# A Hydrogeological Study of Irish Holy Wells

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For I have tasted of that sacred stream

Of science, whose delicious water flows

From nature's bosom

Sir Humphrey Davy: The Collected Works of Sir Humphry Davy, edited by his brother John Davy, Vol 1 - Memoirs of his Life. 1839. Smith, Elder and Co. Cornhill, London

# Declaration

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# Abstract

The overall aim of the research was to characterise the hydrogeology and water chemistry of Irish holy wells. The first main research task was an analysis of the distribution of Irish holy wells (listed in a national database of 2676 wells with grid references) using a Geographical Information System (GIS). Holy wells were shown to be located in all of the main lithological groups and aquifer categories, and they occur as frequently in aquifers classed as poorly productive as they do in the regionally important aquifers, e.g. 68% of the wells are in poorly productive aquifers that underlie 72% of the land area of the Republic of Ireland. However, there is a higher density of holy wells in areas classed as having Extreme or High groundwater vulnerability than in the Moderate or Low vulnerability areas.

Field surveys were then carried out at 215 holy well and five spa well sites. A report was prepared on each well, containing details of the well dimensions, accessibility, water level, site geology, maps, photos, physico-chemical parameters (pH, electrical conductivity and water temperature measured on site), and whether a water sample was collected for laboratory analysis. The data from the surveyed wells were subjected to similar GIS analyses as for the full database. The surveyed wells fell into all of the main physiographical, lithological, aquifer and groundwater vulnerability categories identified in the full dataset. The surveys confirmed that the majority of holy wells are small springs and seepages, which issue from shallow unconfined aquifers where the groundwater vulnerability is often classed as Extreme or High.

A total of 238 water samples were collected for analysis from 167 holy wells and five spa wells. These included duplicates, repeat samples, and samples from four wells selected for monitoring over a 2-year period. The samples were analysed for 60 parameters, comprising major and minor ions and trace elements. As expected, the main water type was calcium-bicarbonate. Parametric and non-parametric statistical tests showed that there were significant differences in water chemistry between different lithological groups, especially between the carbonate lithologies (pure and impure limestones, sands and gravels, and mixed bedrock and gravel groups) and non-carbonate lithologies (non-calcareous sedimentary, igneous and metamorphic bedrock groups). Proximity to the sea was also a major influence on chemistry, with elevated major ions (especially sodium and chloride) in the coastal wells (defined here as within 500 m of the shoreline). As anticipated, of the four monitoring wells, the well in the deep confined

aquifer displayed less seasonal variation in water chemistry compared to the three other wells, which all tap shallow unconfined aquifers.

Nitrate concentrations were above background levels in 52% of the wells, indicating that anthropogenic influences were widespread. However, statistical tests did not show a significant relationship between nitrate values and groundwater vulnerability category. This suggests that shallow open wells at sites where the bedrock aquifer is protected by a low permeability overburden may still be susceptible to contamination from surface runoff.

The chemical analysis results were compared with natural background levels (NBLs) for Irish groundwaters. It was found that many of the samples from holy wells – including wells with low nitrate values – exceeded the relevant NBLs for several parameters. However, the NBLs had been established using monitoring data obtained mainly from a limited number of boreholes and large springs (about 20), generally located in regionally important aquifers, whereas the holy well dataset comprised one-off samples from 167 shallow wells, the majority of which are located in poorly productive aquifers. It is not possible, therefore, to draw definitive conclusions from these comparisons.

Reports of general or specific health cures were found for 57% of the wells surveyed and sampled. The most common of the named cures was for eye ailments (27% of wells), followed by rheumatic or joint pains (11%), toothache (8%) and headaches (7%). Statistical tests did not identify any linkage between the reported cure and the water chemistry in the majority of cases. However, sodium and chloride values in wells with reputations for eye cures were significantly different compared to the other wells, the median concentrations of both ions being higher in the eye wells. This is an interesting finding, because bathing irritated eyes with a weak sodium chloride solution is a modern medical treatment. Eye wells were found to be more common close to the coast, where elevated sodium and chloride values would be expected in local groundwaters. The potential nutritional benefits of drinking water from holy wells were also examined, and it was shown that a water supply from a well could provide useful contributions to the recommended daily intake of calcium, magnesium and iron, especially where diets are poor. However, it is widely regarded as being unlucky to use a holy well for a domestic water supply, and usually only a small amount of water is drunk from a holy well as part of the ritual.

The value of holy wells as therapeutic landscapes, heritage sites and community amenities was also examined, noting that many holy wells have been covered over or infilled over the years. The thesis ends with a set of recommendations regarding the management, protection and cataloguing of holy wells, with specific recommendations for including holy wells as County Geological Sites.

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# 1 Introduction

## 1.1 Background and research objectives

In view of the essential nature of water for human livelihood and wellbeing, it is unsurprising that wells have become associated with religious beliefs in many societies. As Oestigaard (2013) observed: 'water plays a fundamental role in many religious practices of the world's religions and is an important element in many of their underlying concepts'. Sacred wells and springs occur across the world, from India to Africa, from Australia to Central America, and from Eastern Europe to Britain and Ireland (Ray, 2020a). They are especially abundant in Britain and Ireland: Bord and Bord (1985) estimated that there are 2000 holy wells in England, more than 1000 each in Scotland and Wales, and a further 3000 in Ireland. The total in Britain and Ireland may therefore be around 8000 but, as noted by the same authors, 'only a fraction now survives and can be visited'.

Much has been written about the social and cultural significance of holy wells in Ireland and elsewhere, including their reputed health benefits (see literature review in Chapter 2). However, no detailed research has been carried out previously into the hydrogeological settings or water chemistries of Irish holy wells, or of the possible linkages between the characteristics of the water and the perceived health benefits.

The principal research questions for this author were therefore:

1. Are Irish holy wells more common in some physiographical, geological or hydrogeological settings than in others?
2. Are there aspects of the water chemistry of Irish holy wells that differ from the water chemistry of other wells in similar hydrogeological surroundings?
3. Are there any linkages between the water chemical characteristics of Irish holy wells and their reputed health benefits?

To address these research questions, the research objectives were to:

a) Investigate the hydrogeological settings of holy wells in Ireland using a combination of Geographical Information System (GIS) applications and field surveys.
b) Sample and analyse the major ion and trace element water chemistry of holy wells in a variety of hydrogeological locations.

c) Compare water chemical characteristics of holy wells with chemistry data from other wells in Ireland, to see if there are any special characteristics in the water quality of holy wells.
d) Examine the relationship between the water chemistry of holy wells and the perceived benefits in terms of health and wellbeing.

This research constitutes an original contribution to knowledge, as no such study has been attempted previously.

In addition to the specific research objectives, it was anticipated that the research would add to the knowledge of the hydrochemistry of shallow aquifer systems in Ireland, especially spring waters. However, whilst the collection and analysis of water samples was an important aspect of the research, this should not be regarded as a hydrochemistry thesis; rather, it is a thesis about holy wells, in which water chemistry forms an important part.

It was also expected that the research would consider some of the heritage aspects of holy wells, and hence lead to recommendations for increased measures to preserve holy wells as part of our geological heritage.

## 1.2 Research methodology

The research initially comprised an extensive literature review on wells, holy wells and Irish hydrogeology, the results of which are included in the relevant chapters that follow this introduction. More than 300 references are cited in the thesis.

A hydrogeological characterisation of Ireland's holy wells was undertaken using GIS software (including ArcMap 10.3). Layers for physiography, soils, geology, groundwater vulnerability and aquifer classes were obtained from the Geological Survey of Ireland, whilst the layer with the locations of holy wells was produced by the National Monuments Service and provided by Maynooth University. At the outset of the research, it was recognised that a GIS-based analysis alone would not be sufficient to characterise the wells' hydrogeology fully. Many of the wells in the database may no longer exist, or their grid references may not always be accurate. Moreover, holy wells are generally shallow and may tap into superficial and/or bedrock aquifers,

and the groundwater source may not be apparent solely from the available mapping (small areas of gravel, for example, may not be mapped as an aquifer).

Field surveys were therefore essential. Some 215 holy wells were surveyed across the country over a 3-year period. Five spa wells were also surveyed for comparison. A hydrogeological report was prepared on each well site. As discussed in Chapter 4, the surveyed wells provided a good representation of the total numbers of holy wells within the main lithological groupings in Ireland. In addition to those wells surveyed, many other sites were visited where the wells were either not found, or access was not available.

Water samples were collected for full chemical analysis from 167 of the holy wells plus the five spa wells. (Some holy wells could not be sampled either because they were dry, or because of access issues). In addition, four holy wells of contrasting hydrogeology were selected for monitoring over a 2-year period to provide information on temporal variations in hydrochemistry. A total of 238 water samples were analysed throughout the course of the project; these included multiple samples from the monitored wells, other repeat samples, and duplicates for quality assurance checks.

## 1.3 Thesis outline

Chapter 2 begins with an overview of water wells and their importance to society, before moving on to the topic of holy wells. Following a discussion of what constitutes a holy well, international and Irish literature on holy wells is reviewed. Spa wells are also considered in Chapter 2, since there has been a significant body of scientific data collected in relation to the hydrogeology of spas, and these data have some relevance to this study of Irish holy wells.

Chapter 3 provides background information on the geology and hydrogeology of Ireland. A hydrogeological characterisation of holy wells is then presented. This is based on an analysis of holy well sites in relation to geological and hydrogeological maps using a GIS approach. A total of 2676 wells that have grid references were included in this analysis.

Chapter 4 includes the methodology and overall results of the field surveys of holy wells. The data were analysed using a similar GIS approach to that applied to the full holy wells database in the previous chapter.

In Chapter 5, the hydrogeology of individual wells is described. The wells included here were selected as examples of wells from the main lithological groupings used for the GIS analyses in Chapter 3 and Chapter 4, plus wells in particular situations relevant to their hydrogeological characterisation, such as confined aquifer conditions or coastal locations.

Chapter 6 concerns groundwater chemistry. The linkages (well established or otherwise) between human health and the chemical elements and ions found in groundwaters are discussed, followed by an account of the natural background levels of these parameters in Irish groundwaters. Selected relevant previous studies of groundwater chemistry in Ireland are summarised.

The chemical analyses carried out in this research are described in Chapter 7. The field sampling and laboratory analysis methods are discussed in detail, together with an account of the quality assurance checks and the statistical treatment of the data. The major ions and trace element results are presented for each of the main lithological groupings, and for coastal versus non-coastal settings. The results from the holy wells and spa wells are compared with natural background levels and with the findings from previous hydrochemical studies. Various ionic and trace element relationships are examined. The chemical data from four holy wells monitored over a 2-year period are reviewed for their seasonal variations.

Chapter 8 discusses in more detail the existing literature concerning holy wells and reputed health cures, including the cures associated with the wells studied during this research, then considers the findings of the hydrochemical surveys described in Chapter 7 in relation to their health implications. The chemical characteristics of water samples from wells associated with specific cures are compared with those from other wells, using statistical techniques. Potential nutritional benefits from drinking well water - and the possible negative aspects of consuming some waters - are also examined. The importance of holy wells as therapeutic landscapes, heritage sites and community resources are considered at the end of the chapter.

Chapter 9 presents the conclusions of this PhD thesis, and includes recommendations for future research and recommendations on which holy wells might be prioritised for protection as heritage sites from a hydrogeological perspective.

# 2 Wells and holy wells

## 2.1 Water wells

> 'From which type of source, then, is the most commendable water obtained? From wells of course…' (Pliny, writing his *Natural History* in the First century AD, as quoted in Humphrey *et al*., 1998).

A water well can be generally defined as 'any hole in the ground that can be used to obtain a water supply' (Misstear *et al*., 2017). Wells have presumably been around since the time of the first humans. The earliest wells were probably developed at springs or involved shallow excavations along river valleys. However, when humans started to settle in villages and towns, defensive sites on high ground would have assumed greater importance, and so deeper wells would have become more common.

The oldest recorded well is in Cyprus and dates from between 7000 and 9500 BCE (Fagan, 2011). Another ancient well discovered in Europe is a 13 m deep hand-dug well in Germany dating from about 5000 BCE (Houben and Treskatis, 2007). In the Middle East, a well at Sha'ar Hagolan in the Jordan valley dates from about 6300 BCE (Garfinkel *et al*., 2006), whilst in Mesopotamia, wells are known from the 6$^{th}$ millennium BCE (Miller, 1982). Further east, Bromehead (1942) referred to a well in the Indus valley in Pakistan which dates from the third millennium BCE. Also in Asia, early well remains have been found in China, dating from around 3700 BCE (Zhou *et al*., 2011). (Many of the ages quoted have been obtained from carbon-14 dating of wooden well materials or of organic remains found inside the well excavations).

Wells come in many different shapes and sizes. Traditionally, most wells were vertical shafts excavated by hand (referred to nowadays as hand-dug wells – Figure 2.1a). The majority of hand-dug wells are only a few metres deep, although there are some examples of hand-dug wells extending to depths of several tens of metres. In the eastern desert of Ancient Egypt, a well was sunk to over 60 m in 1300 BCE (Bromehead, 1942), and modern examples of deep hand-dug wells are found in countries such as Niger.

A type of horizontal well, or infiltration gallery, originated in Persia around the middle of the first millennium BCE and the technology spread to the Arabian peninsula shortly afterwards

(Wilkinson, 1977; Lightfoot, 2000). This is known as a *qanat* (Persian) or *falaj* (plural *aflaj*, Arabic) and typically involves the construction of a sub-horizontal adit that drains water by gravity from a motherwell source (*umm al falaj*) until it reaches the surface at a settlement (Figure 2.1b); the length of the tunnel section is often several kilometres, and its route can sometimes be traced from the remnants of spoil heaps created at the time of the excavation. In the Sultanate of Oman, this type of falaj is known as a *dawudi falaj*, in accordance with the legend that these aflaj were created by Solomon, son of David (*Sulaiman ibn Duad*), who flew into Oman from Persia on a magic carpet and ordered them to be built (Hawley, 1984) – this is the first of many legends surrounding wells that will be mentioned in this thesis. Falaj building spread across northern Africa and into southern Europe with the Arab conquests from the 7$^{th}$ century CE onwards. Indeed, it is believed that the name Madrid may derive from '*Mayra'*, an old Spanish-Arabic word for falaj (Martinez-Santos and Martinez-Alfaro, 2012).

Modern water wells are mostly drilled by machine (and are often referred to as boreholes) and can reach depths of over 1000 m, although the majority are less than 100 m deep. Whilst most drilled wells are installed with mechanical pumps to lift the water to the surface (Figure 2.1c), some wells tap aquifers that contain groundwater under sufficient pressure that it discharges naturally to the surface (Figure 2.1d). These are known as artesian wells, after the Artois region in France where the first such flowing well was reportedly constructed in the 12$^{th}$ century CE (Bromehead, 1942).

Water wells, whether drilled or hand-dug, have many uses. In addition to providing drinking water – there are more than 150,000 private wells in Ireland alone (Hynds *et al*., 2012) - over 40% of the world's agricultural water is obtained from wells (Margat and van der Gun, 2013). Groundwater is also widely exploited by a range of industries, and is increasingly used as a source of energy – either directly for power generation from high enthalpy (usually greater than 150 $^{o}$C) geothermal sources, or by using low enthalpy shallow systems (usually less than 50 $^{o}$C), which have become popular for heating and cooling buildings in Ireland and elsewhere (Banks, 2012).

Although groundwater sources are generally purer than surface water sources owing to the natural filtration properties of the soil and rock through which the groundwater flows, some wells may be polluted either by natural or human causes. From a health perspective, the most significant naturally occurring (geogenic) chemical pollutants are arsenic and fluoride (see

Section 6.2) – one estimate puts the number of people exposed to elevated arsenic in drinking water (i.e. above the World Health Organization guideline value of 10 µg $l^{-1}$) at 226 million (Murcott, 2012), with particularly large exposures in Bangladesh and West Bengal (World Bank, 2005), whilst more than 200 million people globally drink water with fluoride concentrations above the WHO recommended value of 1.5 mg $l^{-1}$ (Edmunds and Smedley, 2005). There are numerous anthropogenic pollutants from sources such as industry and farming. Common industrial pollutants include fuel oils and solvents (Misstear *et al*., 1998a, 1998b), whilst farming may lead to groundwater contamination by nitrates and microbes. In Ireland, many of the private wells are contaminated by faecal bacteria from agricultural activities or wastewater disposal, often because the wells are poorly located and/or poorly constructed (Hynds *et al*., 2013).



a)



b)




c)



d)

Figure 2.1 Examples of different well types: a) hand-dug well fitted with handpump, Lwengo District Uganda; b) falaj, Birkat al Mawz, Oman; c) drilled well used for abstraction and artificial recharge, Las Vegas, USA; d) artesian well, near Rome, Italy. Photos by Bruce Misstear

## 2.2 Holy wells

### 2.2.1 What is a holy well?

According to Logan (1980): 'If it is necessary to define what is a holy well, it may be said that a holy well is any collection of water which for one reason or another is considered to be holy'. However, such a definition is not specific to a well and could equally apply to a lake or rock pool. Ray (2014) notes that in Ireland, '*toibreacha* (holy wells) and *toibreacha beannaithe* (blessed wells) are water sources, usually springs (but sometimes ponds or lakes), which are sites of religious devotion.' She adds that, unlike shafts and holes excavated by people for the collection of water, 'holy "wells" most commonly appear on their own and can also include seepage pools, or even the hollows of rocks or the cavities of trees…where dew and rain collect'. Again, this definition is not fully satisfactory, as many holy wells include some degree of excavation, often around a pre-existing seepage or spring. Branigan (2012) describes a holy well as 'a location where water issues from the earth and where the site is a focal point for supernatural divination, the curing of illness through ritual, the cursing of third parties, and/or the veneration of early Christian saints, Pagan deities, or elements of nature, specifically the water itself.' This is quite a good definition, although the phrase 'where water issues from the earth' applies more accurately to a spring rather than a well. In an article about the holy wells of County Limerick, Ó Danachair (1955) defined a holy well as 'a well or spring at which prayers and ceremonies of a Christian religious nature have been performed in recent times'. This is satisfactory in that both well and spring are included, but limits holy wells to sites of recent Christian devotion.

For the purposes of this thesis, a holy well is regarded simply as a groundwater well or spring at which religious rituals have been, or are currently, performed. As will be discussed in Section 2.2.3 below, holy wells in Ireland are often dedicated to a local Irish saint (Brigid and Patrick being the two most common examples) or to a saint of the universal Catholic church (especially the Virgin Mary, often representing a rededication of a well from an Irish saint), although some bear a name that reflects the reputed cure of the well (such as *tober sul*, or eye well).

Before leaving this topic of defining a holy well, it is perhaps worth dwelling for a moment on the word 'holy', and how its meaning differs from that of 'sacred'. According to Oestigaard (2013) the word holy implies possession of a divine quality, whereas sacred refers to objects that are respected or venerated. On that basis holy wells might be more properly referred to as

sacred wells. However, Oestigaard also notes that holy water can be regarded as having divine qualities. It is therefore reasonable to refer to a well that contains 'holy water' as a holy well. In any event, the phrase holy well is in common usage in Ireland and so will be retained here.

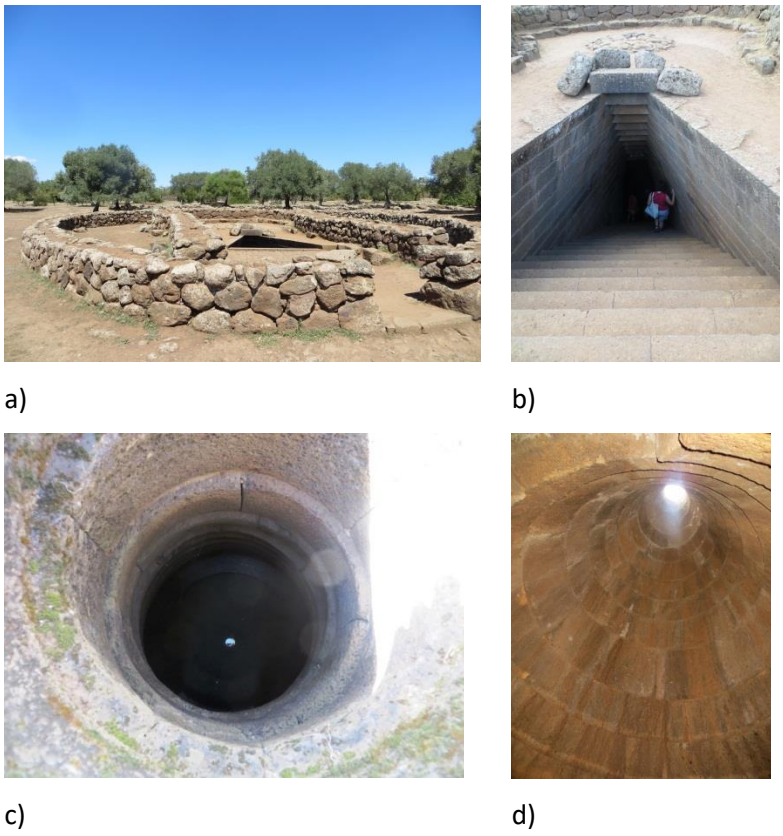
### 2.2.2 Holy wells: An international context

The widespread occurrence of holy wells is highlighted in a recent book '*Sacred Waters: A Cross-Cultural Compendium of Hallowed Springs and Holy Wells*' edited by the US scholar Dr Celeste Ray (Ray, 2020a), as it includes chapters about holy wells and sacred springs in more than 30 countries, located in all six inhabited continents. The publication of such a book, with its 43 authors of 33 chapters, also indicates the current scholarly interest in the topic, especially among academics in the humanities.

Sacred texts such as the Bible and Koran contain many references to water wells – sometimes as a source of conflict (Misstear *et al*., 2017). The Hebrew bible makes 580 references to water, including several to wells (Oestigaard, 2013), whilst the famous Zamzam well in Mecca is visited by millions of people each year as part of the Muslim Hajj pilgrimage (Ghabin, 2020; see Section 8.1). However, sacred wells predate these great monotheistic religions. For example, there are several Bronze Age wells in Sardinia which have religious significance (Varner, 2009), and one such well is illustrated in Figure 2.2. This temple well at Santa Cristina dates from between the 9$^{th}$ and 11$^{th}$ century BCE. Created by the Nuraghi people, the religious importance of this location continued into historical times with the construction of the Christian Santa Cristina church in the 11$^{th}$ century CE (Moravetti, 2003). As will be described later, some Christian holy well sites in Ireland also have their origins in pagan times.

There are many different lithoiatric practices and beliefs in healing, related to both pagan and Christian religions. According to Aliverti (2013) 'Rocks and stones have high symbolic value. They represent an important link between heaven and earth because they may fall from the sky or result from upheaval of the ground, lifted up to the sky or accumulated in the soil, becoming a symbol of Mother Earth and fertility.' He points out that since pre-Christian times, mountains, caves, boulders, gorges, forests and springs have provided locations for shrines. He cites several examples of lithoiatric practices in Italy, some of which involve interactions between stone and water – such as drinking water dripping from rock walls or collecting stone fragments from

streambeds. He infers that the symbolic value, whether magical or related to religion, is independent of whatever physical and chemical properties the rock and stones may possess.



a) b)

c) d)

Figure 2.2 The temple well at Santa Cristina, Sardinia, which dates back to the 9th to 11th century BCE: a) the surface stone work (made out of blocks of volcanic rock [trachyte]) which encloses the vestibule or atrium where votive offerings[1] would have been made; b) the stair room, with steps down to the water level, currently at about 7 m below ground surface: during the March and September equinoxes, the well chamber is lit by sunlight through this stair room; c) view into the well chamber from the surface opening; d) the well chamber (*tholos*) which is about 2.54 m in diameter at its base and narrows to an 0.33 m opening at the surface. Photos by Bruce Misstear; data from Moravetti (2003) and Laner (2004)

Water featured prominently in the religious beliefs of the Iron Age (Celtic) peoples of northwest Europe (Bord and Bord, 1985; Rolleston, 1985; Dooge, 1996; Varner, 2009; Ray, 2014). The 'Celts' believed that spring sources of rivers were a link with the Celtic otherworld which lay

[1] Votives are 'objects left by petitioners to emphasize the sincerity of a request or in thanksgiving for a desired outcome' (Ray, 2020a)

underground. Ó Dochartaigh (2000) noted that shafts sunk in the ground were associated by the Celts with religious practice – there is evidence from votive offerings - and that 'it is a short enough cultural transfer from this ritual use of shafts, which must often have been prone to filling with water, to a belief in a relationship between gods and underground water'. Hence it is easy to understand the development of beliefs, rituals and traditions associated with holy wells.

Nevertheless, not all scholars accept the 'Celtic' origins of some holy wells. Ray (2014) summarises some of the recent debates as to whether the Iron Age peoples of Europe, including Ireland, really did have a Celtic identity and how this has influenced some views about the history of holy wells. She remarks that even though it is widely accepted that water was a substance of veneration in Bronze Age Europe, some scholars argue that wells were not part of religious rituals in the Iron Age, a view she dismisses: 'Perhaps because they have been credited with "Celtic" origins for so long, holy wells/sacred springs have been written out of the period (making the Iron Age unique indeed)'. Ray concludes that archaeological and literary evidence from the late Iron Age confirms pre-Roman votive offerings at springs.

Over the centuries most of the ancient holy wells in Europe have been renamed after Christian saints (Varner, 2009), whilst many others are more recent and date from the Christian period (Ray, 2014). Bord and Bord (1985) speculate on how holy wells were created, noting that many stories indicate that the wells sprang up in response to a saint's prayers. They suggest that saints were possibly skilled in water divining (these authors do not question the efficacy of this technique).

Not all holy wells were regarded as places of worship and healing: there were also cursing wells and some were associated with devils (Ray, 2020b). Moreover, even if wells were not considered as evil, rituals were sometimes discouraged as being contrary to particular religious beliefs. In medieval Britain, the worship of wells and springs was widespread until it was suppressed by Henry VIII in 1536 CE owing to the associations with the Catholic Church (Hardcastle, 1987; Mather 2013). However, despite attempts during the Reformation to suppress water worship in England, 'the cult was so important and such an intrinsic part of culture and religion that it continued for centuries, with nobles and commoners alike, making pilgrimages to the holy wells with the aim of attaining long life and prosperity' (Oestigaard, 2010). Some of these wells have continued as places of ceremony up to the present day: the famous Chalice well at Glastonbury,

which some believe to be the resting place of the Holy Grail, is one example of a much-visited holy well with a history apparently going back 2000 years, even though the nearby abbey was dissolved during the reign of Henry VIII (Varner, 2009); however, Mather (2016) says that this well, which formerly supplied the abbey, was given its present sacred name as recently as 1751, and he thus questions its antiquity as a holy well.

In Austria, water from holy springs has been widely used since the 15th century (Kirschner *et al*., 2012). Here, as in many European countries, the traditions are associated with Catholicism. However, holy well rituals have been popular not just in Catholic societies: Johansen (1997) noted that the use of holy springs was accepted by the Protestant clergy in post-Reformation Denmark, where there are 650 such holy springs, albeit few are in use today (Ray, 2014). Indeed, it is interesting that, in the frontispiece to his 2013 book '*Water, Christianity and the Rise of Capitalism*', Oestigaard included the following quote from 'the father of Protestantism' Martin Luther who wrote (in relation to baptismal water):

> 'The one who believes is the person to whom the blessed, divine water is to be imparted. If you believe that through this water you will be saved, it becomes a fact.'

Apart from religious beliefs associated with the curative power of water, Kirschner *et al*. (2012) point out that, in comparison to unsanitary cities at that time, holy springs were probably of better water quality than the city water sources. Robins and Smedley (2013) also highlight that 'sacred' waters often provided better quality water than other, more contaminated sources, for both drinkers and bathers.

One of the most famous well/spring sites in Europe is at Lourdes which, according to Oestigaard (2013), is the second holiest Christian pilgrimage site after the Vatican City. This is reputed to have been created by Bernadette Soubirous under the guidance of the Virgin in 1858, and it is believed - by the many thousands of people who drink and bathe in its waters each year - to possess healing powers (Varner, 2009; Agnew, 2020). Statues of Our Lady of Lourdes are present at several Irish holy well sites, for example Tobernalt in County Sligo (this is one of the wells in the 'pure limestone' lithological grouping described in Section 5.3).

Holy wells may not always be sources of good quality drinking water, or the water quality may vary throughout the year. One of the few scientific studies of water quality in holy wells is that by Kirschner *et al*. (2012), who investigated the chemical and microbiological quality of holy springs in Eastern Austria (and of holy water in churches and hospital chapels in Vienna). Their studies showed that many of the spring samples were contaminated with faecal bacteria, and that about 20% of the samples had nitrate concentrations above the EU drinking water standard (see Section 8.1.3 for further details of these results). Kirschner *et al*. (2012) concluded their study by recommending that there is a need to increase public awareness that springs potentially can be a source of illness.

The Seokjeong Full Moon well in Seoul in Korea, which was used for baptismal purposes by Catholic missionaries in the late 18th and 19th centuries, reputedly produced 'clear water' water for 15 days a month and 'unclear water' water for the remaining 15 days (Figure 2.3). It is difficult to explain such behaviour in hydrogeological terms. Incidentally, South Korea also possesses about 1460 sacred mineral springs, known as *yaksutŏ*, which are believed to contain minerals of benefit to human health (Yoon, 2020).




a) b)

Figure 2.3 a) the Seokjeong Full Moon Well (the 'half-month stone well') in Bukchon district in Seoul, South Korea; b) the signboard explains that the well was used to provide baptismal water for ceremonies conducted by a Chinese missionary priest, Father Zhou Wenmo in the late 18th century. The well also enjoyed a reputation for helping women who drank its water to have a male child. In addition, as mentioned in the main text, the well apparently produced clear water for 15 days a month and unclear water for the remainder of the month. Photos by Bruce Misstear

Robins and Smedley (2013) observe that many of the bottled waters now popular with consumers developed at sites of holy wells, and some varieties claim medicinal properties. Reimann and Birke (2010) indicate that bottled waters are mainly a life-style choice, since e.g. bottled water may be less safe than drinking water (EU bottled water regulations can be less strict than those for tap water – see Section 6.2; and lack of chlorination makes bottled waters vulnerable to bacterial contamination during storage). They also point out that, paradoxically, the expectation for mineral water amongst many consumers has changed from a highly mineralised (and sometimes purgative) water to a pure water with very low mineral content.

### 2.2.3 Holy wells in Ireland

> 'It is impossible, indeed, for any traveller, to pass over any considerable portion of the country, more especially in the south and west, without meeting with numerous *Holy wells* and other places of superstitious resort, celebrated either for the cure of cattle, or the restoration to health of beings of the human race; and having around them various emblems of superstitious reverence, such as rags and ribbons hung on *holy* places, as memorials of the sacredness of the waters…' (Philip Dixon Hardy, 1836).

#### 2.2.3.1 Number of Irish holy wells

The estimates of the number of holy wells in Ireland (*toibreacha beannaithe*) vary slightly, but centre around 3000: Foley (2010) mentions that there are 3047 extant holy wells on the island but adds that this is probably an underestimate, whereas Ray (2014) gives a figure of 2996 for the Republic of Ireland (based on data from the National Monuments Service), with a further 187 holy wells in Northern Ireland (data from the Northern Ireland Sites and Monuments Record), yielding a total of 3183 holy wells for the whole island. In 2017, Foley mentioned a figure of 263 holy wells for Northern Ireland, which would suggest a total in excess of 3250 for the island (Foley, *pers comm*). In addition to being important cultural sites in themselves, holy wells (and wells in general) have also been an important influence on place names: there are 163 townlands in the Irish Townlands Index that include the word *tobar* or some variation of this word (Healy, 2001).

Whereas holy wells are marked on the Ordnance Survey maps produced from the 1820s onwards, many holy wells have been destroyed in the past century by farming, forestation, urbanisation or developments such as road schemes, and it is not known how many wells survive and are accessible. In her article on the rounding traditions at holy wells, Ray (2015) mentions having visited about 800 Irish holy wells, probably the largest number visited by any one individual researcher.

#### 2.2.3.2 Origins and perspectives

Ray provided an archaeological perspective on Irish holy wells in her 2014 book, noting that very little archaeological work has been done on holy wells in Ireland (less than 1% of the well sites have been excavated). One of the problems hindering archaeological investigations is that many of the holy wells are still in use. A second issue is that holy wells have been regarded as unimportant in terms of their archaeological characteristics, and therefore have been a low priority for archaeological research. What work has been done has been mainly in connection with proposed developments near the wells such as new housing. One well that has been excavated by archaeologists is St Anne's well at Randalstown in Co Meath (Figure 2.4). This well was excavated in the 1970s because of its proximity to a proposed tailings pond for the nearby Tara mines. Ray refers to the excavations yielding Iron Age votives at the site. The finds included a Roman brooch dating from the 1st century CE and a pottery sherd from around the same period (Kelly, 2002). A contemporary example of archaeological investigations is taking place at Disert in Co Donegal, where there is a holy well (dedicated to St Colmcille), an early medieval ecclesiastical enclosure and a graveyard (*cillin*) (Beglane *et al*., 2016; Beglane, 2018; Beglane *et al*., 2018); see Section 5.4.3. The initial investigations included high-resolution aerial photography plus ground geophysics, whilst physical excavations around the well commenced in 2019 and have yielded some evidence of pre-Christian activities[2].

[2] https://ifrglobal.org/program/ireland-disert/ (accessed 4/6/2020)



a) b)

Figure 2.4 St Anne's well Randalstown, where archaeological excavations in the 1970s uncovered a Roman brooch: a) the edge of the Tara Mines tailings dam can be seen in the background of the photo; b) the spring well was dry at the time of this author's visit in August 2018; a photo with the well containing water is included in Ray's 2014 book on Irish holy wells. Photos by Bruce Misstear

One of the most comprehensive (and readable) accounts of holy wells in Ireland is by Logan (1980). He covers the history of these wells, the pagan and Christian practices associated with them, the supposed cures and the significance of objects such as trees, animals, stones and votive offerings. He describes their geographical settings in terms of major landscape features such as the seashore, mountains and hilltops, and bogs – albeit he does not extend this analysis to the geology or hydrogeology of the well sites. Based on studies of rituals and traditions at more than 500 holy wells, Brenneman and Brenneman (1995) also considered their geographical settings, although these authors' focus was on describing the place or *tuath* that apparently gave power to the well during 'Celtic times', rather than in providing more detailed accounts of the topographic setting. They indicate that there are three main settings, or contexts, in which the wells are found: a) in meadows or boggy areas 'at the center (*sic*) of some bowlike formation' (they refer to these as umbilicus or navel wells); b) in rocky or mountainous areas; and c) on or close to the seashore. The Brennemans argue that the location is relevant to the healing power of the well, with wells in rocky or mountainous locations often being associated with cures for aching limbs or teeth, whereas wells in shoreline locations were noted for cures for barrenness. The same authors also noted that perhaps half of the holy well sites in Ireland contain a sacred tree - known as the *bile*, and commonly hawthorn, ash or hazel (Bord and Bord [1985] mention that hazel is associated with wells and water in Celtic folklore) - and venerated stones (including bullaun stones), in addition to the well or spring (examples of rag trees and bullaun stones from the authors' own well surveys are illustrated in Figure 2.5). More recently, Ray (2020c) describes

holy wells as sites of biocultural diversity, and discusses how their flora can add to the cures associated with the wells.



a)



b)



c)



d)

Figure 2.5 a) rag trees at Killeigh springs, Co Offaly; b) ash tree inside Tobernacogany well at Fore, Co Westmeath, decorated with rags, ribbons and other tokens, plus there are coins pressed into its bark (which have damaged the tree); c) bullaun stone at St Kieran's well at Kilkieran, Co Kilkenny; here the bullaun stone is used as a holy water font for a 'cure for headache'; d) bullaun stone that forms the so-called Wart well at Timoleague, Co Cork. Photos by Bruce Misstear

Whilst it is generally believed that many Irish holy wells have pre-Christian origins, not all scholars accept this. For example, in his book dealing with Irish holy wells and Catholic devotion, Carroll (1999) argued that 'not only were holy well cults and rounding rituals not a part of *Celtic* tradition in Ireland, they were not an important part of the *Christian* tradition in Ireland through to the sixteenth century'. According to Ray – who also includes that quote from Carroll in her 2014 book - this denial ignores the archaeological evidence of votive offerings from Iron Age times found in holy wells in Ireland, Scandinavia and elsewhere. It also ignores evidence from some of the earliest hagiographies of Irish saints: for example, Ray (2013) recounts how

Adomnán's 7th century narrative '*Life of St Columba*' includes stories about the blessing of wells by Colmcille, whilst the 10th century (and possibly earlier) '*Tripartite Life of Saint Patrick*' has several accounts of Patrick creating new wells. McCormick (2009, 2011) also counters Carroll's arguments against a Pagan-origin model for holy wells, using evidence from the large Struell wells complex at Downpatrick in County Down. In a more recent paper on bathing in the Struell wells, which also discusses the origins of Irish holy wells, McCormick refers to an 8th century text describing St Patrick singing psalms when immersed in the well at night (McCormick, 2017). In her new book '*Pilgrimages of Faith*', Nugent (2020) comments that, whilst it is impossible to know in most cases when holy wells became pilgrimage sites, 'Certainly, devotions at some Irish wells began as early as the Iron Age'. Nugent adds that 'Some of the oldest wells became Christian places in the early medieval period, but others came into existence throughout the late medieval period and in later centuries following the Reformation'.

Brenneman (2005) describes many of the beliefs and rituals surrounding the sacredness of water in Celtic society, noting that the central role of fertility in the use of sacred springs was superseded by the role of healing after the coming of St Patrick. O'Sullivan and Downey (2006) mention medieval writings in Latin and Irish that link holy wells to early Irish Christianity 'and indeed early mythology' and also refer to the presence of holy wells close to ancient sites such as Tara in County Meath (the Well of the White Cow at Tara was one of the wells surveyed and sampled in this research – see Section 5.2.1.1). In Wales, 62 holy wells are at sites associated with stone megaliths (Jones, 1954, as cited in Bord and Bord, 1985), whilst many others occur at sites with early Christian churches (Bord and Bord, 1985). In Ireland, Harbison speculated that the existence of a sacred well may have been a major factor in selecting the site for many early Christian monasteries 'in order to achieve a felicitous and frictionless continuity from Pagan to Christian cult' (Harbison, 1991). As will be seen from the well surveys described later in this thesis, there are many holy wells located in or close to early Christian monastic establishments in Ireland (see Section 8.3.2).

Despite there being much convincing evidence for the pre-Christian origins of holy wells, it would be incorrect to assume that all or most holy wells have pagan origins. Ray (2014) points out that whereas there are indeed many holy wells that date from the pre-Christian era, some holy wells were only dedicated as holy wells much more recently, in some cases as late as the 19th century. Those wells adopted by the early Christians were subsequently given the name of a Christian saint 'in the Irish tradition'; in many cases, the wells were subsequently rededicated

to a 'universal' saint by church reformers in later centuries. Nevertheless, many of the extant holy wells still bear a dedication to a local saint – this applies to more than 50% of the 238 holy wells in Co Clare, for example, with dedications to saints such as Senan, Flannan, Caoidhe, Mochulla and Mac Duagh (Houlihan, 2015).

As in other European countries (see Section 2.2.2), attitudes of the church and state in Ireland towards holy wells have varied over the centuries: under Penal Codes in the early 18th century, during the reign of Queen Anne, a person could be 'fined or whipped for attending pilgrimages to holy wells' (Ray, 2013). Although visiting holy wells was one of the 'main expressions of Catholic devotion in pre-Famine Ireland' (O'Sullivan and Downey, 2006), the church in Ireland has maintained 'an ambivalent attitude to holy wells' (Foley, 2010), with concerns at various times about hydrolatry, profane rituals and antisocial behaviour. In the 19th century, one (Protestant) author went as far as to say that holy wells 'are not only opposed in their nature and tendency to every precept of the moral law and of the Catholic religion, but are so many stains on the character of a civilized and even nominally Christian people, and consequently a disgrace to the age and to the country in which we live' (Hardy, 1836). Nevertheless, Logan (1980) observed that the Catholic Church in contemporary Ireland encourages visits and praying at holy wells, whilst Ray (2015) reports that, following the various child abuse scandals investigated at religious institutions in the previous decade, some priests are using gatherings around holy wells as a means of attracting people back into the congregation.

A very useful source of local information on Irish holy wells is the survey carried out under the auspices of the Irish Folklore Commission in the 1930s, and known as the Schools' Folklore Scheme. This involved 50,000 schoolchildren from 5000 primary schools across the Irish Free State collecting information on folklore in their area, including folklore and traditions surrounding holy wells. The information from the Schools' Collection – comprising 450,000 pages in bound volumes - is nowadays available for download from the dúchas website (Irish Folklore Commission, 1937-38)[3]. To update this type of information, in 2017 the noted scholar on holy wells, Dr Celeste Ray, launched a website: 'Ireland's Holy Wells: County by County' where members of the public are able to upload details of holy wells[4].

[3] https://www.duchas.ie/en/cbes (accessed 1/6/2020)
[4] http://ihwcbc.omeka.net/instructions (accessed 1/6/2020)

In the last 20 years there have been several illustrated texts published on Irish holy wells. Some of these books are aimed mainly at the general reader but include much useful information for the interested researcher. The publications by Healy (2001) and Rackard and O'Callaghan (2001) give accounts of selected holy wells across the country and their associated rituals. Books with a more local focus include those by Branigan (2012) on the sacred wells of the Dublin area, French (2012) on County Meath holy wells, Houlihan (2015) on the holy wells of County Clare, and Broderick (2016) and Keane (2018), both of whom write about the holy wells of County Waterford. Accounts of Irish holy wells are also included in various regional guides on history and archaeology, including e.g. Conlon (1999 and 2000) on County Louth, Roberts (2009) on West Cork, and Nugent and Scriven (2015) on Cork city. These books and articles not only contain useful information on holy wells, they also contribute towards the preservation of holy wells as part of the country's rich archaeological and cultural heritage. The need for this is evident from French's (2012) book, in which he notes that of the 130 or so holy wells in County Meath only three wells are protected in the County Development Plan (see Section 8.3.3).

Certain holy wells have been the location of very large pilgrimages, and not always in the distant past. St Moling's well by the Barrow in Co Carlow was visited by several thousands of pilgrims in the plague year 1348 (Clyn, 2007; Nugent, 2020), whilst as many as 20,000 pilgrims visited Lady's Well on Lady's Island (Co Wexford) as recently as on 15 August 1978 (Logan, 1980). The 'catchment' for the holy well could range from local to national (Foley, 2010). Foley quotes Harbison (1991) saying that 'Historically people came from the parish and had local affiliations with the well with a nominal catchment of 20 miles'. Foley notes that nomadic communities, such as the Travelling Community in Ireland, have a particular regard for holy wells, and mentions St Brigid's well and Father Moore's well in Kildare as being popular with Travellers (see Section 5.7).

Foley (2010, 2011) provides a cultural and health geography perspective on Ireland's holy wells. In his 2010 book, Foley considers holy wells and historic spas (along with sea bathing, Turkish baths, sweat-houses and modern spas) as therapeutic landscapes, places that provide physical, mental and spiritual healing and wellbeing. He describes the various 'performances of health' associated with these waters, namely bodily performances (including physical/medical and psychological/faith cure aspects), cultural performances (encompassing social, cultural and political influences and religious and profane rituals), spatial performances (the influence of location and setting) and economic performances (especially relevant to some of the spas, but

holy wells could also include some economic activities such as selling of souvenirs and food). Ten holy wells are described in detail in the contexts of these performances.

Some of the terminology and concepts surrounding therapeutic landscapes with respect to holy wells are developed further by Foley in his 2011 paper. Here he describes the 'therapeutic assemblage' that links material aspects of wells, people and cures, with metaphors of cultures and beliefs, and with inhabitation of place. These concepts are illustrated with reference to the 10 wells covered in the 2010 book. In a 2015 paper, Foley extends his analysis beyond water to folk medicine more generally. He considers the roles of sweat houses, herbal remedies and travelling healers - as well as water - in folk medicine and compares the relationships of these informal practices with more mainstream medicine (Foley, 2015).

A contemporary example of a holy well as a therapeutic landscape can be found in Co Kerry, where people are reportedly seeking solace during the Covid-19 pandemic by visiting St Finian's well on the Iveragh Peninsula[5]. The 6th century St Finian (or Fíonnán) had a reputation for protecting people from the plague.

#### 2.2.3.3 Rituals

Religious practices at holy wells typically involve prayers (which may include saying decades of the rosary at the Stations of the Cross) and the giving of votive offerings. The rounding or pattern rituals vary from well to well. They may be part of a larger pilgrimage (or *turas*) incorporating stations at local monuments, such as at Glencolmcille in County Donegal (Ray, 2013) – St Colmcille's well at Glencolmcille is one of the wells described in Section 5.6. These rituals are most commonly carried out on the Saint's or pattern (patron) day, when they are believed to be most efficacious. There are many different types of ritual and votive offerings associated with them e.g. the pilgrim may dip a rag in the well (often red by tradition, a colour believed to ward off evil spirits – Logan, 1980), bathe the affected body part with the wet rag and attach the rag to a tree (Figure 2.6a). Some pilgrims believe that by leaving a rag behind, they are leaving the ailment behind too, and that the ailment will disappear as the rag rots away. Whereas the intention of leaving a rag behind is to deposit a concern at the well, the giving of a votive such

[5] https://www.rte.ie/news/ireland/2020/0504/1136435-kerry-locals-seek-solace-in-holy-wells-during-pandemic/ (accessed 15/7/2020)

as a statue can be interpreted as the leaving of a gift to help ensure that the pilgrim's prayers are answered by the saint (Ray, 2010).




a) b) c)

d) e)

Figure 2.6 St Brigid's well County Kildare: a) the well, with tree in background containing rags and other tokens; b) the water from the well flows under an arch decorated with St Brigid's cross; c) the stations for the pattern day rituals; d) rags, ribbons, scarves, photos and other tokens hanging on the tree beside the well; e) a sign at a small tree planted near the well by community workers from Drumcree, at the time of the 1997 conflicts over the right to hold commemorative marches through that town. Photos by Bruce Misstear

Offerings at holy wells seen by the author of this thesis include coins, buttons, bracelets, stones, statues, rosary beads, candles, children's dolls, cards and photos (Figure 2.6d); at one well there was even a crutch left behind (Father Moore's well in Kildare), an observation also made elsewhere by Logan (1980). The offerings may be specific to a particular time in history, such as the memorial plaque and tree placed by Drumcree march protestors at St Brigid's well in Kildare in 1997 (Figure 2.6e). Sometimes offerings like coins and buttons are dropped into the well, or larger objects are placed on the ground beside the well, or the cloths, trinkets and photos are hung on a bush or tree. Ray (2013) notes that the tossing of coins into a well is more often

associated with modern tourism – where the holy well is regarded as a form of wishing well – rather than representing a traditional votive practice. It is most common to drink the water or to dip rags, but some well rituals included bathing e.g. at Struell in Co Down – and one site visited by this researcher, at Cranavane in County Carlow, includes a coffin trough, where a corpse was immersed prior to burial in the nearby graveyard (see Appendix B). Another oft-quoted belief is that if a fish is seen in the well after performing the round (and the round is always done in a clockwise direction - *diseal*), then the petitioner's prayers will be answered (Ray, 2020c).

#### 2.2.3.4 Cures and healing reputations

Some wells are associated with several cures whilst others are linked to specific cures – for example, mental health in the case of Father Moore's well in Kildare (Father Moore being an example of a 19th century 'healing priest'; Ray, 2013) or eye diseases at Tobar na Sul near Lough Hyne in Cork. (Varner [2009] noted – albeit not specifically in relation to Ireland - that treatment of eye diseases is the most common cure associated with holy wells, and speculates that this may be due to the pilgrims having insufficient Vitamin A in their diet, leading to the dry eye condition xerophthalmia). In addition to mental health disorders or eye diseases, ailments with which holy well cures (or protections against) are associated include: back ache, rheumatism, sprains, toothache, headaches, warts, whooping cough, influenza, plague, child illnesses, and lack of fertility (O'Sullivan and Downey, 2006; Ray 2013). Indeed, Bord and Bord (1985) found 75 different ailments for which cures were associated at particular holy wells (see Section 8.1).

Foley (2010) and others emphasise that faith in the healing properties of the water and its religious significance are key in the 'embodied performances of health' i.e. in the water cure. According to Foley 'The forms of health which lie at the heart of the holy well are spiritual in their foundations, yet also speak to wider holistic understandings of healing and wellbeing', noting the affective presence of wells as places of peace and contemplation. Foley says 'it is not too fanciful to see the holy well as the people's spa', in view of its 'presence as a public and free site of care and as a watering place for the masses'. He develops this connection between holy wells and spas further by suggesting that holy wells were an early type of spa, and that the development of spa culture was to some extent linked to the decline in the importance of holy wells.

From the point of view of the current research, it is important to recognise that although the ritual and spiritual dimensions are central to the perceived curative powers of holy wells, drinking the water is also common practice at many holy wells, as will be discussed later in this thesis (Section 8.2). Moreover, water is often collected for consumption in the home, sometimes in connection with specific cures – Ray (2013) mentions bottles of 'head well', 'eye well' and 'sore throat well' water being stored in kitchen pantries.

## 2.3 Spa wells

The word spa is derived from Spa in Belgium, itself derived from the Walloon word for fountain *espa* (Mather, 2013). At many spas people seek health benefits by both drinking and swimming in the waters, which are often highly mineralised. As long ago as 400 BCE Hippocrates recognised the importance of a pure, potable water supply for good health, whereas two thousand years later, during the age of enlightenment, many regarded the highly mineralised waters found at spas as being beneficial, and were unaware that such waters might also have harmful properties (Bergman, 2013).

In Britain, the spas grew up at thermal springs in Roman times, were suppressed or at least discouraged during the Middle Ages – when bathing in warm water was considered sinful - and enjoyed their peak popularity in the 18$^{th}$ century (Mather, 2013). Between 1560 and 1815, there were 173 spas in England, albeit not all of them were in operation at the same time (Oestigaard, 2013). Robins and Smedley (2013) discuss the healing power of springs at Bath, the city having been founded in 863 BCE when Prince Bladud reputedly was cured of leprosy by immersing himself in a warm mud spring. (It is also alleged that Robert the Bruce was cured in a similar manner by immersing himself in waters issuing from a Devonian Sandstone spring at Scotlandwell in Fife - Robins *et al*., 2004). From the late 17$^{th}$ century, Bath spa developed a reputation for treating rheumatism, gout, infertility and skin diseases, leading to the establishment of a Mineral Water Hospital there in 1739. Robins and Smedley (2013) observed that American native Indians used to seek treatment for rheumatism in waters at the site that became the spa town of Bath in West Virginia. At some sites in Britain, spas developed at the same sites as holy wells (Bord and Bord, 1985). An example is Malvern spa, where there are two holy wells (including an eye well) in the vicinity.

Although many of the healing properties claimed for groundwater are questionable, Robins and Smedley (2013) suggest that exposure to clean cold water may alleviate symptoms of leprosy and rheumatism, whilst drinking highly mineralized water containing Epsom salts (hydrated magnesium sulphate) at spas has a purging effect which may be beneficial in some cases, albeit often with unpleasant side effects. (In their paper, they point out that it is difficult to distinguish any strictly medicinal benefits of groundwater from the health benefits of exposure to 'clean and wholesome water for drinking and bathing').

In Scotland in the 19th century, around 20 hydropathic resorts were established in response to declining water and air quality in cities and towns (Spence and Robins, 2004). These provided customers with access to clean drinking water and good air. In contrast to many of the heritage spa sites in Britain and elsewhere, the waters at these sites were not highly mineralised, but instead offered relatively pure, potable groundwater.

Foley (2010) considered the development of spa towns in Ireland as part of his work on healing waters and therapeutic landscapes. He notes that spa development was fairly limited in Ireland compared to Britain and continental Europe as there was only one mildly hot spring (at Mallow - 20 $^{o}$C). Spa towns developed from late 17th century and reached their peak popularity in late 18th to mid-19th centuries. An 18th century study by Rutty 1757, quoted in Foley (2010), classified the different spa waters, the two most common of which were chalybeate (iron-rich) and sulphur spas, with others including magnesium and saline. There were about 200 spas across the country, only a few of which led to the growth of towns around them (e.g. Lucan, Lisdoonvarna and Mallow). Lucan, for example, was initially a chalybeate spa but a second source developed there was sulphurous in character. At Lisdoonvarna, the different spa wells provided waters rich in iron, sulphur, magnesium and even copper (Drew, 2001).

Spas offered treatments for a variety of ailments, ranging from gout to infertility, from dysentery to leprosy (Section 8.1). Treatments were performed by ingestion and immersion, and the purging effects of mineralised waters were noted. The spring source at Mallow developed into a warm-water spa in the late 17th and early 18th centuries. It has been the subject of hydrogeological and hydrochemical study owing to its elevated groundwater temperature (Brück *et al*., 1986; Aldwell, 1995 and 2001). The former spa wells at Lisdoonvarna and Mallow were among those surveyed and sampled in this thesis (see Section 5.11). The Mallow spa had

its origins as a holy well (Lady's well), an example of where the identities of holy wells and spas are blurred.

It is interesting to note that whereas spa treatments are generally regarded as a form of alternative medicine in countries like the UK and Ireland, spa cures are often considered as a *bona fide* supplement to conventional modern medical treatments in continental European countries (Coccheri *et al*., 2008). In a study of patients attending nearly 300 spa resorts in Italy, Coccheri *et al*. (2008) found some positive evidence that spa treatments resulted in health benefits in relation to several ailments (rheumatic, dermatologic, respiratory, etc), and hence that further research – including randomised controlled studies – would be warranted.

The importance of the spa industry today is evident from information published by the Global Wellness Institute (2018), which indicated that there were more than 34,000 thermal/mineral springs operating in 127 countries in 2017, with revenues of $56.2 billion[6]. Most of these are in Asia or Europe, with large numbers especially in countries such as Japan, China, Germany, Italy and Hungary.

[6] The GWI defines the thermal/mineral springs industry as 'revenue-earning business establishments associated with the wellness, recreational, and therapeutic uses of waters with special properties'

# 3 Hydrogeological characterisation of holy wells

In the introduction to this chapter the (relatively small amount of) literature available on the hydrogeology of holy wells in Britain and Ireland is reviewed, plus the more extensive literature on the hydrogeology of spa wells. (Britain is included in this review since some of its geology and hydrogeology is similar to that in Ireland). This is followed by an account of the geology and main hydrogeological characteristics of aquifers in Ireland. The main part of the chapter covers an analysis of the distribution of Irish holy wells according to their physiography, geology, aquifers and groundwater vulnerability. This analysis was performed using a geographical information system (GIS).

## 3.1 Introduction

### 3.1.1 Previous hydrogeological studies of holy wells and spa wells in Britain

A detailed hydrogeological characterisation of holy wells has not been attempted previously. Indeed, very few of the many books and papers on holy wells pay much attention to their geological surroundings. One of the few texts to refer to geology is the historical account of (mainly English) holy wells by Rattue (1995), in which he considered the density of holy wells by county. In the case of Dorset, he included a map showing the distribution of holy wells by geology and observed that wells are most abundant in formations such as the Lias clays and Oolitic limestones, and less common in the chalk and in sand and gravel. He then extrapolated these observations to the east of England to explain the relative scarcity of holy wells there: 'Considering that the whole of eastern England is composed of gravels, chalks and sands – apart from the Kentish Weald, always sparsely inhabited – this, coupled with lower rainfall, must account for some of its scarcity of wells'. From a hydrogeological perspective, this deduction is somewhat surprising, as the chalk is the main aquifer of England, accounting for over half of the groundwater withdrawals for public water supply (and a higher proportion in east and southeast England; Environment Agency, 2007).

Perhaps the low density of holy wells observed by Rattue (1995) in chalk is partly a reflection of the relatively deep water tables that sometimes occur in the chalk aquifer where it occupies high ground (as in the Chiltern Hills and the North and South Downs). However, this explanation would not apply to sands and gravel aquifers which normally are found in river valleys and have

shallow water tables. Whilst, clearly, there are many other, non-hydrogeological, factors that can account for the distribution of holy wells, including population density, soil type and land use – and also differences in the survival rates of wells in different regions - Mather (2016) in a more recent article gives a possible explanation for the lower density of holy wells in the more productive aquifers. He presents a table showing the density of holy wells by region in England and Wales (using data from Harte, 2008), together with an indication of the geology of each region. Mather uses just three geology divisions: basement, older cover and younger cover. The basement is described as comprising hard rocks of low permeability; the older cover comprises hard rocks with minor aquifers (presumably Devonian, Carboniferous and other pre-Permian sedimentary rocks); and the younger cover comprises Permian to Quaternary deposits, which thus includes the main aquifer formations – namely, the Sherwood Sandstone, chalk, greensands and sands and gravels. Mather notes that the density of holy wells is highest in Cornwall and Wales (18 and 17 wells per 250 square miles, respectively), and lowest in the east and southeast of England (1.5 to 3.1 wells per 250 square miles). He attributes these variations to the influence of geology: the aquifer characteristics are poorer and groundwater is less abundant in Cornwall and Wales, and hence, it is argued, good wells would have been more strongly valued than in the east and southeast, where groundwater supplies are more abundant. However, it is also possible that the densities of holy wells are higher in southwest England and Wales for other reasons, including a stronger legacy of Iron Age influences in these regions. The density of holy wells in England and Wales is discussed further in Section 3.3.6, where it is compared with the distribution in Ireland.

In contrast to holy wells, spa sites in Britain have been subjected to far greater hydrogeological scrutiny. Banks (1997) described the hydrogeological settings and hydrochemistry of many of the spas of England, whilst Mather (2013) has made a hydrogeological appraisal of spa wells in Britain and provides a general hydrogeological grouping (as will be discussed below). Existing or former spas described by Banks include the saline springs of Mercia and Cheshire (with geologies characterised by evaporite deposits), the Carboniferous limestone spas in the Peak District of Derbyshire and South Yorkshire, and the spa wells around London - there were more than 30 in this area alone, mainly supplied from shallow gravel aquifers or from sandy horizons within the London Clay; the hydrogeological setting of one of these sites, the heavily mineralised ‘purging wells’ at Shooter’s Hill in Kent, has been described subsequently by Mather and Duffin (2017). Banks (1997) also included a detailed account of the thermal spa at Bath; this is ‘probably the oldest and certainly the best known of the English spas’, and dates from Roman times (but

with evidence of settlement there going back perhaps as far as 5000 BCE). The history of geochemistry and the origins of the water at Bath are described further by Edmunds (2004).

Many of the spa wells in Britain were originally free-flowing springs, but were converted into wells by the construction of lined tanks from which the water was withdrawn (Mather, 2013). The hydrogeological settings of 14 heritage spa sites are considered by Mather (2013). They range from iron-rich chalybeate springs issuing from Lower Cretaceous sand beds in the Weald at Tunbridge Wells (described in detail by Fuller, 2004), to thermal springs originating from the deep (>2000 m) confined Carboniferous limestone aquifer below Bath (this 10,000 year old water reaches the surface via gravels which infill hollows in the Mesozoic sediments that overly the limestones), and to potable, low mineralisation waters issuing from a shallow aquifer within Precambrian metamorphic rocks at Great Malvern.

Mather (2013) divides the heritage spas in Britain into three groups: 1) those spa locations strongly influenced by distinctive hydrogeological conditions at that site; 2) spa locations that have less distinctive hydrogeology, but rather owe their origins to factors such as local entrepreneurial initiatives or chance; and 3) spa locations that owe their origins to human interference with groundwater flow systems through mining or mineral exploration. The first group is characterised by long flow paths, and by very old and highly mineralised waters, and includes the spa springs at Bath and Buxton. The second group is the largest group in Britain, encompasses many different water types, and includes the chalybeate springs (rich in hydrous iron oxides) at Tunbridge wells and the shallow fresh water springs at Great Malvern. An example of the third group is the surface discharge of mineralized water at Woodhall Spa from a coal exploration shaft that was constructed in the early 19$^{th}$ century.

The hydrogeological settings of the Scottish hydropathic sites established during the 19$^{th}$ century are varied, with the largest number tapping Devonian sandstone aquifers (9 out of 20 sites) and smaller numbers exploiting Dalradian and Lower Palaeozoic metamorphic aquifers (seven sites), and Carboniferous limestone or Permian sandstone aquifers (four establishments; Spence and Robins, 2004). Unlike many of the heritage spas in Britain or continental Europe, where the waters are heavily mineralised (see Mather's first grouping above), Spence and Robins (2004) point out that the groundwaters at these hydropathic establishments are only weakly or moderately mineralised, and their chemistries are typical of other Scottish groundwaters.

### 3.1.2 Previous hydrogeological studies of holy wells and spa wells in Ireland

The only previous hydrogeological study of holy wells in Ireland was a taught-course MSc project by Buckley (2012), carried out under the supervision of this author. Buckley sampled 12 holy wells (and three spa wells) for major ions and 10 minor ions or trace elements. Although the results were generally inconclusive in terms of establishing links between the chemical characteristics of the water and the reputed health benefits, perhaps Buckley's most interesting observations were in relation to elevated lithium in Tobar na nGealt near Camp in County Kerry and in the Swanlinbar spa well in County Cavan. Both Tobar na nGealt and the spa well at Swanlinbar have a reputation for curing mental health problems: the links between lithium and mental health are well known to medical practitioners, as lithium is used for treating mood disorders and it may also reduce the risk of dementia (Terao *et al*., 2014; see Section 6.2.2). The reported elevated lithium in Tobar na nGealt, and the stories surrounding health cures at the well, were also the subject of a documentary broadcast on TG4 in late 2012 (Buckley's dissertation included the results of lithium analyses carried out by Southern Scientific, which were referred to in that programme).

There have been a number of hydrogeological studies relating to Irish spa wells, including those spa wells known for their thermal waters. Aldwell and Burdon (1980) described hydrogeothermal conditions in Ireland, with accounts of the chemistry and possible origins of the thermal waters at sites such as Mallow Spa and the many warm springs in Leinster, including those at Louisa Bridge in County Kildare, and St Gorman's holy well near Enfield in County Meath. The water chemistry of the spa well in Mallow (known as Lady's well because the spa developed at the site of a former holy well) was monitored in the 1980s by Brück *et al*. (1986), whilst the thermal wells in Leinster (including the spa well in Leixlip and St Gorman's well in Co Meath) were studied more recently by Blake as part of her doctoral research programme (Blake *et al*., 2016).

Apart from the thermal spa wells and springs mentioned above, probably the best known former spa wells in Ireland are those at Lisdoonvarna in County Clare (Foley, 2010). A brief account of the geology and hydrogeology of these wells was given by Drew (2001). The wells are characterised by having different chemical characteristics, as indicated by their different names: sulphur, chalybeate (i.e. iron-rich), copperas (i.e. copper-rich) and magnesia wells.

The different wells referred to in this section – including Tobar na nGealt in Kerry, St Gorman's well in Meath and the former spa wells at Swanlinbar, Mallow, Leixlip and Lisdoonvarna – were also visited and sampled during the present research project, and therefore are described further in the relevant sections of Chapters 5, 6 and 7.

## 3.2 Background to Ireland's geology and hydrogeology

The geology of the Republic of Ireland comprises Precambrian and Palaeozoic bedrock overlain by a varied overburden. The Precambrian and Lower Palaeozoic rocks include igneous intrusives, volcanic rocks, metasediments, shales and sandstones, whilst the Upper Palaeozoic (Carboniferous) contains the country's main limestone formations (Holland and Sanders, 2009). The older rocks generally form a rim of higher ground around the coast, with mountains composed of granite and quartzite rising to about 1000 m above Ordnance Datum (OD). The Carboniferous limestones mainly occupy lower ground in the Midlands and west, typically at elevations of 50 to 200 m OD, although the famous limestone hills of the Burren in County Clare achieve elevations above 300 m OD.

There are more than 1400 bedrock geological formations and stratigraphic members mapped in Ireland (Drew, 2018). The Groundwater Division of the Geological Survey of Ireland (GSI) has combined these into 27 rock units using characteristics that are relevant to their hydrogeology including the type of permeability, the nature of the bedding and, in the case of carbonate rocks, their relative purity (GSI, 2009). Thus the main Ordovician metasediments, in which weathering and open fractures are generally restricted to their upper few metres, and which therefore generally possess poor aquifer properties, are distinguished from the Ordovician volcanics which are characterised by more extensive fracture and groundwater flow systems that can provide much more productive aquifers. In the case of the Silurian bedrock, the relatively minor volcanics are included within the Silurian metasediments and volcanics unit as they have similar hydrogeological properties. Within the carbonate rocks, 'impure' limestones are distinguished from 'pure' limestones, and the latter comprise two main units according to whether they are well-bedded (and hence potentially more fractured and with greater karstification potential) or massive unbedded formations. The main Groundwater Rock Unit Groups (GRUGs) are shown in Figure 3.1.

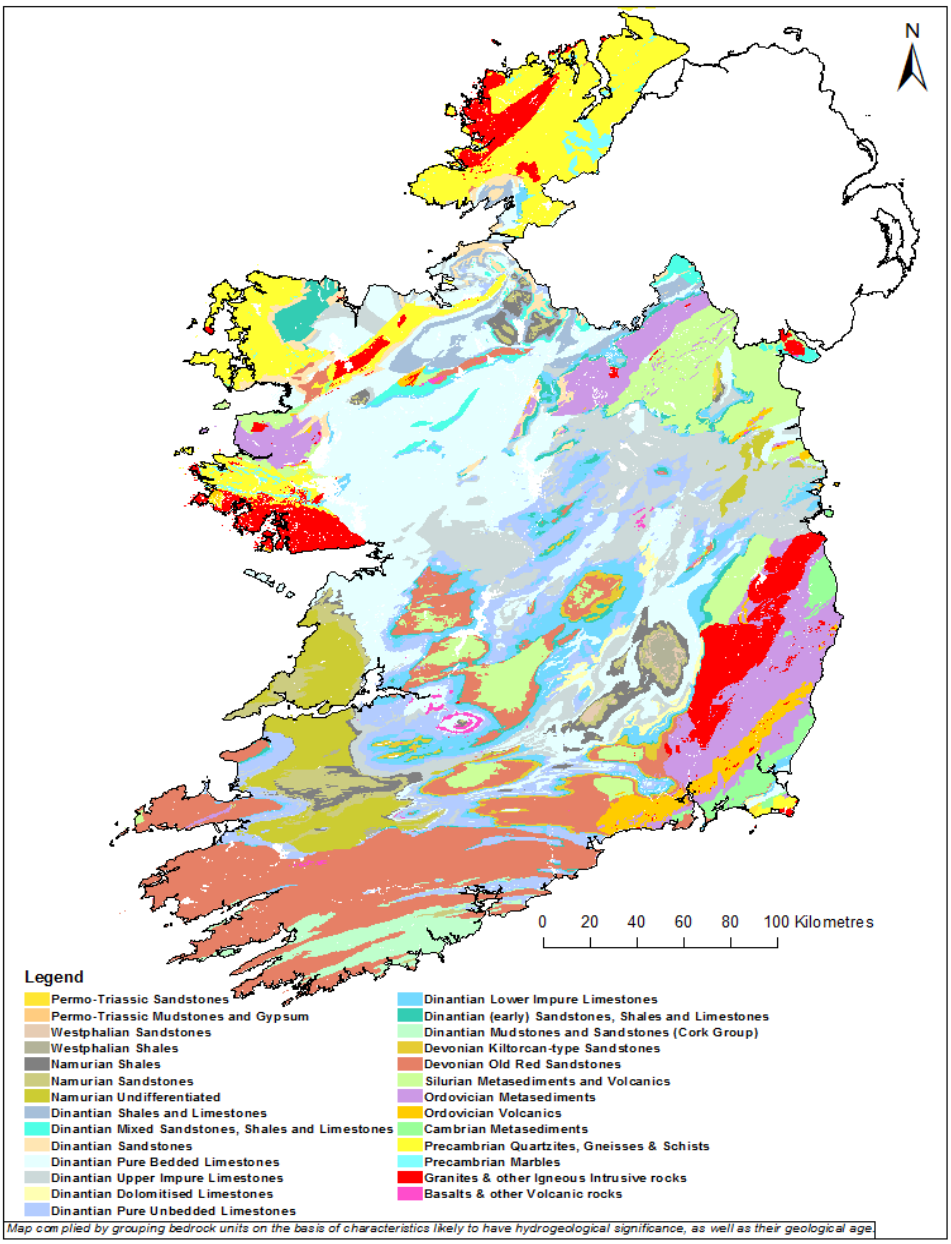



Figure 3.1 Simplified bedrock geology map of Ireland, showing the Groundwater Rock Unit Groups (Geological Survey of Ireland)

The overburden consists of glacial deposits, alluvium, lacustrine deposits and peat. The glacial deposits include tills and glacio-fluvial sands and gravels, and often form prominent landscape features such as drumlins and eskers.

It is helpful to group geological formations into a small number of lithological groups when describing their main hydrogeological and hydrochemical characteristics (Table 3.1 and Figure 3.2). The most productive aquifers in the country occur within the Carboniferous limestones

('pure limestones' in Figure 3.2), Devonian sandstones (part of the non-calcareous sedimentary lithological grouping), Ordovician volcanic formations (especially those in County Waterford, within the igneous lithological grouping), and in sands and gravels. The aquifers are classified into three main classes and ten sub-classes according to their extent and productivity (Table 3.2). For more detail on the classification criteria, the reader is referred to Geological Survey of Ireland (2009).

Table 3.1 Main lithological groups and Groundwater Rock Unit Groups (based on GSI 2009 and Tedd *et al*., 2017)

| *Lithological group* | *Groundwater Rock Unit Group* |
|---|---|
| Impure limestones | Dinantian (early) sandstones, shales and limestones |
| | Dinantian lower impure limestones |
| | Dinantian mixed sandstones, shales and limestones |
| | Dinantian shales and limestones |
| | Dinantian upper impure limestones |
| Pure limestones | Dinantian pure bedded limestones |
| | Dinantian pure unbedded limestones |
| | Dinantian dolomitised limestones |
| Non-calcareous sedimentary | Devonian Kiltorcan-type sandstones |
| | Devonian Old Red Sandstones |
| | Dinantian mudstones and sandstones (Cork Group) |
| | Dinantian sandstones |
| | Namurian shales |
| | Namurian sandstones |
| | Namurian undifferentiated |
| | Permo-Triassic sandstones |
| | Permo-Triassic mudstones and gypsum |
| | Westphalian sandstones |
| | Westphalian shales |
| Igneous | Basalts and other volcanic rocks |
| | Granites and other igneous intrusive rocks |
| | Ordovician volcanics |
| Metamorphic | Cambrian metasediments |
| | Ordovician metasediments |
| | Precambrian quartzites, gneisses and schists |
| | Precambrian marble |
| | Silurian metasediments and volcanics |

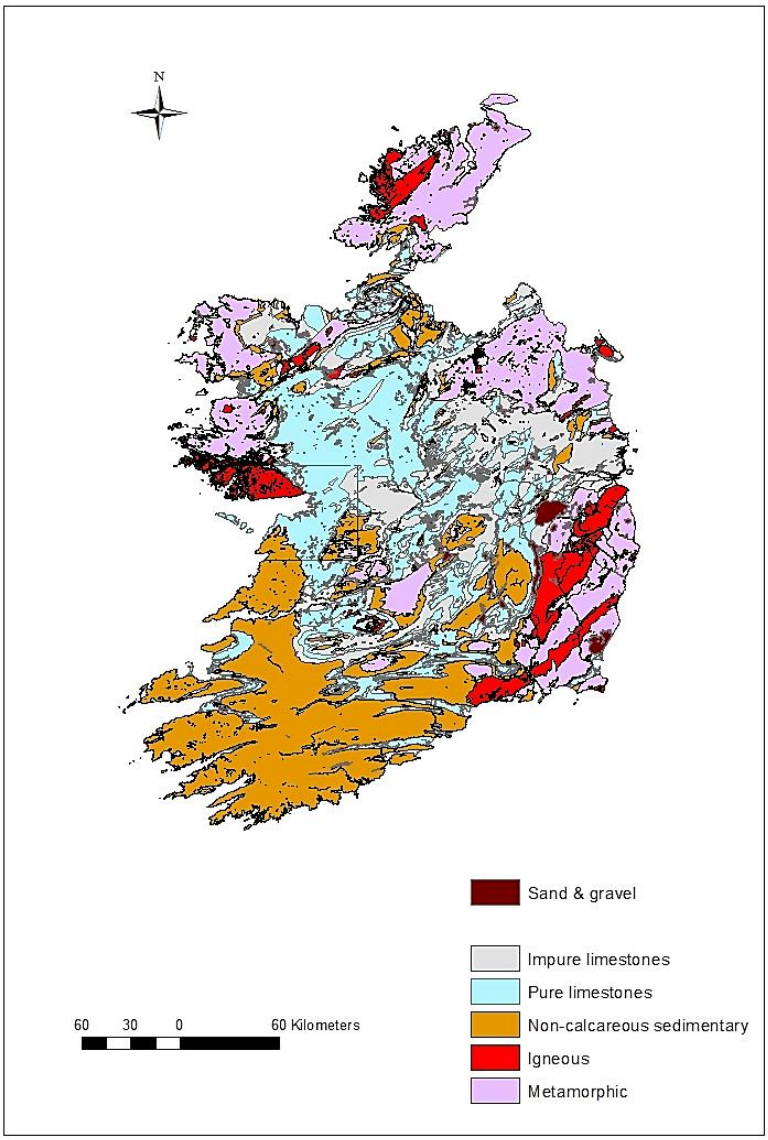



Figure 3.2 Simplified geology of Ireland showing the main lithological groups. (Map prepared in ArcGIS using GSI shapefiles)

The distribution of the main aquifer classes is illustrated in Figure 3.3. It can be seen from the map that about two-thirds of the country is underlain by aquifers that can be described as 'poorly productive' – a grouping that comprises the Pu, Pl and Ll classes in Table 3.2 (Moe *et al*., 2010). Although the most productive aquifers are restricted to certain areas of the country (especially parts of the Midlands and south), this is not reflected in the distribution of wells: low-yielding private wells occur in all aquifer types across the land (Hynds *et al*., 2013), and it might be expected that holy wells will be found in most lithologies too (as will be shown in Section 3.3).

Table 3.2 Aquifer classification in the Republic of Ireland (updated from Misstear and Daly, 2000)

| | *Regionally Important (R)* | Locally Important (L) | Poor (P) Aquifers |
|---|---|---|---|
| Sub-categories | • Karstified aquifers where conduit flow is dominant (Rkc)<br>• Karstified aquifers where flow is mainly diffuse (RKd)<br>• Fractured bedrock aquifers (Rf)<br>• Extensive sand/gravel aquifers (Rg) | • Sand/gravel (Lg)<br>• Generally moderately productive (Lm)<br>• Moderately productive only in local zones (Ll)<br>• Locally important karstified (Lk) | • Generally unproductive except for local zones (Pl)<br>• Generally unproductive (Pu) |
| Criteria for main aquifer categories (selected criteria only) | Areal extent > 25 $km^2$ | Areal extent < 25 $km^2$ | |
| | Well yields > 400 $m^3 d^{-1}$ | Well yields 100 - 400 $m^3 d^{-1}$ (or higher yields where aquifer extent is < 25 $km^2$) | Well yields generally < 100 $m^3 d^{-1}$ (and < 40 $m^3 d^{-1}$ in Pu sub-category) |
| | Specific capacities > 40 $m^3 d^{-1} m^{-1}$ | | |
| | Occurrence of large springs | Some large springs (Lm & Lk) | No large springs |
| Examples | Quaternary sand and gravel (where extensive) | Quaternary sand and gravel (local deposits) | Glacial till |
| | Wexford Limestone Formation | Westphalian sandstones | |
| | Ballyadams/Culahill Limestone | Lucan Formation (Calp) limestones (Midlands/east) | Ballysteen Limestone (Midlands) |
| | Waulsortian Limestone (South) | Waulsortian Limestone (North) | |
| | Kiltorcan Sandstone | Old Red Sandstone (except Kiltorcan Sandstone) | |
| | Ordovician volcanics (Waterford) | | |
| | | | Lower Palaeozoic sediments |
| | | | Precambrian and Lower Palaeozoic granites and metamorphics |

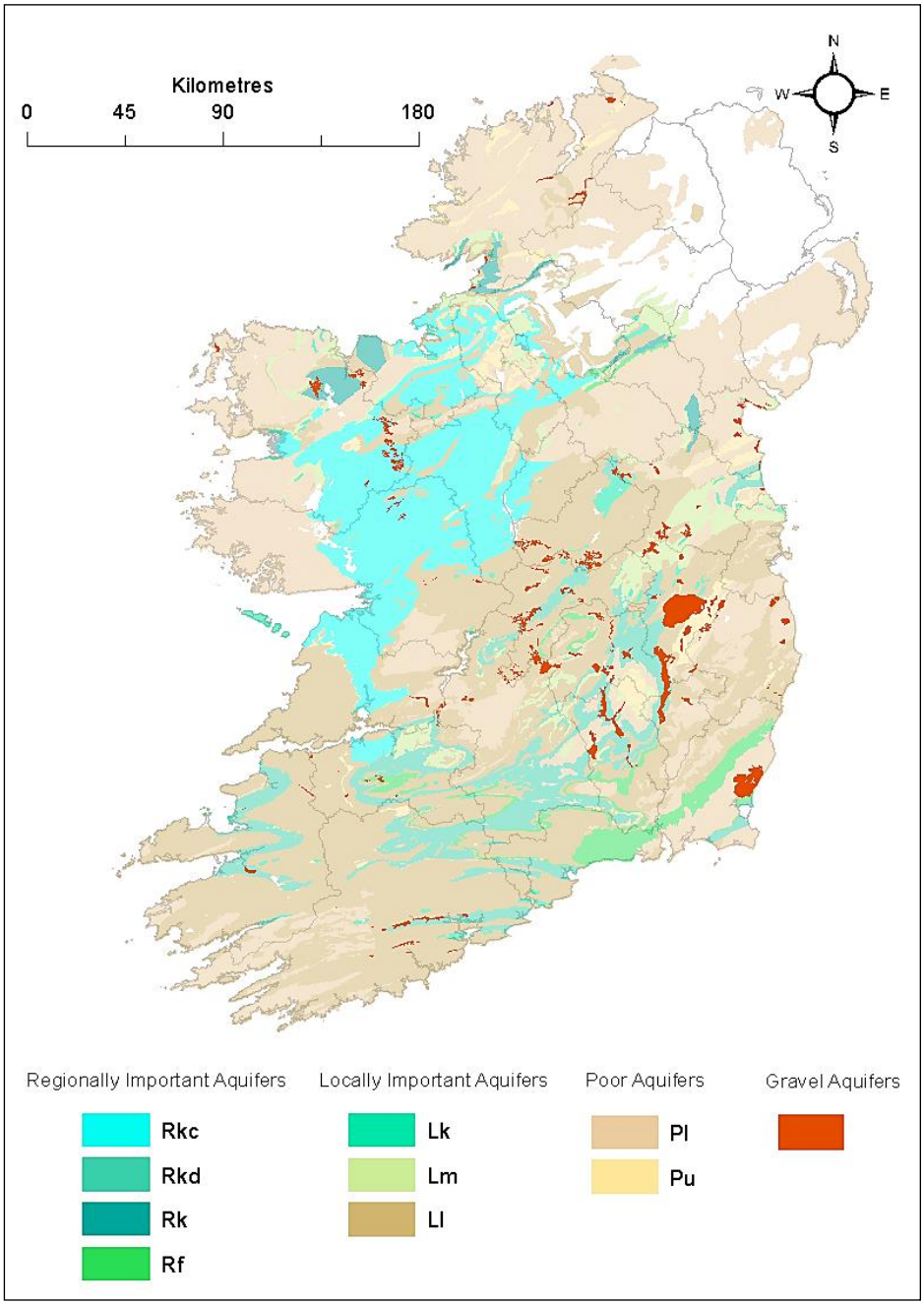



Figure 3.3 Aquifer map of Ireland (Geological Survey of Ireland)

So far, the main lithological units, aquifers and aquifer classes in Ireland have been discussed (albeit briefly), but not their groundwater flow characteristics. Whereas the sand and gravel aquifers possess primary porosity and permeability, the bedrock aquifers are characterised by secondary porosity and permeability, with groundwater flow occurring only within the fracture systems produced by jointing (including bedding plane joints) and/or faulting. The frequency

and characteristics of joints and faults are influenced by aspects of the geology such as rock type, bed thickness, and the stresses and strains to which the rocks have been subjected (Dunphy, 2003; Hunter Williams *et al*., 2019). In the carbonate rocks, some of the fracture apertures have been enhanced through dissolution of soluble calcium carbonate by groundwater, which tends to be slightly acidic close to recharge areas. This dissolution process can lead to the development of major karst features such as those that form the dramatic Burren landscape in Counties Clare and Galway (Drew, 2018). Even where karstification is not evident on the land surface, it may be present at depth, and some of Ireland's highest yielding wells and largest springs are found in karst aquifer systems. Another process that can enhance aquifer permeability is dolomitisation, in which calcium carbonate (calcite) mineral is replaced by calcium-magnesium carbonate (dolomite). Dolomite has a smaller crystal structure than calcite and hence dolomitisation can lead to an increase in porosity and permeability. Dolomites, therefore, can exhibit some of the characteristics of primary porosity and permeability aquifers. In addition to dolomites, a further example of a bedrock aquifer possessing some primary - as well as fissure - permeability is the Devonian Kiltorcan-type sandstone unit (Hunter Williams *et al*., 2019).

Groundwater circulation within the most productive limestone aquifers can occur to depths of several tens or even several hundreds of metres. In contrast, deep groundwater flow paths are rare in the low permeability crystalline and clayey sedimentary or metasedimentary rocks that make up the poorly productive aquifers, and flow is mainly restricted to shallow depths where fractures and weathering tend to be most developed. Recent research has highlighted the important role of the so-called *transition zone* in the flow of groundwater (and pollutants) in such aquifers (Comte *et al*., 2012; Archbold *et al*., 2016). The transition zone is a highly weathered zone of broken rock mixed with soil or subsoil (Figure 3.4). Interest in the transition zone is such that the Geological Survey of Ireland have launched an on-line story map with more than 80 illustrations of the transition zone in different geological settings[7]. As noted by Hunter Williams *et al*. (2019), the water in the transition zone may be perched above the main aquifer water table, and may frequently be dry. For the present research it was anticipated that the transition zone would be an important hydrogeological feature at many of the holy wells and springs located in poorly productive aquifers, and this indeed was found to be the case (see Chapter 5).

[7] Available at http://j.mp/groundwaterstorymap (accessed 5/1/2021)

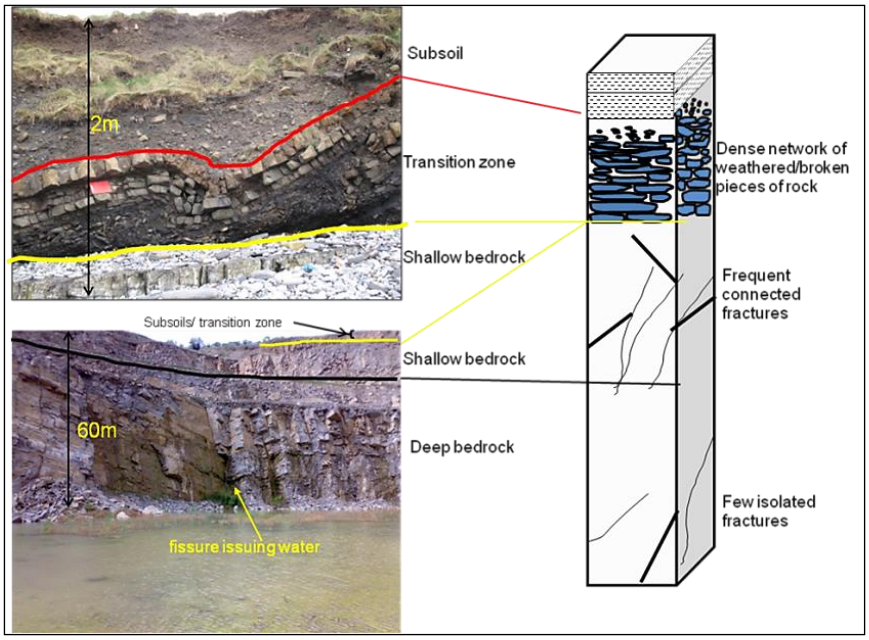



Figure 3.4 Groundwater pathways in fractured bedrock aquifers overlain by subsoils at two contrasting scales (top photograph by Monika Kabza and bottom photograph by Robert Meehan). In the bottom photograph, the subsoils and transition zone occupy a 1-3m zone above the shallow bedrock (from Kelly *et al*., 2015)

Apart from the limited groundwater circulation at depth, in poorly productive aquifers the flow path *length* is also restricted. Studies by Fitzsimons *et al*. (2005), RPS (2008) and Tedd *et al*. (2015) have estimated horizontal flow paths in these PPAs of between 50 and 800 m. These estimates are based both on surface drainage density (by taking half the average stream separation distance in the study catchments as being equal to the distance from the groundwater divide to the stream) and on Darcy throughflow calculations, using typical values of recharge rates, transmissivity values and hydraulic gradients.

The superficial deposits have a significant hydrogeological role even where they do not form aquifers themselves, in that they provide a protective cover to the underlying bedrock aquifers. The national groundwater protection scheme divides vulnerability into four categories, based mainly on the thickness and permeability of the subsoil cover: Extreme, High, Moderate and Low (Daly and Warren, 1998; DoELG *et al*., 1999; Misstear and Daly, 2000). Other factors that determine vulnerability are the type of recharge (point or diffuse), the presence of karst features and the presence of an unsaturated zone (Table 3.3). Of the various factors that influence vulnerability, modelling studies by Fitzsimons and Misstear (2006) showed that subsoil

permeability is especially important. Several of the features that control groundwater vulnerability also influence aquifer recharge, including subsoil thickness and permeability, and a methodology has been developed that uses GIS-based vulnerability mapping to produce recharge maps (Misstear *et al*., 2009a; Hunter Williams *et al*., 2013).

Table 3.3 Aquifer vulnerability classes (after DoELG *et al*., 1999)

| Vulnerability Rating | Hydrogeological conditions | | | | |
|---|---|---|---|---|---|
| | Subsoil permeability and thickness | | | Unsaturated zone (sand/gravel aquifers only) | Karst features (<30 m radius) |
| | High permeability | Moderate permeability | Low permeability | | |
| Extreme | 0 - 3.0 m | 0 - 3.0 m | 0 – 3.0 m | 0 - 3.0 m | Yes |
| High | >3.0 m | 3.0 - 10.0 m | 3.0 - 5.0 m | >3.0 m | N/A |
| Moderate | N/A | >10.0 m | 5.0 - 10.0 | N/A | N/A |
| Low | N/A | N/A | >10.0 m | N/A | N/A |

Note N/A = not applicable.

## 3.3 Hydrogeological characterisation of Irish holy wells using GIS

### 3.3.1 Methodology

An analysis of the distribution of holy wells was carried out using ArcGIS with ArcMap 10.3 (and subsequently ArcMap 10.7). The data on holy wells were contained in a National Monuments shape file – this had data on 2996 wells, for which grid references were available for 2676 wells[8]. The analyses were performed using only those wells that had grid references. The distribution of holy wells was investigated by:

- county
- elevation
- physiographic unit
- bedrock unit
- main lithological grouping

[8] Source: National Monuments Service, Department of Arts, Heritage, Regional, Rural and Gaeltacht Affairs. Licensed for reuse under Creative Commons Attribution 4.0 International licence

- aquifer category
- groundwater vulnerability

The geological information, comprising shape files for the various GIS layers, were sourced from the Web Viewer on the Geological Survey of Ireland website[9]. The shape files were all in vector (polygon) format. The shapefile with the elevation data, which was in raster format, was obtained from Dr R Foley at Maynooth University[10].

An attributes table containing the topographical and geological information for the holy wells was built up during the GIS analysis. The process can be illustrated by taking bedrock geology as an example. The shapefile showing the bedrock geology was opened in ArcMap 10.3, and the shapefile with the holy wells was then added. A new field 'Bedrock Unit' was added to the attributes table of the holy wells layer. A particular bedrock unit such as Ordovician volcanics was selected from the bedrock map (using 'Select by Attributes' and the 'Lithological Group =' commands). The holy wells layer was then highlighted as the target layer and, using the 'Select by Location' command, the wells that 'are within the source layer feature' (in this case the Ordovician volcanics) of the source layer (the bedrock map) were identified. The attributes table for the wells layer was opened and, using the 'Field Calculator' option, the relevant bedrock label (in this example Ordovician volcanics) was added to the Bedrock Unit field. This process was repeated for all 27 lithological units in the bedrock map layer.

A similar process was carried out for the other features analysed in the GIS. In the case of sands and gravels, these are mapped as a separate GIS layer to the bedrock units. Using the attributes table for the holy wells layer, the sand and gravel wells (n= 49) were subtracted from the list of bedrock wells to avoid double counting. Similarly, areas of sands and gravels were deducted from areas of bedrock units when looking at the main lithological groupings of wells by area (see Section 3.3.6).

The shapefile with elevation data was in raster format. In order to perform a similar analysis to that described above for the geological layers, the raster file was converted into a vector

[9] http://www.dccae.gov.ie/en-ie/natural-resources/topics/Geological-Survey-of-Ireland/data/Pages/Data-Downloads.aspx

[10] This was a 90 m resolution GRID layer, downloaded from a global model devised jointly by NASA and the Japanese Agency METI through their product ASTER - Advanced Spaceborne Thermal Emission and Reflection Radiometer: https://asterweb.jpl.nasa.gov/gdem.asp).

(polygon) file. As the original raster file was rather large (nearly 7 million cells), it was first reclassified into a simpler raster file by defining 10 elevation bands, and this new file was then converted into a vector file which enabled the 'Select by Attributes' process to be followed. The reclassification and file conversion actions were performed using the Arc Tool Box 'Spatial Analyst' and 'Conversion Tools' functions.

The results of the GIS analysis are described in the following paragraphs. It is worth adding a few caveats here:

a) Not all holy wells are included in the analysis. As mentioned above, the 320 wells without grid references were excluded. Moreover, not all holy wells are included in the full National Monuments database.
b) The analysis was carried out for the Republic of Ireland only.
c) The distribution of a small number of the wells was not picked up in each analysis. Thus, for example, of the 2676 wells with grid references analysed for bedrock geology, a total of 101 wells were not included. The number of omissions in the different analyses varied from 48 to 107, representing only 1.8 to 4% of the total. In most cases, these appeared to be wells on shorelines or other map boundaries.
d) The resolution of the digital maps and the original geological mapping will have had an influence on the accuracy of the analysis, as will the accuracy of the locations of the holy wells. For example, the raster file with the elevation data had a cell size of 84 m x 84 m, whilst the bedrock geology layer in the GSI Groundwater Viewer is based on mapping at a scale of 1:100,000.

The distribution of holy wells across the Republic of Ireland is shown in Figure 3.5. The distribution by counties is discussed in the next section.

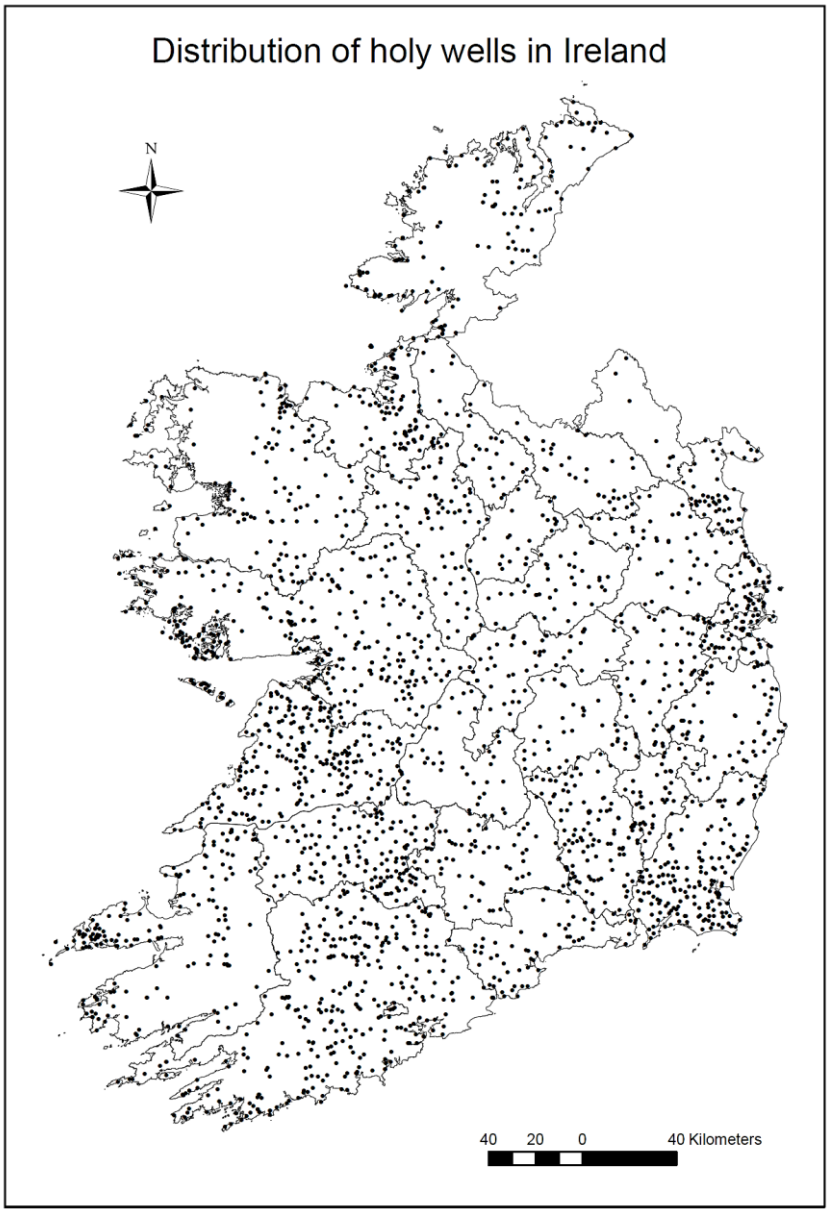
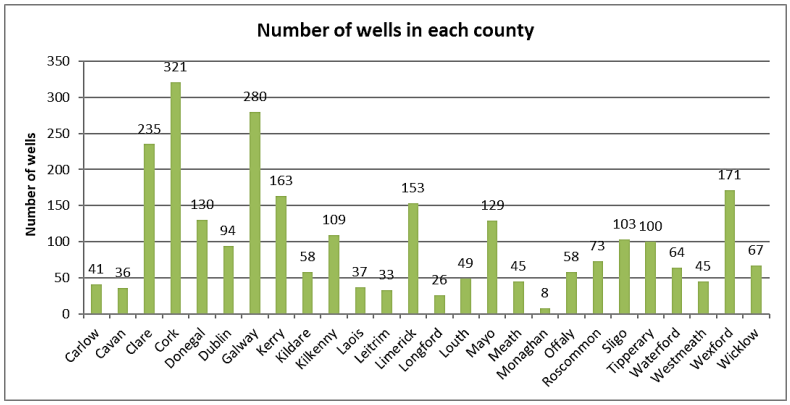


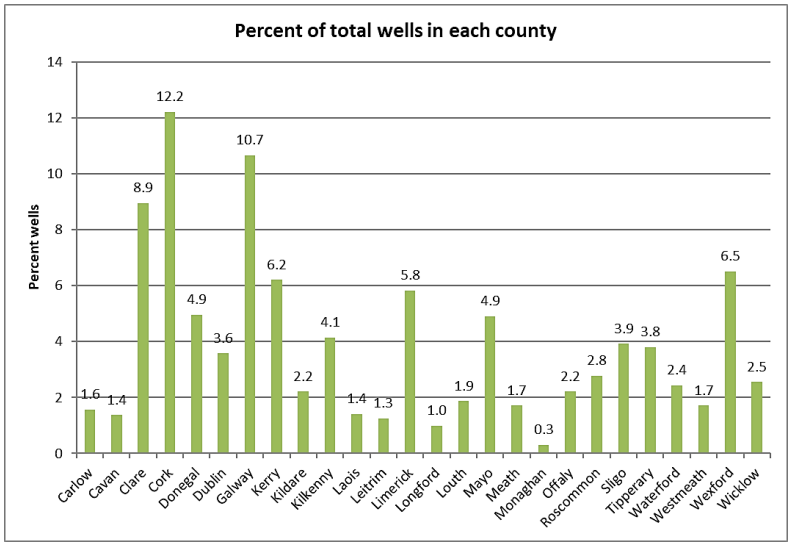

Figure 3.5 Distribution of holy wells in the Republic of Ireland (based on GIS shape file from the National Monuments Service)

### 3.3.2 Distribution of wells by county

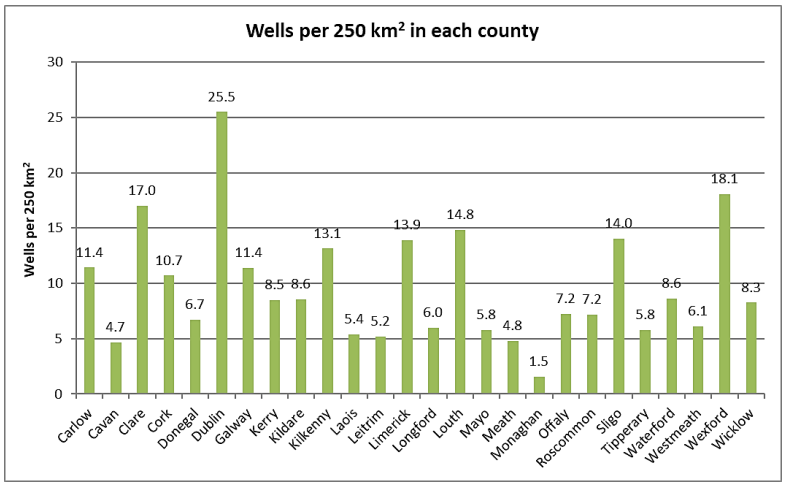
The distribution of wells by county is shown in Figure 3.6, with the lower graph showing the number of wells per 250 km$^2$ in each county. The largest number of wells is in County Cork (321), and the lowest in County Monaghan (8).




a)




b)




c)

Figure 3.6 Holy wells by county: a) number of wells in each county; b) percent of total wells in each county; c) wells per 250 km$^2$ (n = 2628)

The distribution of holy wells is compared with historical population density in Figure 3.7. The population data were obtained from Irish Historical Statistics (Vaughan and Fitzpatrick, 1978), and were from the 1841 census i.e. before the major depopulation caused by the Great Famine. (The data were normalised by this writer to population per km$^2$). Obviously, population densities will have varied over the centuries, but it is interesting to note, for example, that whereas the highest well and population densities were both found in Dublin, the lowest well frequency is in Co Monaghan which actually had a relatively high population density. This suggests that other factors, including geology, have an important bearing on the frequency of holy wells.

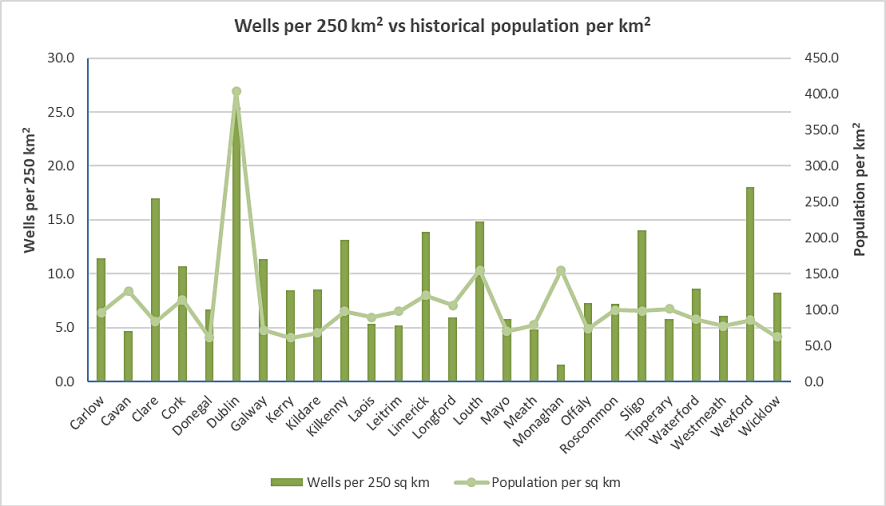



Figure 3.7 Holy wells per 250 km$^2$ versus historical population per km$^2$ in each county (n = 2628)

The distribution of holy wells by region in England and Wales is shown in Figure 3.8. This graph has been prepared by adapting a table in Mather (2016), in which he presented the well frequencies as wells per 250 square miles (converted to wells per 250 km$^2$ in Figure 3.8), using source data from Harte (2008). As noted in Section 3.1, the density is highest in Wales and the west country, and lowest in the east and south. The average density of holy wells in England and Wales is 2.4 holy wells per 250 km$^2$. This is much lower than the mean density in Ireland of about 9.4 holy wells per 250 km$^2$, where the frequency varies from 1.5 wells per 250 km$^2$ in Monaghan to 25.5 wells per 250 km$^2$ in Dublin. Possible explanations for the different frequencies of holy wells are discussed in Section 3.3.6 below.

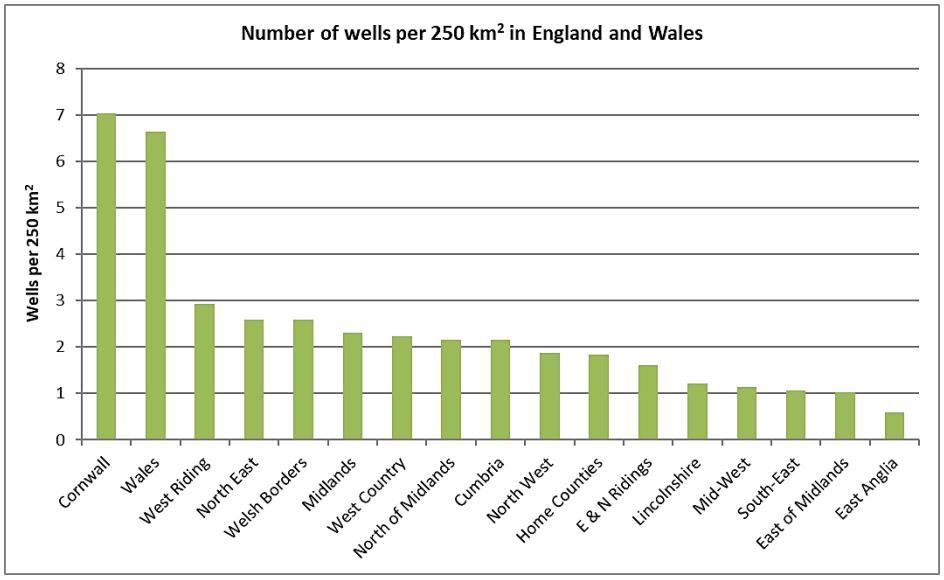



Figure 3.8 Occurrence of holy wells in England and Wales (based on data in Mather, 2016)

### 3.3.3 Distribution of wells by elevation

The distribution of holy wells according to topographic elevation is illustrated in Figure 3.9.

From the analysis of wells by topographic elevation (Figure 3.10), 74% of wells are at elevations between sea level and 100 m OD. Of the 19 the wells identified as having elevations below Ordnance Datum, all of these, as expected, are shoreline wells: six in Kerry, five Donegal, three Cork, two each in Waterford and Galway, and one in Wexford. One of these 19 wells is on an island – Baile Iarthach Thuaidh in County Cork. In addition, many of the 958 wells in the 0 - 50 m OD elevation range are at or close to shorelines. From a hydrogeological perspective, the location of wells close to the seashore, and often close to the high water level mark or in the intertidal zone, is not surprising, since groundwater, being less dense than sea water, often discharges to the sea in such areas and hence is easily accessible as a spring or via a shallow well. St Colman's well at Salterstown and St Denis's well at Clogher, both in County Louth, are two such examples (see Section 5.10).

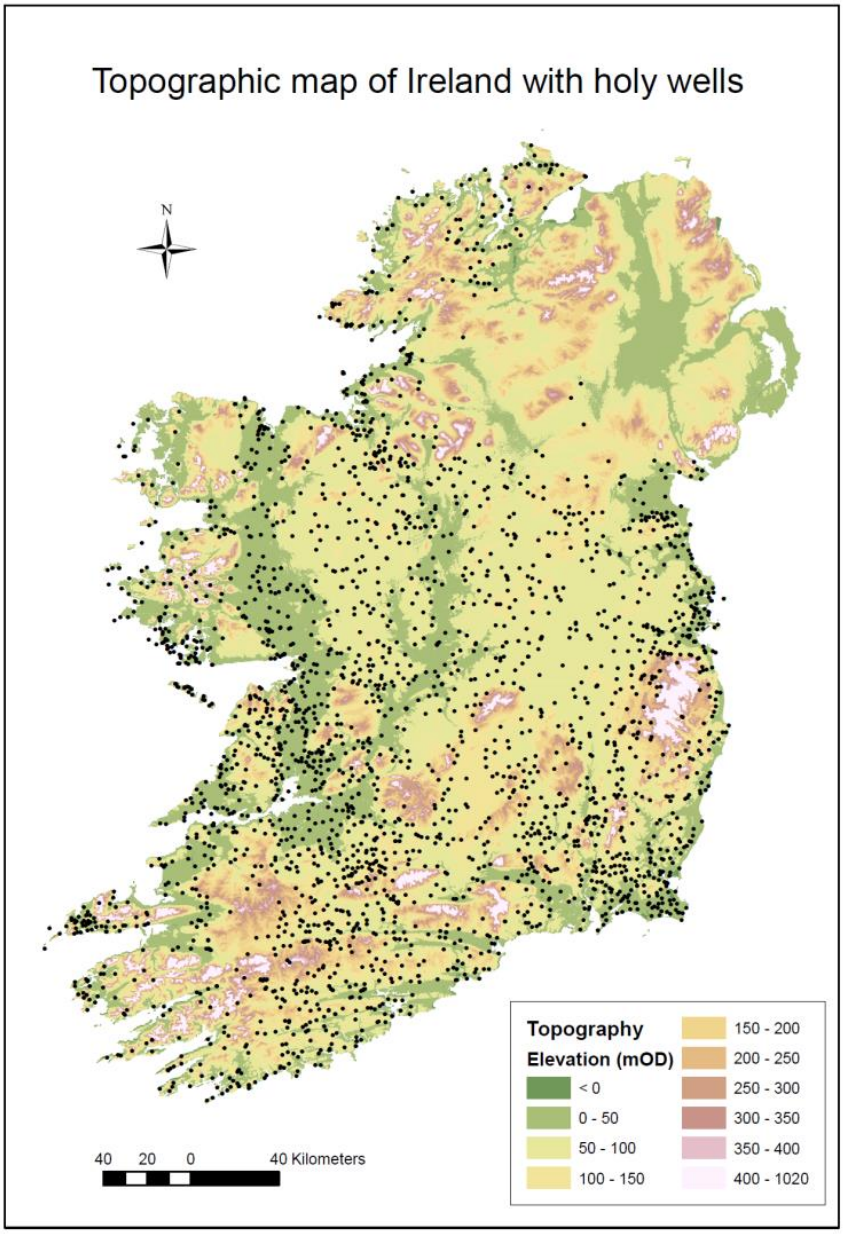
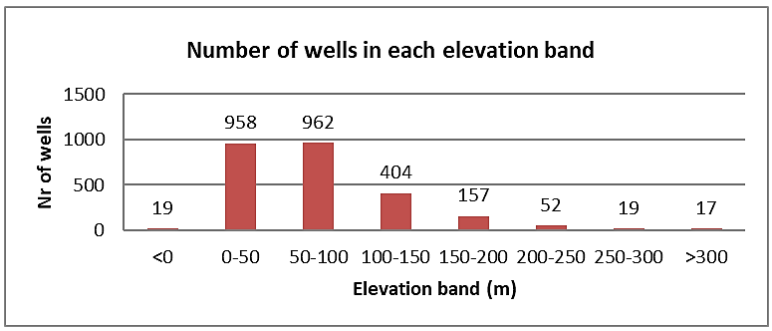


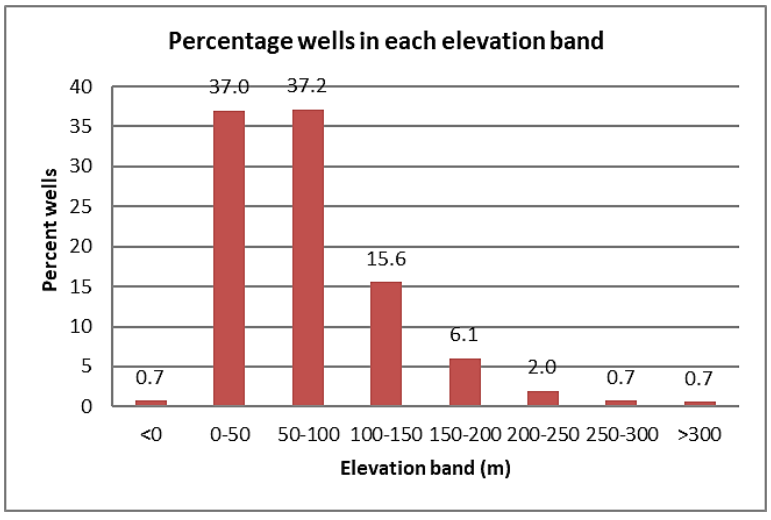

Figure 3.9 Distribution of holy wells according to topography

Ó Giolláin (2005), in discussing well locations and the earlier work of Brenneman and Brenneman (1995), mentions that 'Other than those near the Medieval parish church, most wells are either on a height or by the seashore. Many are on the tops of hills or mountains'. However, the current GIS analysis would suggest a more uniform topographical distribution, albeit that many medieval parish churches (probably the majority) probably lie in the elevation bands containing the largest numbers of wells – 90% of wells lie between sea level and 150 m OD.

Thirteen wells have elevations above 400 m OD: five in Cork, four in Donegal, two in Kerry and one each in Galway and Wicklow. Most of these are between 400 and 500 m OD. The highest well is St Brendan's well at Baile an Chnocin (Cill Chuain) on Cnoc Bréanainn (Mount Brandon) on the Dingle Peninsula, which is at approximately 950 m OD. This is part of Cosán na Naomh, the Saint's Path, a well-known pilgrim route. Unsurprisingly, in view of their hill and mountain locations, all 13 of the highest wells lie in the Extreme (mainly X) vulnerability category, indicating that bedrock is at or close (within 3 m) to the ground surface. The high elevation Cork and Kerry wells are all in Devonian Old Red Sandstone, whereas the Donegal wells are in Precambrian crystalline rocks (quartzites, gneisses and schists). The high elevation Galway well (Gowlaunlee) is in Precambrian marbles, and the Wicklow well (Ballymoney) is in Lower Palaeozoic granite. In terms of aquifer class, eleven of the elevated wells are classed as Poor (Pl or Pu) and two are in locally important Ll category.




a)




b)

Figure 3.10 Distribution of Irish holy wells according to elevation: a) number of wells in each elevation band; b) percent wells in each elevation band (n = 2588)

### 3.3.4 Distribution of holy wells by physiographic unit

In 2018 the Geological Survey of Ireland's Quaternary Programme launched a new three-tier classification of physiographic units, accompanied by maps and downloadable GIS shape files in their web viewer (GSI, 2018; Pellicer and Sheehy, 2018). As background, the GSI report notes that 'The Irish physical landscape is a geological product of the interaction between 'older' bedrock and 'younger' Quaternary sediment cover and the processes of erosion, deposition and deformation that have been acting upon them throughout Earth's history'. The three-tier classification of physiographical units represents three levels of complexity, comprising 6, 15 and 28 physiographic units, respectively. Details of how the units were derived can be found in GSI (2018), and only a brief explanation will be given here. The physiographic unit maps were compiled at 1:100,000 scale based on visual analysis of bedrock maps, Quaternary maps, digital elevation maps, and high-resolution digital globe orthophotography. The Level 1 and Level 2 classifications are shown in Table 3.4 and a national map for Level 1 is reproduced in Figure 3.11.

Table 3.4 Main physiographic units (Levels 1 and 2), also showing the number of holy wells within each unit

| Level 1 | Nr of wells | Level 2 | Nr of wells |
|---|---|---|---|
| Mountain to hill | 623 | Mountain rounded | 228 |
| | | Mountain plateau | 126 |
| | | Mountain ridge | 114 |
| | | Mountain ice-sculpted | 155 |
| Hill to rolling lowland bedrock | 480 | Hill to rolling lowland rounded bedrock | 250 |
| | | Hill to rolling lowland bedrock ridge | 230 |
| Bedrock plain | 150 | Bedrock plain | 150 |
| Rolling ice-moulded sediments | 645 | Drumlin and ribbed moraine topography | 451 |
| | | Rolling ice-moulded topography | 194 |
| Flat to undulating sediments | 588 | Flat to gently undulating ice-moulded topography | 421 |
| | | Coastal plain | 66 |
| | | Bog plain | 38 |
| | | Flat fluvial-lacustrine plain | 63 |
| Hummocky sediments | 123 | Hummocky glaciofluvial sediment topography | 120 |
| | | Hummocky to undulating aeolian sand topography | 3 |
| TOTAL | 2609 | TOTAL | 2609 |

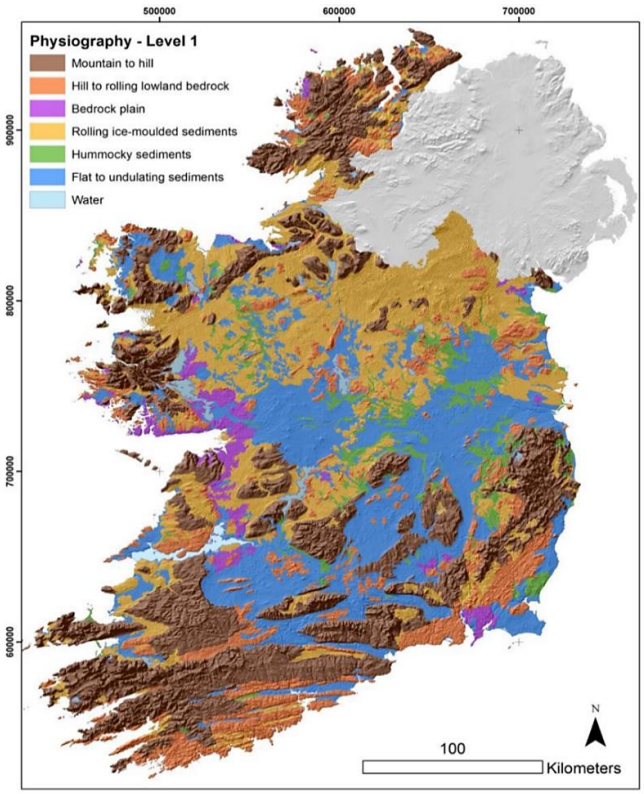
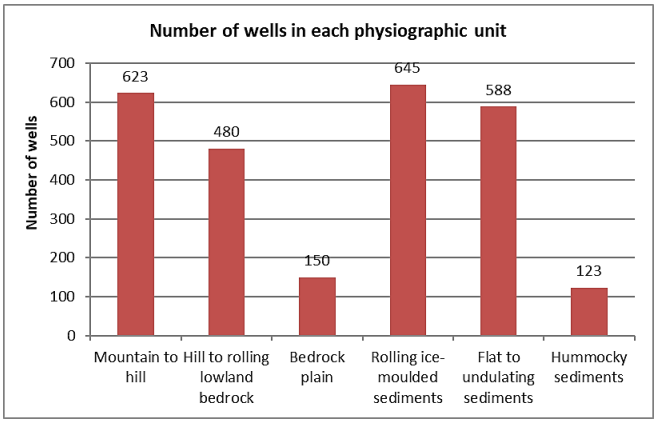



Figure 3.11 Level 1 physiographic units map of Ireland (from Pellicer and Sheehy, 2018)

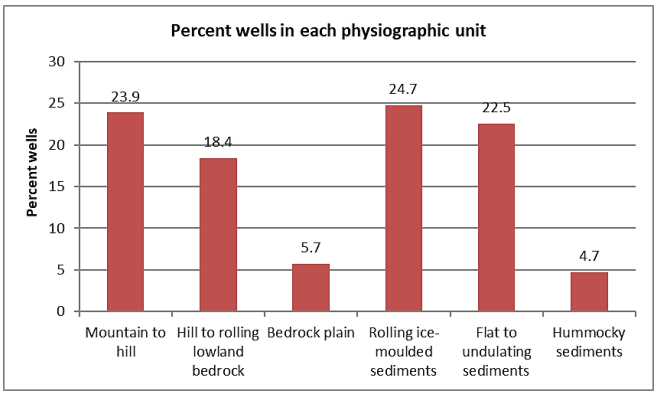
In the GSI methodology, the distinction between mountains and hills was generally taken at 300 m elevation - although the methodology makes clear that 'a systematic threshold for mountain cannot be determined from these maps' - and follows a UN Environment Programme approach which defines a mountain as 'Elevation of at least 300 m, with a 300 m elevation range within 7 km' - whereas prominent landforms with elevations between 100 m and 300 m OD were classed as hills (GSI, 2018). Landscapes with elevations below 100 m OD were classified on the basis of the main sediment type and landform. It can be seen in Figure 3.11 that, as expected, the mountain to hill unit dominates the elevated coastal rim of the country, whereas flat to gently undulating sediments and rolling ice-moulded sediments occupy much of the Midlands.

The distribution of holy wells (in the national database) by physiographic unit was analysed in GIS using the same methodology as before, and the results are included in Table 3.4 and Figure 3.12. Reassuringly, the total numbers of wells within the Level 1 and the Level 2 subdivisions were in agreement. Of the 2676 wells in the database with grid references, the analysis picked up 2609 wells in the physiographic units plus 11 wells classed as being 'Water' (which were mapped as being close to shorelines). Although direct comparisons between physiographic units

and elevation bands are not appropriate, the number of wells above an elevation of 100 m in Section 3.3.3 (649) is in broad agreement with the number of wells in the mountain to hill category (623) determined here.




a)




b)

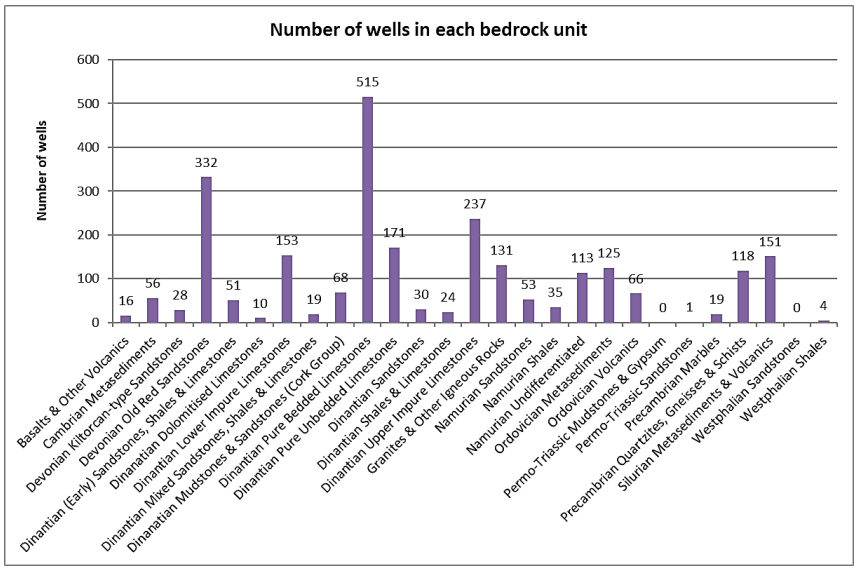
Figure 3.12 Distribution of Irish holy wells according to Level 1 physiographic unit: a) number of wells within Level 1 unit; b) percent wells within Level 1 unit (n = 2609)

It should be added here that the influence of physiographic setting is likely to be more important at the local scale than the regional scale discussed here. For example, a change in slope may be a stronger influence on the location of a particular spring rather than its location in a physiographic unit such as mountain to hill or hill to valley lowland (see Section 4.2.3).

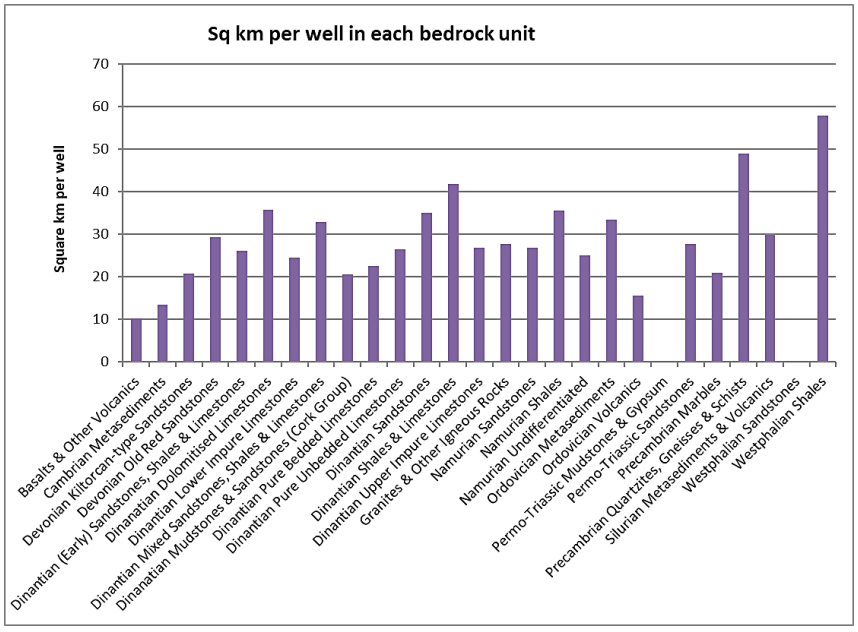
### 3.3.5 Distribution of wells by bedrock unit

The distribution of holy wells according to the 27 Groundwater Rock Unit Groups (GRUGs) is shown in Figure 3.13. The largest number of wells is found in the Dinantian pure bedded

limestones (515), Devonian Old Red Sandstones (332) and Dinantian upper impure limestones (237). The following bedrock units contain fewer than 10 holy wells: Westphalian shales (4), Permo-Triassic sandstones (1), Permo-Triassic mudstones and gypsum, and Westphalian sandstones (zero in both units). In the case of the Permo-Triassic units, in particular, these cover very small areas within the Irish Republic, and they are mainly of relevance to Northern Ireland.




a)




b)

Figure 3.13 Distribution of holy wells according to bedrock unit: a) number of wells in each bedrock unit; b) normalised data, indicating the square kilometre per well in each bedrock unit (n = 2526)

### 3.3.6 Distribution of wells by main lithological groupings

To investigate the distribution of holy wells according to geology, it is helpful to group the similar bedrock units together, and also include the wells in sands and gravel deposits (Figures 3.14 and 3.15). As discussed in Section 3.2, a 6-fold grouping has been adopted here. This is the same system that was used by Tedd *et al*. (2017) for lithological groupings in the analysis of natural background levels (NBLs) of water quality parameters in their study (see Section 6.3.2).

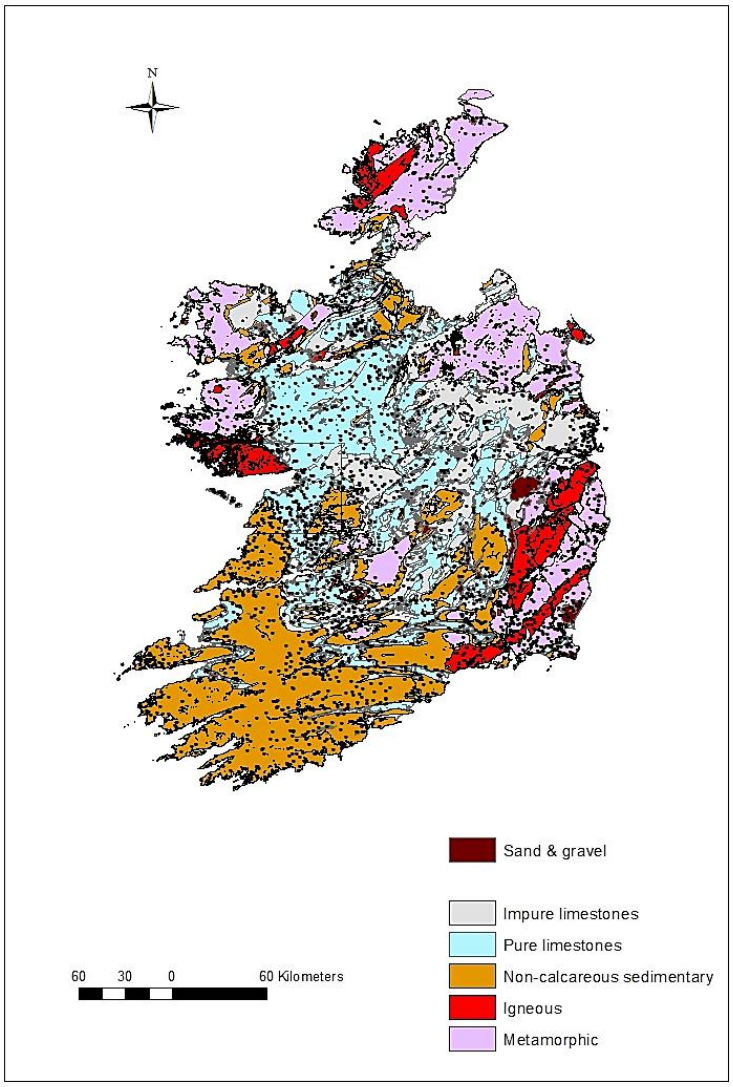
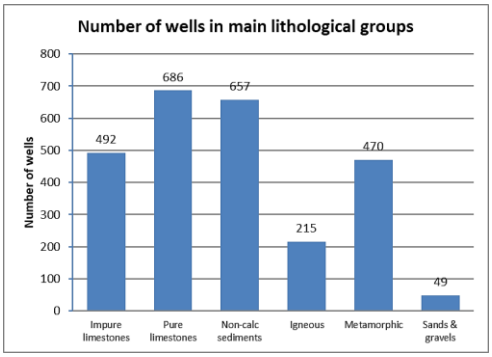
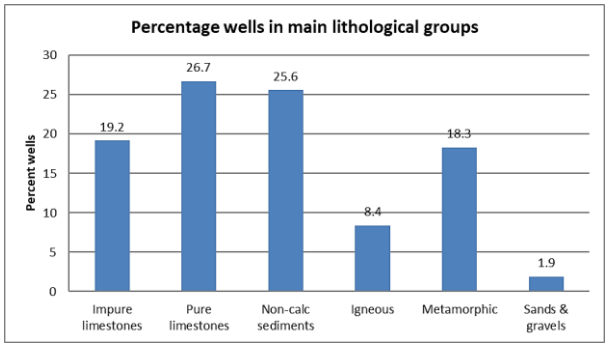


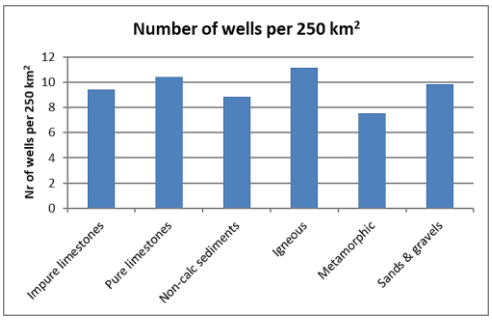

Figure 3.14 Map showing the distribution of holy wells according to the main lithological groups. (Map prepared in ArcGIS using GSI shapefiles)



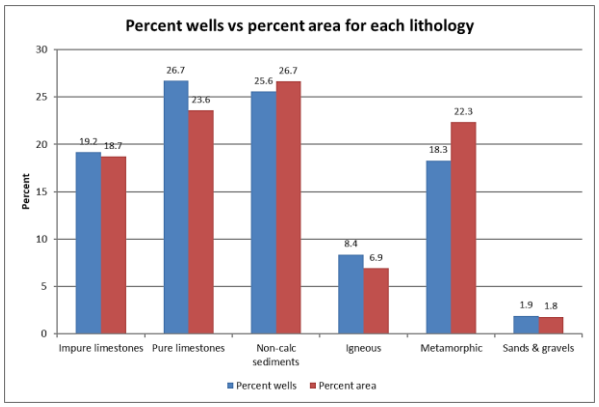

a)




b)




c)




d)

Figure 3.15 Distribution of holy wells according to the main lithological groupings: a) number of wells within each group; b) percent wells within each group; c) number of wells per 250 km$^2$ of each group; d) percent wells versus percent area of each lithological group (n = 2569)

It can be seen from Figure 3.15 that holy wells occur in all six main groupings, with higher densities in the pure limestone group (which might be expected as these form some of the most productive aquifers), but also in the igneous rocks (which have poor aquifer characteristics).

As noted in Section 3.1.1, Mather (2016) looked at the distribution of holy wells in regions of England and Wales according to three simple geological groupings based on hydrogeological characteristics (Table 3.5). The first group comprises basement rocks (B) which generally have low porosities and permeabilities, and are characterised by fracture flow. This grouping is broadly equivalent to the igneous and metamorphic rock units used in the Irish groupings above, but also includes some low permeability sedimentary rocks (he refers to Devonian shales as being part of the basement in Cornwall). The second grouping is termed older cover (OC), and would mainly comprise Devonian sandstone and, especially, Carboniferous limestone and sandstone rocks. This second grouping is again mainly characterised by secondary permeability

aquifers. The OC would likely encompass the pure limestones, impure limestones and (most of) the non-calcareous sedimentary groups in the Irish classification. The third group is the younger cover (YC), which includes the major Permo-Triassic Sherwood Sandstone and Cretaceous chalk aquifers. Whilst these are not present in the Republic of Ireland (save for a small area of Permian sandstone near the border), the YC group also includes sand and gravel deposits, which is one of the six lithological groupings discussed above for Ireland.

Table 3.5 Distribution of holy wells by region in England and Wales (based on Mather, 2016)

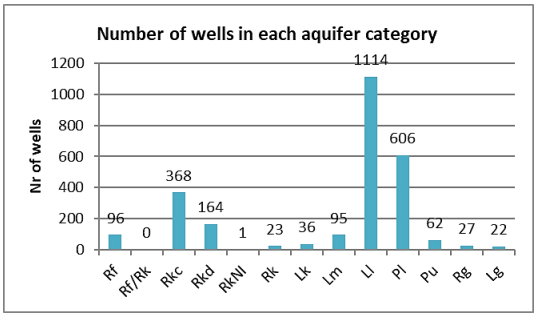
| REGION | Wells per 250 miles$^2$ | Wells per 250 km$^2$ | Geology |
|---|---|---|---|
| Cornwall | 18 | 7.0 | B |
| Wales | 17 | 6.6 | B/OC |
| West Riding | 7.5 | 2.9 | OC |
| North East | 6.6 | 2.6 | OC |
| Welsh Borders | 6.6 | 2.6 | OC/YC/B |
| Midlands | 5.9 | 2.3 | YC/OC |
| West Country | 5.7 | 2.2 | OC/YC/B |
| North of Midlands | 5.5 | 2.1 | YC/OC |
| Cumbria | 5.5 | 2.1 | B/OC/YC |
| North West | 4.8 | 1.9 | YC/OC |
| Home Counties | 4.7 | 1.8 | YC |
| E & N Ridings | 4.1 | 1.6 | YC/OC |
| Lincolnshire | 3.1 | 1.2 | YC |
| Mid-West | 2.9 | 1.1 | YC |
| South-East | 2.7 | 1.1 | YC |
| East of Midlands | 2.6 | 1.0 | YC |
| East Anglia | 1.5 | 0.6 | YC |
| Average | 6.2 | 2.4 | |

Mather argues that the geology played an important role in the frequency of holy wells: where groundwater is scarce, such as in the basement aquifers of Wales and Cornwall, it would have been highly valued as a resource and hence more likely to become ‘sanctified’; in contrast, where groundwater is more abundant, such as in the east and southeast of England, it was ‘taken for granted’. However, other explanations for the differences in well frequencies are possible. For example, groundwater flow paths in basement aquifers generally may be shorter than those in the the more productive chalk and sandstone aquifer, and hence the springs and seeps that gave rise to many holy wells may be more common (see Section 3.2). It may also be the case that the frequencies of holy wells are higher in southwest England and Wales because

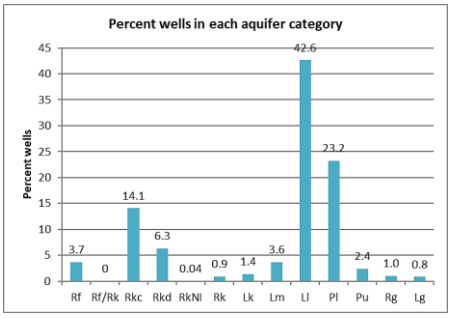
of better survival rates of wells in these areas and/or a stronger Iron Age legacy in these regions. Regarding survival rates, there is less intensive agricultural development and urbanisation in the west and southwest of Britain compared to the east. In relation to Iron Age influences, of possible relevance, perhaps, is the observation by Binnal (1945) that eye wells are most common in those western areas of England where the 'Celtic influences' were strongest (he reviewed 78 wells in England with reputations for curing sore eyes, and found that 43 are in the western half of the country, 15 in the midlands, 10 in the north, six in the east and only four in the south and southeast). The Irish data certainly would suggest a more uniform distribution of holy wells across both productive and poorly productive aquifers.

### 3.3.7 Distribution of wells by aquifer category

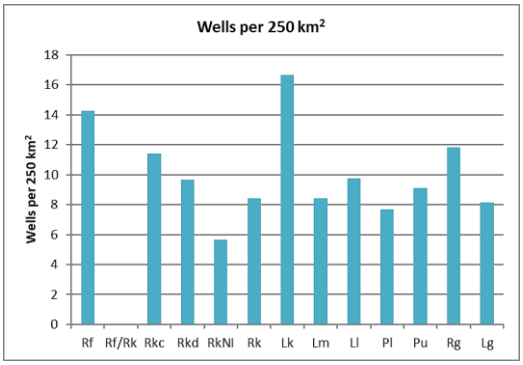
The distribution of holy wells by aquifer category in Ireland is shown in Figure 3.16.



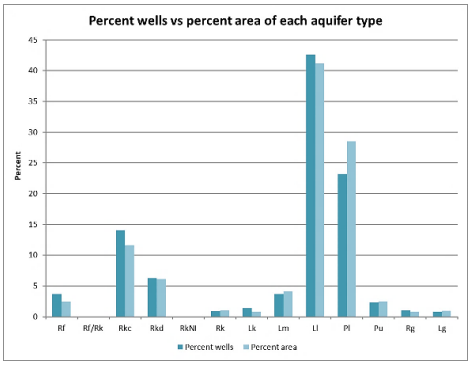

a)




b)




c)



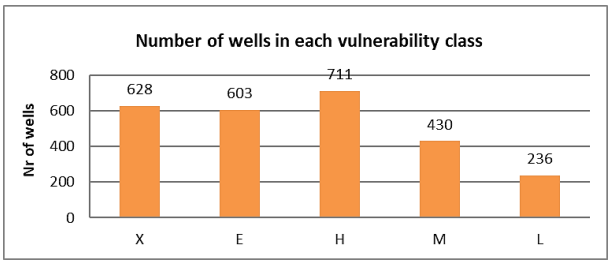

d)

Figure 3.16 Distribution of holy wells according to aquifer category: a) number of wells within each category; b) percent wells within each category; c) number of wells per 250 km$^2$ in each category; d) percent wells against percent area of each aquifer category (n = 2614)

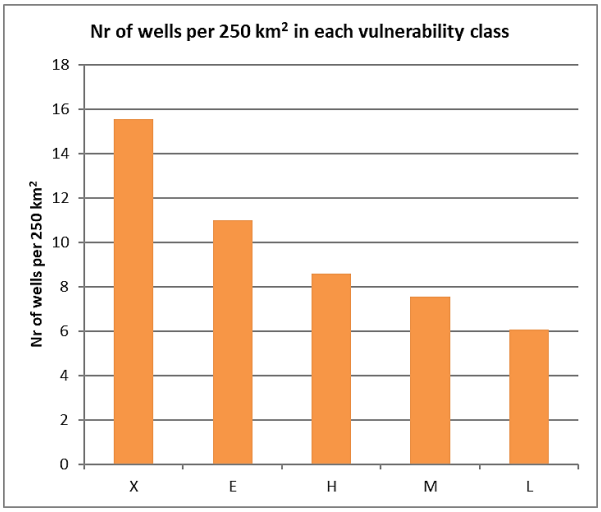
The majority of wells (68%) are located in poorly productive aquifers (Ll, Pl and Pu categories), which underlie about 72% of the country, but there are also relatively high densities in the regionally important and locally important (Lm and Lk categories) bedrock aquifers and in the sands and gravels. Thus, there is no apparent relationship between the occurrence of holy wells and the relative productivity of the aquifer: holy wells are just as likely to be found in poorly productive aquifers as in the aquifers with higher transmissivities.

### 3.3.8 Distribution of wells by groundwater vulnerability class

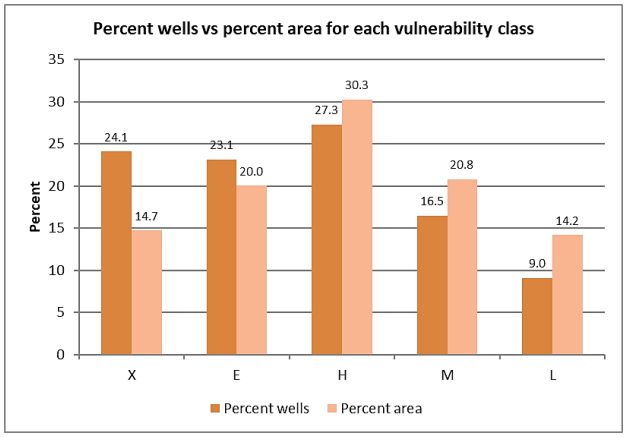
The distribution of holy wells with respect to groundwater vulnerability category (Figure 3.17) shows a clear pattern, with wells more frequent in the X and E Extreme and in the High vulnerability categories than in the Moderate and Low categories. This finding is not surprising, since the majority of holy wells (based on this researcher's surveys – see Chapters 4 and 5) are springs or very shallow wells, and hence are more likely to be found where the subsoil cover is thin or absent, and the aquifer is close to ground surface (i.e. the X and E vulnerability categories especially).




a)




b)




c)

Figure 3.17 Distribution of holy wells according to groundwater vulnerability category: a) number of wells within each category; b) number of wells per 250 km$^2$ of each category; c) Percent wells against percent area of each vulnerability category (n = 2608)

## 3.4 Concluding remarks

In this chapter, the distribution of holy wells was investigated according to their different physiographical, geological and hydrogeological settings. A summary of this work has now been published (Misstear *et al*., 2020). The GIS analysis showed that the distribution of holy wells is not particularly sensitive to the type of geology or aquifer class – holy wells are as common in poorly productive aquifers as they are in the regionally important aquifers. One trend, however, is clear: there is a greater frequency of holy wells in areas classed as having Extreme or High groundwater vulnerability compared to wells in Moderate and Low categories. As will become clear in the next two chapters this is because the majority of holy wells are in fact shallow springs, where the subsoil cover is generally thin or is absent altogether.

Whilst bedrock geology is unlikely to have varied over the long period from the origins of our oldest holy wells (e.g. Iron Age in Ireland: approximately 500 BCE to 400 CE) to the present day, the superficial geology (soils) may have changed somewhat, and the topography more so – due to flooding and erosion, for example. Then there are the impacts of human development to be considered. In consequence, the physiographical and hydrogeological settings analysed here may have changed since the time when the rituals and cures associated with the wells first came into practice. A spring may have dried up, or its flow may have increased; biogeochemical

processes may have changed the natural water quality over time; and human impacts may have resulted in pollution.

The GIS analyses described in this chapter were based on the National Monuments Service database of holy wells, itself based on the 19th century mapping carried out by the Ordnance Survey of Ireland. As such, many of the wells included in this GIS analysis may no longer exist, whilst there are other holy wells in existence which were not included in the OS mapping, or in the National Monuments' records. For these reasons, it was essential to carry out field surveys of holy wells, and to apply a similar GIS analysis to these wells, as described in the next chapter.

# 4 Well surveys

Following the general hydrogeological characterisation of Irish holy wells in the previous chapter, which was carried out using a GIS and the full National Monuments Records (NMR) shapefile of holy wells, this chapter introduces the extensive field surveys of holy wells undertaken as part of this research. The survey methodology is described in Section 4.1, with details of the numbers of wells surveyed, the type of data collected, and the selection of monitoring wells. Section 4.2 presents the results of a GIS-based analysis of the survey data, using a similar approach to that adopted for the full NMR dataset in Chapter 3. Some summary statistics of water depths and water levels are given at the end of this section. Descriptions of individual wells are not included in this chapter, but rather are the focus of Chapter 5.

## 4.1 Methodology

### 4.1.1 Number of wells surveyed

Some 215 holy wells were surveyed across all 26 of the traditional counties of the Republic of Ireland (Figure 4.1). The wells were chosen to give a good representation of the variety of lithologies and hydrogeological settings of holy wells in Ireland (see below). Geological and topographical maps, together with information on holy wells found in publications or internet sources, were consulted in the selection process. In addition, the surveys included five spa wells (a location map is included with the descriptions of these spa wells in Section 5.11), plus a well near Taughmaconnell in County Roscommon which was surveyed and sampled because it had the appearance of an old holy well, but subsequent investigations did not reveal any evidence of sacred associations. Of the 221 sites surveyed, 27 wells were either dry, abandoned or otherwise inaccessible for sampling. A full list of the wells surveyed is included in Appendix A, whilst the details of the chemical sampling are covered in Chapter 7.

Before describing the scope of the well surveys it is worth considering the survey size and how representative this may be of the total number of holy wells. There are a number of standard methods available for examining the size of a survey in relation to the total population, for a particular confidence level and margin of error (precision). One of the most commonly used methods is that by Cochran (1977). For large populations, the sample size is given by:

$$n_0 = \frac{Z^2 pq}{(e)^2} \quad (4.1)$$

where $n_0$ is the sample size, $Z$ is a factor related to the confidence level (and applies to a normal distribution), $p$ is the proportion of population with a particular attribute (normally taken as 0.5), $q$ = 1-$p$ and $e$ is the margin of error. For small populations the Cochran formula is modified to:

$$n = \frac{n_0}{1+\frac{(n_0-1)}{N}} \quad (4.2)$$

where $N$ is the total population size and $n$ is the new, adjusted sample size.

In applying Equation 4.2 here, the total population – i.e. the number of holy wells – is not known accurately. As discussed in Section 2.2.3, the number of holy wells in the Republic of Ireland is generally reported to be in the region of 3000 (Foley, 2010; Ray, 2014). This number is based on the records in the National Monuments Service database (which itself is based on the results of mapping surveys by the Ordnance Survey during the 19th century). However, many of these wells no longer exist, whilst some holy wells that do exist were not included on the original topographic maps or in the National Monuments archive. In the GIS analysis in Chapter 3, the NM database containing 2996 wells was used, although only 2676 of these wells had grid references. For the purposes of this exercise, the total population (number of wells) is taken as 3000 and, assuming a confidence interval of 95%, the resultant margin of error ($e$) can be calculated as 6.44%. (If only the 2676 wells with grid references are taken as the population, then the error reduces slightly to 6.41%).

In relation to the main lithological groupings, the number of wells surveyed and the resulting calculated margins of error (for a 95% confidence level) are summarised in Table 4.1 (the distribution of wells by lithology is discussed in Section 4.2.5). The $e$ values range from 13.5 to 32%. The highest $e$ values – i.e. lowest survey precision – are for the sand and gravel lithological group, which has the lowest sample population. However, it should be noted that the margin of error calculations do not include the mixed bedrock and gravel lithological group, since this group was not part of the GIS analysis of the total well population in Chapter 3; several of these wells would fall in the sand and gravel group, which would thus reduce the margin of error.

The meaningfulness of these estimates of survey precision is questionable, since the surveys involved the recording of a wide range of attributes of the wells and well sites, as described below. Nevertheless, they do provide some quantitative assessment of the relative survey errors. The Cochran method will be used again when considering the number of wells sampled for water chemical analyses in Chapter 7.

Table 4.1 Calculated margins of error for well surveys (using Cochran's method)

| Lithological group | Number of wells in GIS analysis (Chapter 3) | Number of wells surveyed | Calculated margin of error (%) |
|---|---|---|---|
| Impure limestone | 492 | 35 | 16.0 |
| Pure limestone | 686 | 49 | 13.5 |
| Non calcareous sedimentary | 657 | 47 | 13.8 |
| Igneous | 215 | 16 | 23.6 |
| Metamorphic | 470 | 46 | 13.7 |
| Sand & gravel | 49 | 8 | 32.0 |
| Mixed bedrock & gravel | - | 13 | N/A |
| TOTAL | 2569 | 214[1] | N/A |

Note: The total surveyed wells is 214 and not 215 because the Wart well at Timoleague was excluded, as this is bullaun stone rather than a well

### 4.1.2 Scope of well surveys

At each well site details of the location, topography and geology were noted. The well dimensions, depth to water, depth of well and the main physico-chemical water quality parameters (EC, pH and temperature) were also recorded. Where the well water was accessible for sampling, water samples were collected for analysis, either during this first visit or during a return visit (see Section 7.1). A standard proforma was used for recording information during the field surveys (Table 4.2). A total of 215 holy well sites were surveyed. A list of the wells, including grid references, is included in Appendix A.

Site measurements included: grid reference, elevation, well and well house dimensions, depth to water and depth of water (usually by tape, because wells were generally very shallow, but sometimes using a water level dipper when needed), electrical conductivity (EC), water temperature and pH (see Chapter 7 for details of chemical sampling). Three grid references were recorded at each site: the Irish Grid, the ITM (Irish Transverse Mercator) and the

latitude/longitude. The GPS instrument was a Satmap Systems Active 12 with the OSI 1:50,000 OSI mapping on an SD card. The claimed instrumental accuracy was down to 1 m, although this can vary according to conditions. For elevation, the GPS instrument was set to the 'Elevation from maps' option, as it was impracticable to calibrate the barometric altimeter repeatedly to obtain accurate readings from atmospheric pressure. Each holy well was logged on the GPS as a 'Point of interest'. The surveys also included observations on well accessibility, topography, any geological features (such as rock outcrops, joint directions), potential pollution sources near to the well, whether or not the well was sampled, the water sample reference number, the sample appearance, and weather conditions.

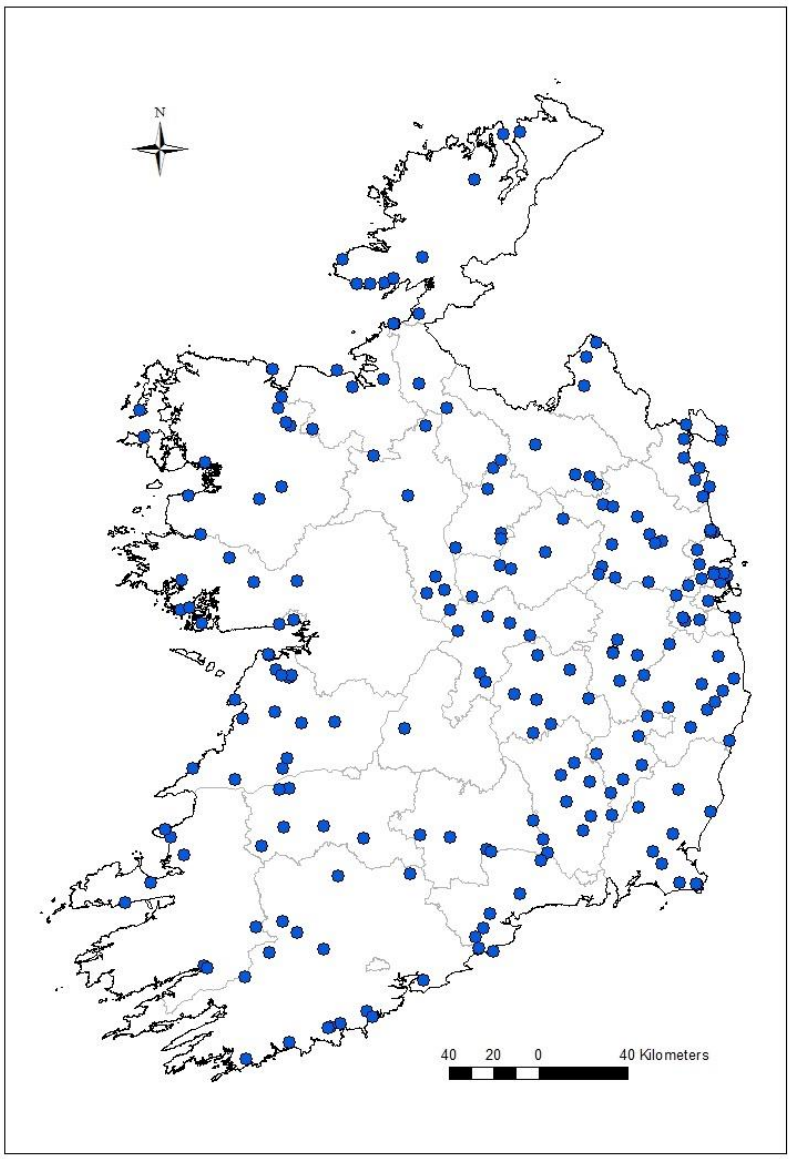



Figure 4.1 Location of surveyed holy wells (n = 215)

## Table 4.2 Well survey proforma

| | | | | |
|---|---|---|---|---|
| Location / Townland | | | | |
| Grid reference | Irish Grid | | | |
| | ITM | | | |
| Latitude / Longitude (degrees) | | | OSI Discovery Map Nr | |
| Date(s) visited: | | | | |
| Access | | | | |
| Well description | | | | |
| Reputed cures | | | | |
| Topography | | | | |
| Elevation (m above OD) | | | | |
| Geology | Superficial | | | |
| | Bedrock | | | |
| | Structural features | | | |
| Hydrogeology | Description | | | |
| | Depth to water<br>(m below ref point) | | | |
| | Aquifer class | | | |
| | Vulnerability | | | |
| Water quality | EC ($\mu S\ cm^{-1}$) | | | |
| | Temperature (°C) | | | |
| | pH | | | |
| | Sample collected? | | | |
| | Sample appearance | | | |
| | Weather conditions | | | |
| Potential pollution sources nearby? | | | | |
| Additional comments | | | | |

There were issues in gaining access to certain wells (Figure 4.2). These arose from a variety of reasons, including: the site was overgrown; the well house was locked; or the landowner did not permit access.




a) b)

c) d)

e) f) g)

Figure 4.2 Some of the practical difficulties surrounding well surveys: a) Private land sign near St Fiachra's well, Kilfera, Co Kilkenny; b) Sign warning of bull in field containing St Saran's well, Co Offaly; c) The former site of St Patrick's well, Arklow, Co Wicklow, now a quarry site; d) Evidence of deep mud near Sunday's well Ballymore, Co Westmeath; e) Rotted timbers (plus pallet and barbed wire at far end) impeding access to St Lastra's well, Co Monaghan; f) The Irish weather; and g) Dry well, Tobar na Molt (Well of the Wethers), Ardfert, Co Kerry. Photos by Bruce Misstear (except f), taken by Gillian Misstear)

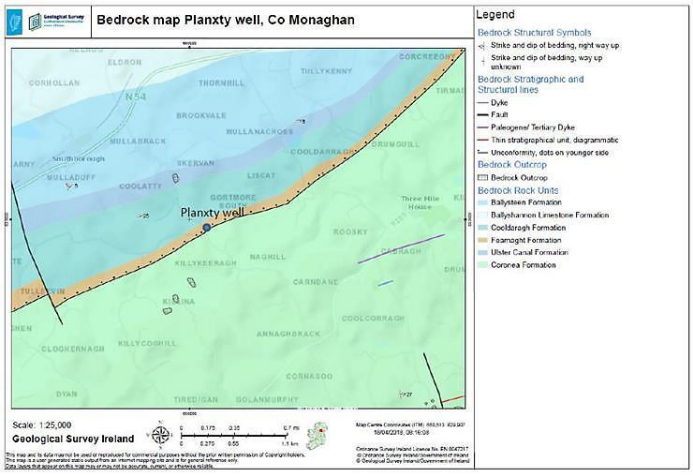
### 4.1.3 Well survey reports

A well survey report was prepared for each well. Each report includes a summary of information gathered during the site visit, together with more details about the well's history, including information on reputed cures. This additional information was drawn from several sources: publications, including national or local books and articles on holy wells (see Section 2.2.3), web sites – there are an increasing number of web blogs available that contain varying amounts of information about individual holy wells – and from discussions with local people. Each completed report includes photos taken by the researcher, plus several maps that were downloaded from the GSI Groundwater Data Viewer: subsoils, bedrock geology, groundwater vulnerability and aquifer classification. The OSI Digital Globe image was normally used to prepare the location map, although sometimes the OSI Ortho image (2010) was used if this was clearer; both of these images are available in Basemap Gallery in the Groundwater Data Viewer. The Basemap Gallery also includes the contemporary OSI 1:50,000 Discovery mapping, the OSI Historic black and white 6 inch mapping (dating from 1829-1841) and the OSI Historic 25 inch mapping (1897-1913). On all reports, a note was made as to whether or not the well is marked on the contemporary or historical maps.

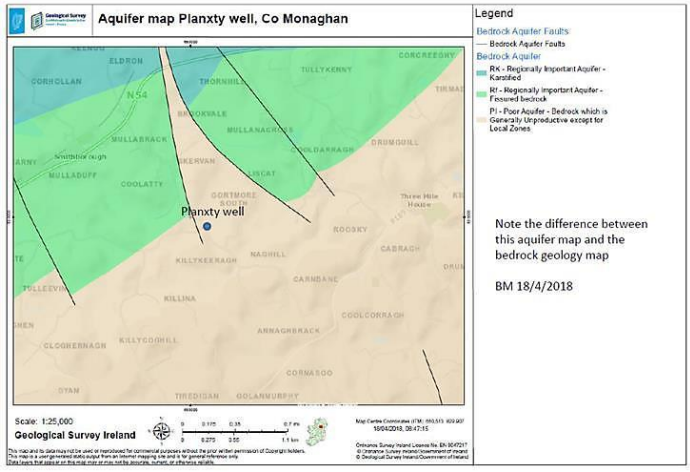
A total of 221 well reports, each 5 to 8 pages in length (typically 6 pages), were completed. Three examples are included in Appendix B. Within the GSI's Groundwater Viewer, the Quaternary and bedrock maps are available to print at 1:10,000 or larger scales, whereas the groundwater rock unit, vulnerability and aquifer (groundwater resources) maps can be printed at 1:25,000 or smaller scales. In general, most of the maps in the survey reports were reproduced at 1:25,000 scale, except where more detail was required, especially in the case of Quaternary (subsoil) maps, for which a scale of 1;10,000 was used. It should be emphasised here that the actual scale of the original mapping is different e.g. the bedrock maps were generally prepared by the GSI at a scale of 1:100,000.

There were also issues (only very occasionally) where there were inconsistencies between different geological maps. For example, at the Planxty well near Smithborough in County Monaghan, the bedrock geology and aquifer maps show significant differences in the vicinity of the well (Figure 4.3). According to the bedrock map (Figure 4.3a), the well appears to be on, or very close to, the unconformable contact between the sandstones and conglomerates of the Dinantian Fearnaght Formation (Dinantian sandstones in the Groundwater Rock Unit Group

classification) with the underlying Ordovician turbidites of the Coronea Formation, part of the Longford-Down inlier (Ordovician metasediments). If the bedrock map is accurate, then the well appears to be located just within the Dinantian sandstones and conglomerates. However, the aquifer map (and the Groundwater Rock Unit map) show some major differences in the geology and hydrogeology compared to the bedrock map, with the former maps indicating a 'slice' of Ordovician metasediments extending northwards into the Dinantian strata, which contains the well site (Figure 4.3b). According to the GSI (Hunter Williams, *pers comm*), the bedrock map is likely to be more accurate, as it was updated based on Tellus information (airborne geophysics) and re-mapping at 1:50,000.




a)




b)

Figure 4.3 Bedrock geology (a) and aquifer (b) maps for the area around Planxty well in Co Monaghan, illustrating the differences in geological interpretations between the two maps. (Maps prepared using GSI Groundwater Data Viewer)

The GSI Groundwater Data Viewer went through several modifications during the course of the research, especially a major upgrade in the summer of 2017. This resulted in different map formats. For consistency, all the maps and well survey reports produced prior to the upgrade of the mapper in the summer of 2017 were redone using the new format.

### 4.1.4 Monitoring wells

Four of the surveyed wells were selected for monitoring of temporal variations in water level and chemistry. The wells were chosen as representative of a range of hydrogeological settings:

1. St Brigid's well Tully, Co Kildare: this is in the Curragh sand and gravel aquifer, and it is probably the best known holy well in Kildare.
2. St Kieran's well Castlekeeran, Co Meath: this is a karst limestone site (and thus unusual for the east of Ireland), and comprises three small springs, each with its own reputed cures.
3. Bride's well Calgath (Kilcock), Co Meath: this is at a raised location (the highest point in a field) – indicating a deep source, perhaps - and has a reputation as a warm water well; the geology belongs to the impure limestone grouping.
4. St Moling's well St Mullin's, Co Carlow: the spring issues from weathered granite; it is one of the most famous holy wells in Ireland, and its pattern day in July still attracts large gatherings.

Accessibility was also a criterion when selecting these monitoring wells: they were all located within a maximum of two hours' drive from the researcher's base at Trinity College Dublin. The wells were visited every three months or so for repeat sampling, amounting to between nine and 11 visits over a two to three year period which commenced in the summer of 2016. The hydrogeology of these four monitoring well sites is described in the relevant sections of Chapter 5 (where the well descriptions are organised according to the main lithological units).

The chosen monitoring wells represented examples of wells in four of the six main lithological groups described in Chapter 3. Whilst there were no monitoring wells in the other two main lithologies, several wells in the non-calcareous sedimentary and metamorphic groups were the subject of repeat visits during the research, including St Declan's well at Ardmore in Co

Waterford (non-calcareous sedimentary; Section 5.4.1.1) and St Brigid's well at Faughart in Co Louth (metamorphic; Section 5.6.3). Water levels and basic physico-chemical parameters such as EC and water temperature were recorded during each of the return visits.

## 4.2 Analysis of survey results

In this section, the results of the well surveys are presented in the same sequence as that followed in Chapter 3 for the GIS analysis of the full NMR dataset. This review considers only the holy wells surveyed (n = 215). The five spa wells are not included here, but they are considered separately in Section 5.11.

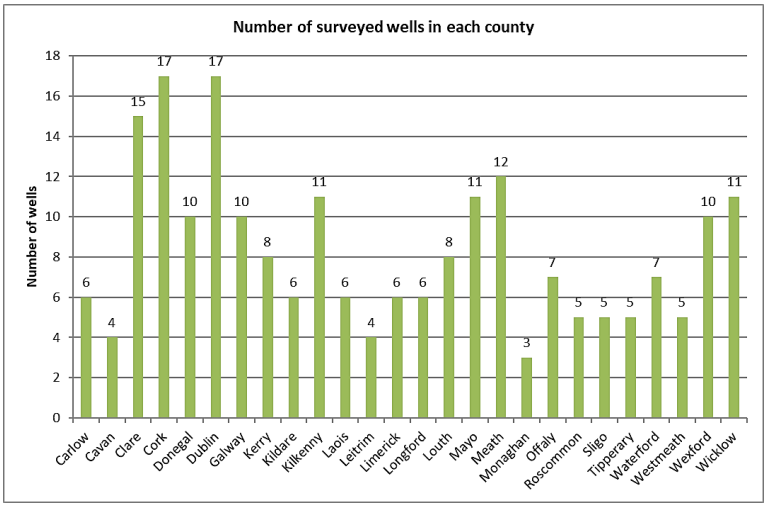
### 4.2.1 Distribution of surveyed wells by county

The numbers of wells surveyed in each county are shown in Table 4.3 and Figure 4.4a. Figure 4.4b compares the percent holy wells surveyed in each county (n = 215), with the percent wells in each county from the GIS analysis (n = 2628, see Section 3.3.2). However, it should be noted that some of the wells surveyed were not included in the GIS analysis i.e. they were not amongst the wells listed in the National Monuments database (or at least, were not among those wells with grid references).

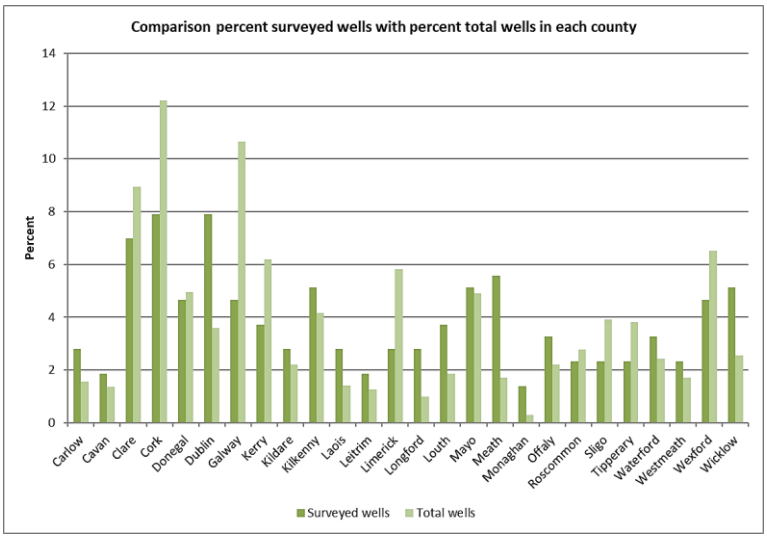
Table 4.3 Number of surveyed wells in each county

| County | Number of wells | County | Number of wells |
|---|---|---|---|
| Carlow | 6 | Longford | 6 |
| Cavan | 4 | Louth | 8 |
| Clare | 15 | Mayo | 11 |
| Cork | 17 | Meath | 12 |
| Donegal | 10 | Monaghan | 3 |
| Dublin | 17 | Offaly | 7 |
| Galway | 10 | Roscommon | 5 |
| Kerry | 8 | Sligo | 5 |
| Kildare | 6 | Tipperary | 5 |
| Kilkenny | 11 | Waterford | 7 |
| Laois | 6 | Westmeath | 5 |
| Leitrim | 4 | Wexford | 10 |
| Limerick | 6 | Wicklow | 11 |

Of the total wells surveyed (215), the largest numbers visited by county were 17 (in both Cork and Dublin) and 15 in Clare. In the GIS analysis of the full NMR dataset, the largest numbers of holy wells were in Cork (321), Galway (280) and Clare (235). This would suggest that wells in Dublin were overrepresented in the surveys. However, it was not possible to sample many of these wells (owing to the wells being either dry or having access issues), and only seven of these 17 wells were sampled, which is the same number as those sampled in Co Galway (seven out of 10 wells). In Co Clare it was possible to sample 12 of the 15 wells and in Cork samples were collected from 12 out of 17 wells surveyed.




a)




b)

Figure 4.4 Distribution of surveyed holy wells by county: a) number of holy wells surveyed in each county; b) surveyed wells as a percentage of the total holy wells in each county (n = 215)

The smallest number of wells surveyed was in Co Monaghan (three wells) which is the county with fewest holy wells (eight wells) according to the GIS analysis. The next smallest number of surveyed wells was in Cavan and Leitrim (four each), again in line with these counties possessing amongst the fewest wells (Figure 4.4b).

### 4.2.2 Distribution of surveyed wells by elevation

Summary statistics of the distribution of surveyed wells by elevation are included in Table 4.4.

Table 4.4 Survey results: well elevations in m OD (n = 215)

| | |
|---|---|
| Average | 72 |
| Median | 62 |
| Std dev | 58 |
| Maximum | 358 |
| Minimum | 0 |
| 5th percentile | 8 |
| 95th percentile | 174 |

In Section 3.3.3, it was shown that the largest numbers of wells were in the 0-50 and 50-100 m elevation bands, and the survey results are consistent with this overall pattern, with an average elevation of 72 m OD. The highest well visited (at 358 m OD) was St John's well on the side of Mushera Mountain, near Millstreet in Co Cork. There were only seven other wells surveyed with elevations greater than 200 m OD, four of which are in Co Wicklow, including St Kevin's well at Glasnamullen (elevation 283 m OD) and Our Lady's well at Ballymanus (248 m OD). Other elevated wells include Lady's well at Corbally in the Dublin hills (232 m OD) and St Eigne's well at Urris in the Mamore Gap on the Inishowen peninsula, Co Donegal (229 m OD).

Several wells were visited that have coastal settings (including locations on small islands), 13 of which have elevations of less than 10 m OD; examples include Abbey well in Ballyshannon Co Donegal, Shaver's well at Tullaghan (Co Leitrim), St Begnet's well on Dalkey Island (Co Dublin), St Joseph's well at Lennaun (Co Galway), St Colman's well at Salterstown (Co Louth) and St Brendan's well at Roskeen (Co Mayo; see Section 5.10 for descriptions of selected coastal wells).

### 4.2.3 Distribution of surveyed wells by physiographic unit

As explained in Section 3.3.4, the GSI has classified the landscape into physiographic units according to three levels of complexity. Using the physiographic unit mapping tool in the Quaternary section of the GSI web viewer, the surveyed wells were assigned to the Level 1 and Level 2 physiographic units, and the results are shown in Table 4.5. There are 213 wells in total, representing the total surveyed wells (215) less the bullaun stone Wart well in Timoleague Co Cork and St Begnet's well on Dalkey Island in Co Dublin, where the physiographic unit has not been classified.

Table 4.5 Number of surveyed holy wells within the Level 1 and Level 2 physiographic units

| Level 1 | Nr of wells | Level 2 | Nr of wells |
|---|---|---|---|
| Mountain to hill | 52 | Mountain rounded | 13 |
| | | Mountain plateau | 9 |
| | | Mountain ridge | 11 |
| | | Mountain ice-sculpted | 19 |
| Hill to rolling lowland bedrock | 35 | Hill to rolling lowland rounded bedrock | 20 |
| | | Hill to rolling lowland bedrock ridge | 15 |
| Bedrock plain | 9 | Bedrock plain | 9 |
| Rolling ice-moulded sediments | 52 | Drumlin and ribbed moraine topography | 30 |
| | | Rolling ice-moulded topography | 22 |
| Flat to undulating sediments | 54 | Flat to gently undulating ice-moulded topography | 38 |
| | | Coastal plain | 9 |
| | | Bog plain | 2 |
| | | Flat fluvial-lacustrine plain | 5 |
| Hummocky sediments | 11 | Hummocky glaciofluvial sediment topography | 10 |
| | | Hummocky to undulating aeolian sand topography | 1 |
| TOTAL | 213 | TOTAL | 213 |

The percent wells in each of the six Level 1 units is illustrated in Figure 4.5, along with the percent total wells (from the GIS analysis in Section 3.3.4) in these units. It can be seen that the percent surveyed wells and percent total wells in each unit match one another closely, indicating that the well survey was broadly representative in terms of physiographical unit distribution.

The largest percentage of surveyed wells is in the flat to gently undulating sediments Level 1 unit (25.4%); within this Level 1 category, the majority (38 wells) fall in the Level 2 unit 'flat to gently undulating ice-moulded topography'.

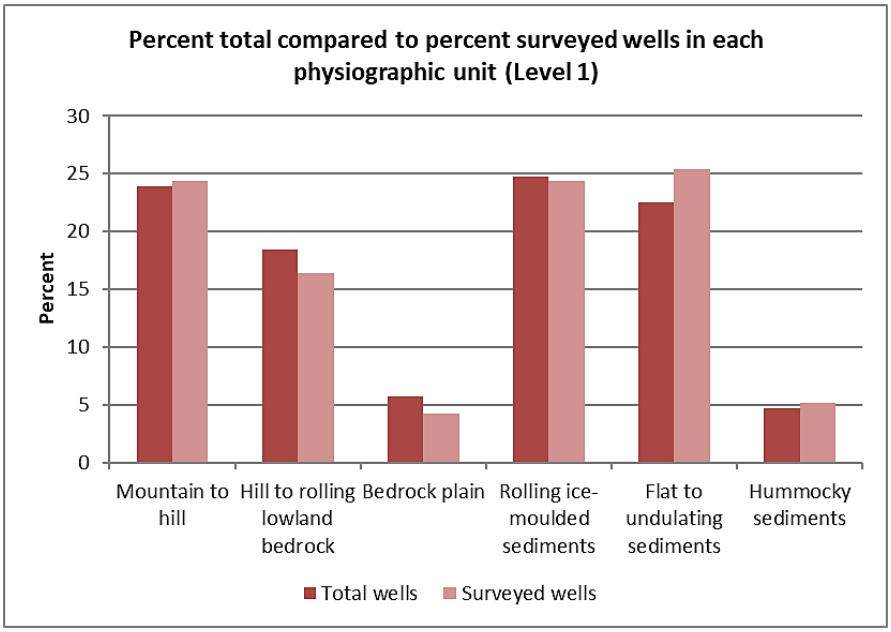



Figure 4.5 Comparison of percent surveyed wells with percent total wells in the Level 1 physiographic units

In terms of elevation, the four units in Level 2 that have 'Mountain' in their title – and which make up the Level 1 mountain to hill unit – contain wells with widely varying elevations, ranging from a maximum of 358 m OD to a minimum of only 8 m OD, with a mean of 119.3 m OD. The highest of the surveyed wells, as noted in Section 4.2.2 above, is St John's well on the side of Mushera Mountain in Co Cork, whilst the lowest elevation well in the mountain to hill unit is St Joseph's well at Lennaun in Co Galway; this shoreline well falls within the mountain ice-sculpted Level 2 unit as it is located at the foot of a mountainous area, and there is no coastal plain or other physiographic unit mapped here. This highlights that, although the distinction between mountain and hill is generally taken as 300 m OD (see Section 3.3.4), the inclusion of the word 'Mountain' in a unit category implies only that the topography in the area rises to that elevation, and not that all the land within that unit is above 300 m OD; indeed, 19 of the 52 wells within the mountain to hill Level 1 unit have elevations below 100 m (the typical minimum elevation for a hill). This is a limitation of the mapping resolution (the maps were prepared at 1:100,000 scale). Some other examples of apparent anomalies (or at least surprises) in the classification are that St Joseph's well at Dulick in Ennis is classed as coastal plain, despite being more than

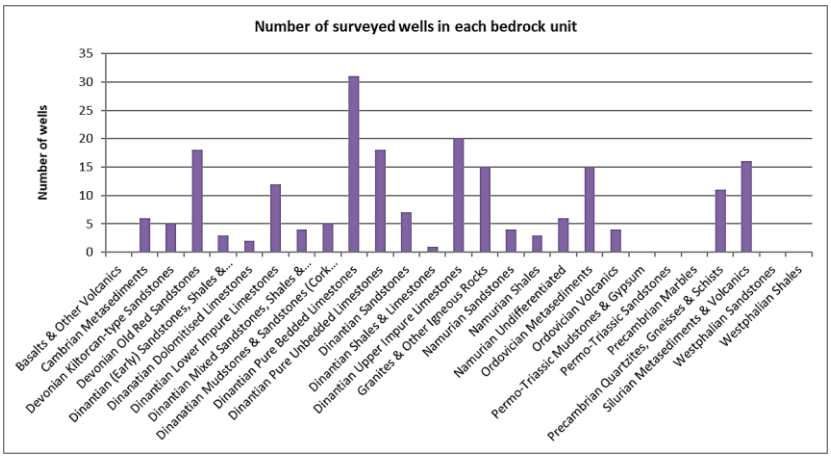
10 km from the sea, whilst St Kieran's well at Castlekeeran in Co Meath, which is a karst limestone spring, falls into the flat fluvial-lacustrine plain unit.

Perhaps of most interest from a hydrogeological perspective is that, when carrying out this analysis, 26 wells (12%) were found to be at or close to (within approximately 100 m of) a boundary, supporting field observations that topography often plays an important role in the location of a holy well (examples are included in Chapter 5).

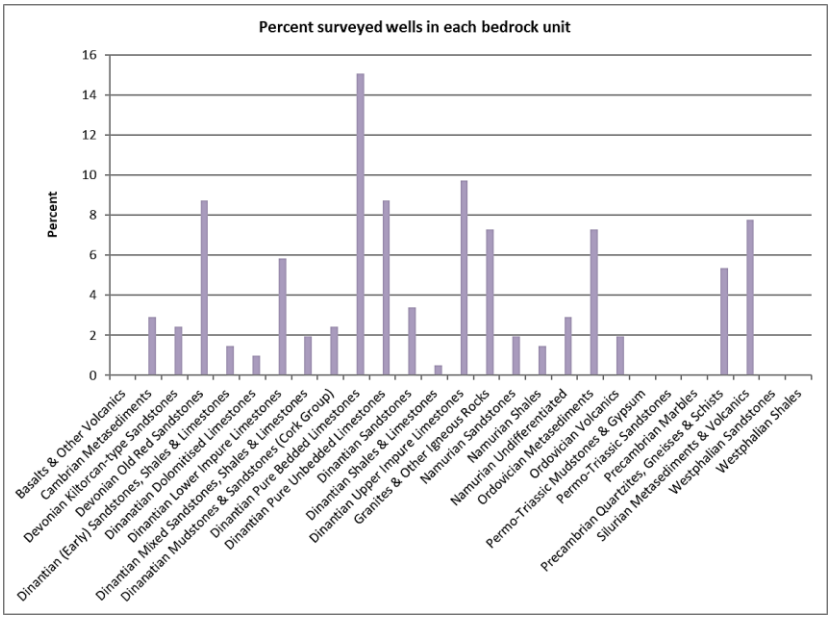
### 4.2.4 Distribution of surveyed wells by bedrock unit

The bedrock geology of the surveyed wells is shown in Figure 4.6 and Table 4.6). The number in this analysis is 206 wells. Of the total survey number of 215 wells, one well was excluded as comprising a bullaun stone rather than a groundwater well (Wart well in Timoleague Co Cork) and eight wells were omitted as being located in sand and gravel deposits. It should be noted here that wells believed to draw their water from a mixture of bedrock and superficial deposits (13 wells, see Section 4.2.5 and Section 5.8) are included in the 206 wells in Table 4.6.

There are 27 bedrock categories in the GSI's Groundwater Rock Unit classification, and at least one well was surveyed in 21 of these units. The six units that did not include a surveyed well comprise only 1.3% of the bedrock area of the Republic of Ireland, and contain only 1.6% of the holy wells (from the GIS analysis of the NMR database); these include, for example, the 'Basalts & other volcanics' group, which occurs mainly in east Co Limerick but extends into neighbouring Co Tipperary. The largest number of wells (31) fall within the Dinantian pure bedded limestones, whose member formations are widely distributed throughout the country and include the Burren Formation in Co Clare and Co Galway, the Kilsheelan Formation in Co Cork and Co Tipperary, the Ballyshannon Limestone Formation in Co Donegal, the Ballyadams Formation in Co Kilkenny and Co Laois, Undifferentiated Visean Limestones of Co Longford and Co Roscommon, the Ballina Limestone and Oakport Limestone Formations in Co Mayo, the Meath Formation in Co Meath, the Dartry Limestone Formation in Co Monaghan and Co Sligo, and the Allenwood Formation in Co Offaly. The next most frequent bedrock type for surveyed holy wells is the Dinantian upper impure limestones (20), which includes the Lucan Formation (Calp rocks) of Counties Dublin, Meath and Kildare. This is followed by the Dinantian pure unbedded limestones (18) and Devonian Old Red Sandstones (18), the latter rock unit being most commonly found in Co Cork and Co Kerry.




a)




b)

Figure 4.6 Distribution of surveyed holy wells by bedrock unit (n = 206)

Table 4.6 Surveyed wells by bedrock category (n = 206)

| Bedrock unit | Nr wells | Percent |
|---|---|---|
| Basalts & other volcanics | 0 | 0.0 |
| Cambrian metasediments | 6 | 2.9 |
| Devonian Kiltorcan-type sandstones | 5 | 2.4 |
| Devonian Old Red Sandstones | 18 | 8.7 |
| Dinantian (early) sandstones, shales & limestones | 3 | 1.5 |
| Dinantian dolomitised limestones | 2 | 1.0 |
| Dinantian lower impure limestones | 12 | 5.8 |
| Dinantian mixed sandstones, shales & limestones | 4 | 1.9 |
| Dinantian mudstones & sandstones (Cork Group) | 5 | 2.4 |
| Dinantian pure bedded limestones | 31 | 15.0 |
| Dinantian pure unbedded limestones | 18 | 8.7 |
| Dinantian sandstones | 7 | 3.4 |
| Dinantian shales & limestones | 1 | 0.5 |
| Dinantian upper impure limestones | 20 | 9.7 |
| Granites & other igneous rocks | 15 | 7.3 |
| Namurian sandstones | 4 | 1.9 |
| Namurian shales | 3 | 1.5 |
| Namurian undifferentiated | 6 | 2.9 |
| Ordovician metasediments | 15 | 7.3 |
| Ordovician volcanics | 4 | 1.9 |
| Permo-Triassic mudstones & gypsum | 0 | 0.0 |
| Permo-Triassic sandstones | 0 | 0.0 |
| Precambrian marbles | 0 | 0.0 |
| Precambrian quartzites, gneisses & schists | 11 | 5.3 |
| Silurian metasediments & volcanics | 16 | 7.8 |
| Westphalian sandstones | 0 | 0.0 |
| Westphalian shales | 0 | 0.0 |
| TOTAL | 206 | 100 |

### 4.2.5 Distribution of surveyed wells by lithological groups

As described in Section 3.2, the bedrock units, together with the sand and gravel deposits, can be grouped into six main lithological units for ease of comparison. Thus, Dinantian pure bedded limestones, Dinantian pure unbedded limestones and Dinantian dolomitised limestones are combined into the pure limestones group, while the non-calcareous sedimentary group includes bedrock units such as Dinantian sandstones, Namurian sandstones and Devonian Kiltorcan-type sandstones and Devonian Old Red Sandstones. The distribution of surveyed wells (n = 214) within these main groups is shown in Figure 4.7 and 4.8a, whilst Figure 4.8b compares the distribution of surveyed wells within each lithological group against the total number of wells in the GIS analysis (n = 2569) of the full NMR database described in Section 3.3.6.

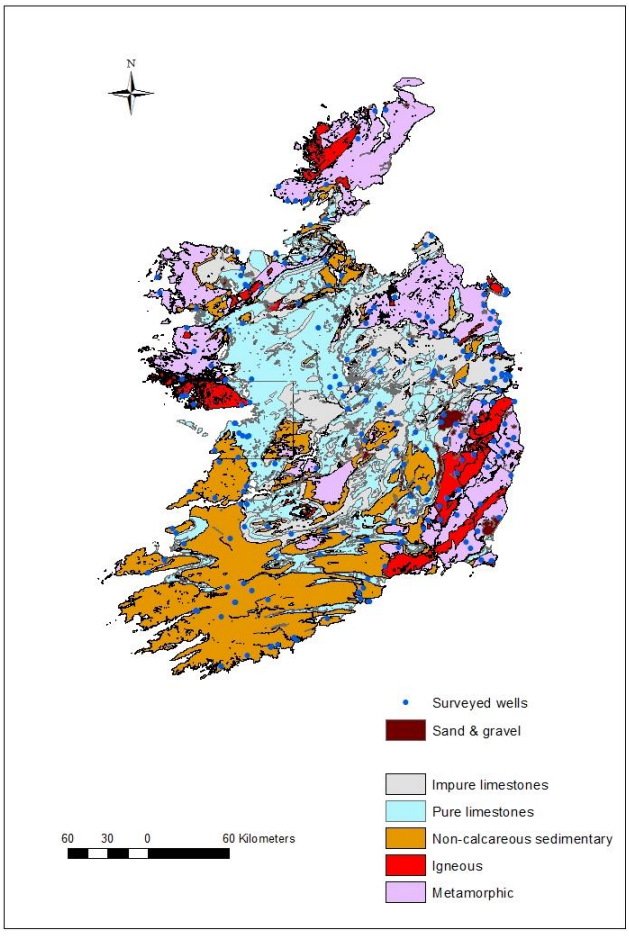
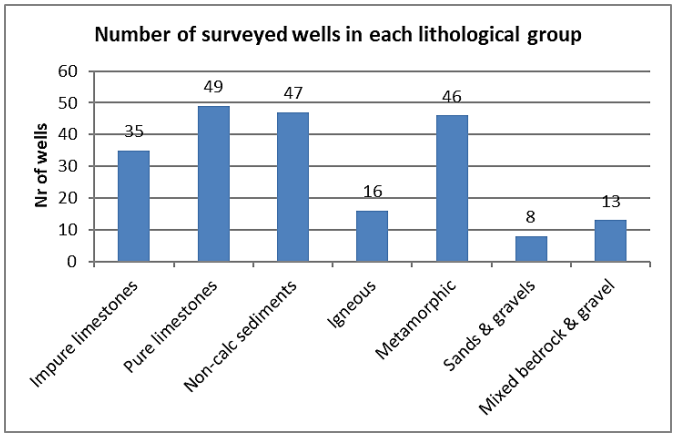
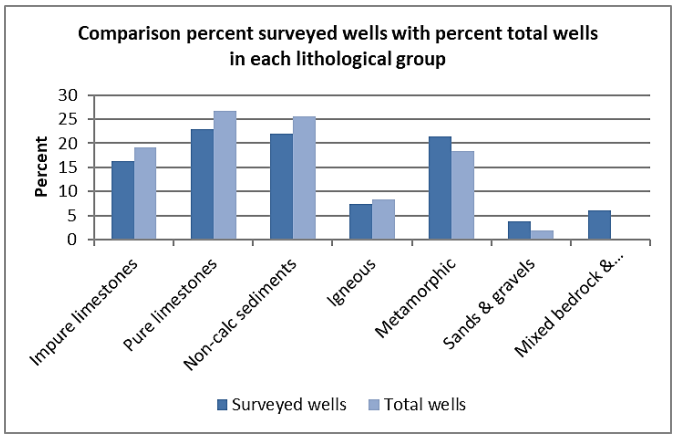



Figure 4.7 Map showing the distribution of surveyed wells according to the main lithological groups. (Map prepared in ArcGIS using GSI shapefiles)

It can be seen that the percent surveyed wells is slightly less than the total percent wells in each of the bedrock categories except the metamorphic group: this is partly because some of the surveyed wells have been assigned instead to a new, additional category, termed 'mixed bedrock and sand and gravel', as described below. The 'over-representation' of wells in the metamorphic category is partly due to the relatively large number of wells being surveyed in Co Wicklow (see Section 4.2.1), where seven of the 11 wells are in this bedrock category (which includes Cambrian, Ordovician and Silurian metasediments).




a)




b)

Figure 4.8 Distribution of surveyed holy wells by lithological group: a) number of wells in each group; b) percent surveyed wells (n= 214) compared to percent total wells in each group

The mixed bedrock and sand and gravel grouping includes those surveyed wells which likely derive their groundwater from a combination of bedrock and overlying superficial deposit. There are 13 such wells in total. In most cases these wells are located in areas where, although

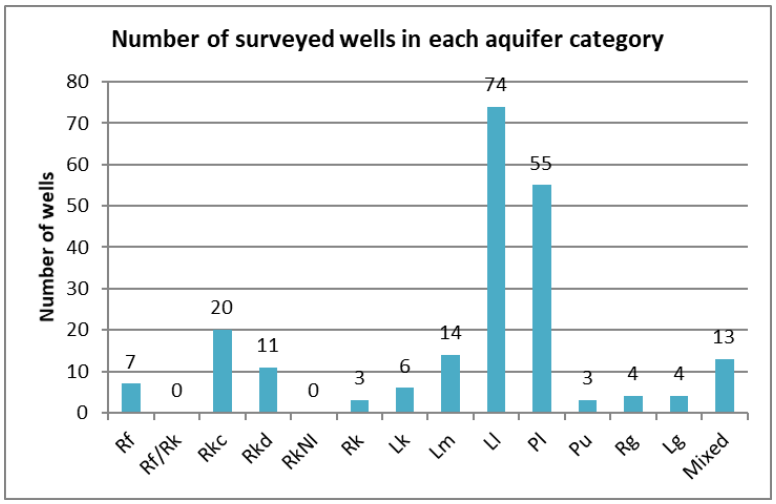
the aquifer map shows only a bedrock aquifer, the Quaternary map shows the presence of local gravel deposits which are insufficiently extensive to be mapped as an Lg aquifer and hence would not have been identified as having a gravel contribution in the GIS analysis of wells in different aquifers in Chapter 3. Examples include Tullowphelim in Co Carlow (gravel overlying granite bedrock), St Joseph's well Lennaun in Co Galway (gravel above metamorphic bedrock), and St Brigid's well at Drum in Co Roscommon (gravel overlying pure limestone bedrock). In the case of St Patrick's well in Trinity College Dublin, it is not the Quaternary map that indicates the presence of gravels (the map shows only tills and made ground, referred to as "Urban"); rather, this information was obtained from ground investigations at the College which showed that the well is close to an old buried channel of the River Stein, and hence probably taps gravels overlying the impure limestone bedrock (Lucan Formation, known as Calp – see Section 5.8). In addition to those wells where local gravel deposits probably contribute to the groundwater source, there are many wells located in or at the side of small valleys where local alluvial deposits may also form part of the groundwater source.

### 4.2.6 Distribution of surveyed wells by aquifer category

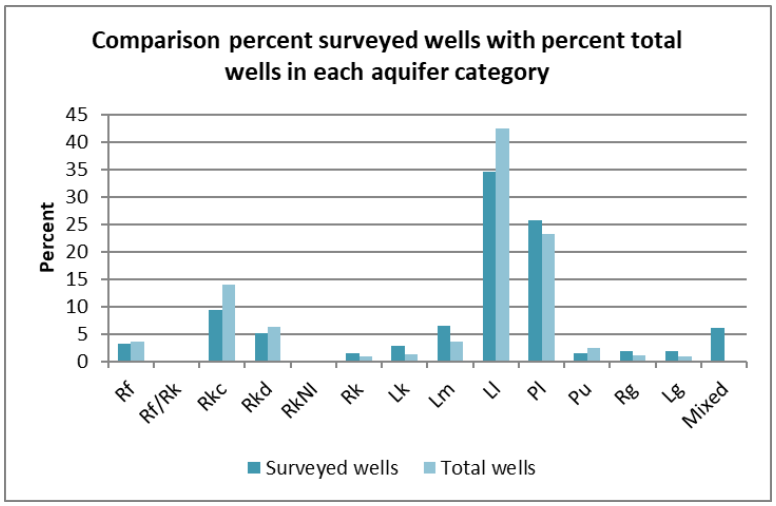
Figure 4.9 shows the number of surveyed wells in each aquifer category, the percent surveyed wells in each category and a comparison of the percent surveyed wells with percent total wells (from the GIS analysis in Section 3.3.7). Similar to the description of wells by lithological category in the previous section, a new "mixed" category has been added which was not included in the GIS analysis in Section 3.3.7. This category includes the 13 wells that are believed to draw their water from a mixture of a bedrock and a gravel source. Again, it should be emphasised that it is likely that other wells that are here classed as having a bedrock source may in reality receive some of their groundwater from a superficial source. There are many situations where spring wells are located in or at the margins of small valleys where there are limited thicknesses of alluvial deposits; also, sandy tills may have moderate permeability (compared to the generally low permeability of clayey tills) and hence form part of the active groundwater flow system.

The majority of the wells surveyed (132 out of 214, or 62%) are in aquifer categories that together can be referred to as poorly productive (categories Ll, Pl and Pu – see Section 3.2 for explanation of aquifer classes), in line with the overall distribution from the GIS analysis (Figure 4.9b). The poorly productive aquifers (PPAs) include Precambrian and Lower Palaeozoic metamorphic and igneous rocks, some Devonian Old Red Sandstone and Carboniferous impure

limestones. Wells in the main karst aquifers (Rkc, Rkd and Rk categories) occur in the mid-west and west of the country (Roscommon, Mayo, Galway, Clare), but are also found in the midlands (Laois, Kilkenny). Notable wells that tap regionally important sand and gravel aquifers include three wells located on the mid-Kildare Curragh aquifer (Section 5.7).




a)



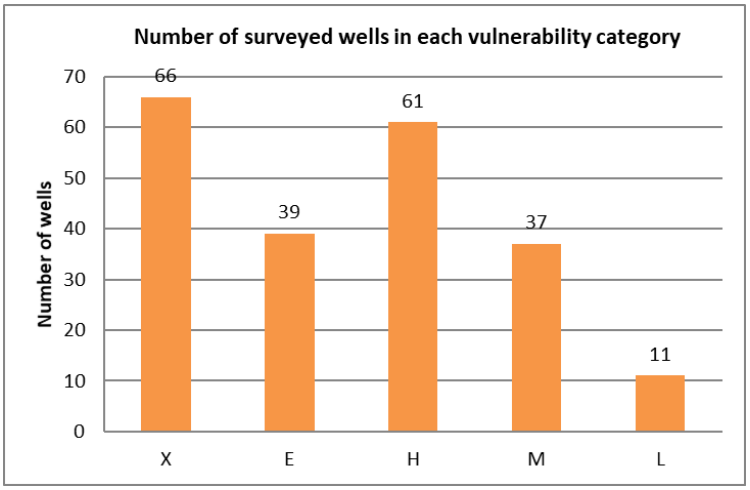

b)

Figure 4.9 Distribution of surveyed holy wells by aquifer category: a) number of wells in each category; b) percent surveyed wells (n = 214) compared to percent total wells in each category

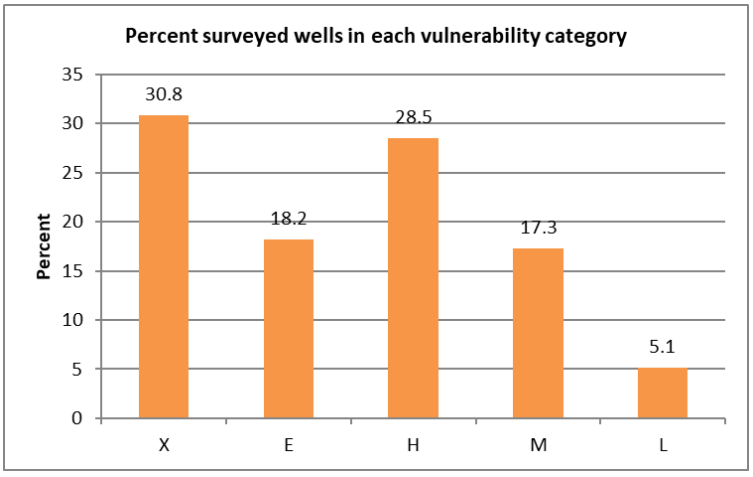
### 4.2.7 Distribution of surveyed wells by groundwater vulnerability class

The number of surveyed holy wells in each vulnerability category is illustrated in Figure 4.10. When the mapping indicated the well location to be at the boundary of two vulnerability

categories, such as X and E Extreme, the higher category was assigned in this analysis i.e. X in this instance.




a)




b)

Figure 4.10 Distribution of surveyed holy wells by groundwater vulnerability category: a) number of wells in each category; b) percent wells in each category (n = 214)

As in the GIS analysis of the total number of wells in the National Monuments database (Section 3.3.8), the largest percentage of surveyed wells falls in the Extreme category (X + E = 49% of surveyed wells, compared to a similar percentage of 47.2% in the full database), followed by the High (28.5% compared to 27.3%), Moderate (17.3% and 16.5%) and Low (5.1% and 9 %).

The well survey data, and site observations, confirm that the majority of holy wells are shallow spring wells, where the aquifer source (usually bedrock) is at or close to the ground surface. This

is consistent with the observation by Bord and Bord (1985), in their account of holy wells of Britain and Ireland, that 'most are not wells at all, but springs which flow into an artificially constructed stone basin'. They also noted that the terms spring, well and fountain were 'virtually interchangeable' in their usage.

### 4.2.8 Water level data from well surveys

At each well both the depth of water in the well and the depth to the water surface were recorded. In 16 cases the well was dry. There were also a few sites where the well was inaccessible (e.g. due to a locked gate at the well portal) and where it was thus not possible to make measurements. Descriptive statistics of the water level data are given in Table 4.7.

Table 4.7 Survey results: water levels

| | Depth of water (m) | Depth to water (m below ref pt) |
|---|---|---|
| Number of values | 174 | 182 |
| Average | 0.34 | 0.22 |
| Median | 0.30 | 0.18 |
| Std dev | 0.22 | 0.21 |
| Max | 1.00 | 1.46 |
| Minimum | 0.01 | 0.00 |
| 5th percentile | 0.04 | 0.00 |
| 95th percentile | 0.70 | 0.56 |

It can be seen from the table that these spring wells are generally shallow, containing on average 0.34 m of water, and they have a maximum water depth of only 1 m. The values of depth to the water surface (in the right hand column of the table) are somewhat arbitrary, in that they are depths measured from different reference points at each well rather than depths below ground level; these reference points were typically a stone lip at the entrance to the well portal, a step leading down to the well, or some other solid structure (the ground level was not taken as the reference point since this was often uneven). Notwithstanding this limitation, the data again illustrate the shallow nature of the wells: the minimum and 5$^{th}$ percentile values of 0 m represent water at the ground surface, whilst the 95$^{th}$ percentile value showed a depth to water

of only 0.56 m. Therefore, when access was available to the well, the water level was normally easily accessible.

## 4.3 Concluding remarks

In this chapter it has been demonstrated that the surveyed holy wells fall into all the main physiographical, lithological and aquifer categories identified in the previous chapter for the full holy wells dataset. With 215 wells surveyed across the country, their distribution can be regarded as being fairly representative of the full number of holy wells described in Chapter 3 (up to 2676 wells were included in that GIS analysis). At a confidence level of 95%, the calculated margin of error for the 215 well survey sample of the estimated total well population was approximately 6% (Section 4.1). The four monitoring wells were chosen as examples of holy wells in four of the six main lithological groups, but cannot necessarily be regarded (owing to their small number) as being representative of the larger well populations within those groups.

One new lithological and aquifer category was added to the GIS analysis of the surveyed wells in this chapter: this is the “mixed” category, where the groundwater source for the holy well is believed to be derived from a combined bedrock and sand and gravel source (Section 4.2.5). A total of 13 wells were assigned to this mixed category, but this is likely an underestimate: there are probably many more wells where the superficial deposits contribute to a groundwater flow that comes mainly from the shallow bedrock and/or transition zone.

# 5 Well descriptions

## 5.1 Introduction

A full list of the sites visited, including their grid references, is provided in Appendix A. The individual reports on the 215 surveyed holy wells and five spa wells prepared by this researcher amount to more than 1200 pages. It is hoped that these reports (subject to any constraints such as land access issues, etc) can be published in the future as a standalone volume, or as a series of online reports on holy wells as geological heritage sites (see Section 8.3.3).

A major challenge was to decide which wells to describe within this chapter, given that the aim of the chapter is to provide an indication of the diversity of well types and their range of hydrogeological settings. A second challenge was how best to organise the descriptions of the selected wells – for example, by physiographic unit, lithology, aquifer category? In Chapter 6, natural background levels (NBLs) of various chemical parameters for Irish groundwaters are presented mainly according to lithological groupings. There are also distinctions made for certain parameters between confined and unconfined aquifer conditions. Therefore, the results of the individual well surveys will be discussed here according to the main lithological groups, but with a section added on wells in confined aquifers (the vast majority of wells in each lithological unit being in unconfined aquifers). Moreover, the physiographical setting is particularly relevant to the hydrogeology (and, most especially, the hydrochemistry) of coastal wells, and a separate section has been included for these wells. At the end of this chapter, the five surveyed spa wells are described.

The locations of the holy wells described in this chapter are shown in Figure 5.1. The name of each well that corresponds to the number shown on the map is given in Table 5.1, together with the relevant report section where it is described. The table also includes a summary of the main lithology, Groundwater Rock Unit Group (GRUG) and aquifer class at each well site.

Although the focus of the chapter is on the geological and hydrogeological settings of the surveyed wells, non-hydrogeological aspects (history, cures etc) of individual wells are mentioned briefly where these are of interest; these aspects are described in more detail in Chapter 8. As such, they provide a snapshot of the condition of holy wells in Ireland in the period 2016-2019.

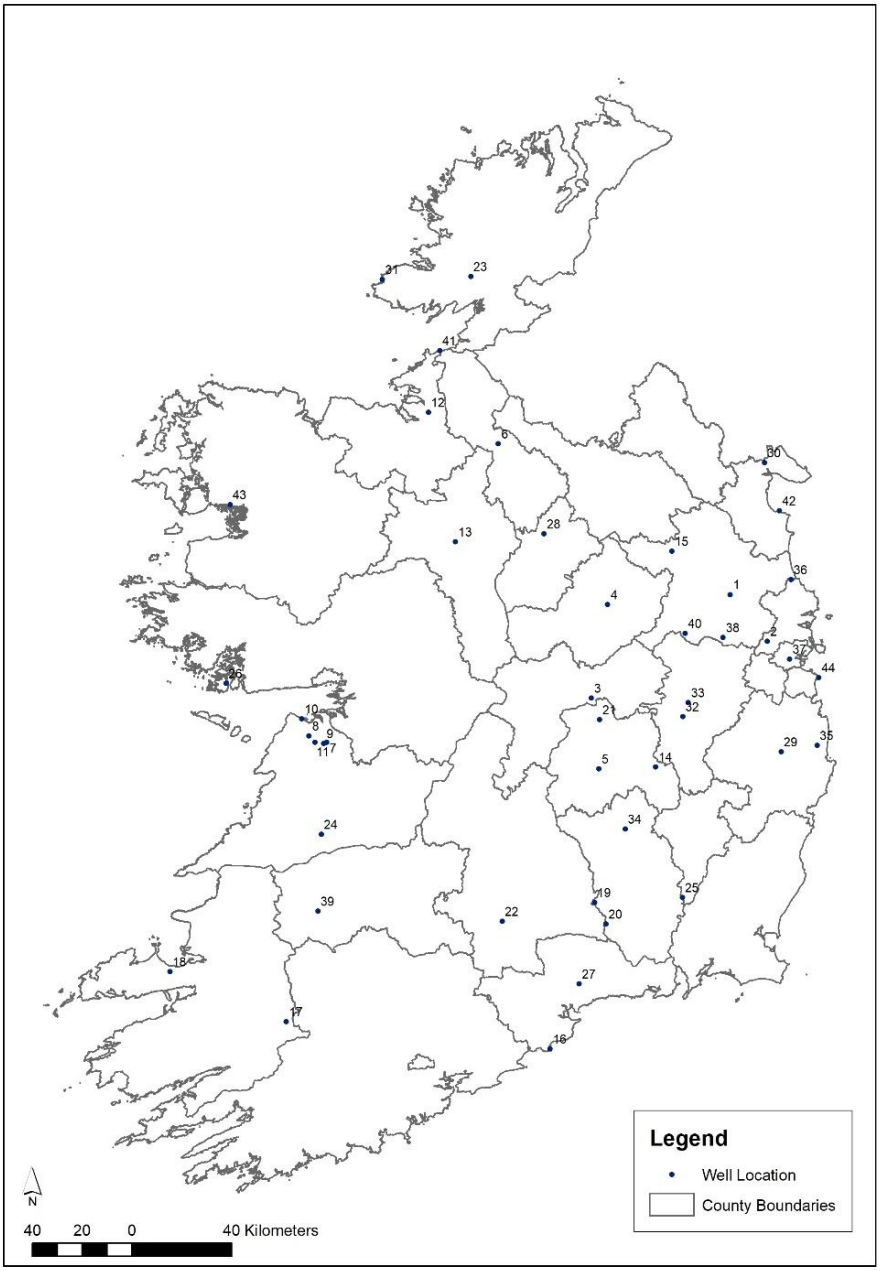



Figure 5.1 Location of holy wells described in Chapter 5. See Table 5.1 for a key to the well numbers. (This map was prepared by Dr Ronan Foley)

Table 5.1 Summary of the holy wells described in Chapter 5. (See Figure 5.1 for a location map)

| Nr | Chapter Section | Well name | County | Lithology | Groundwater Rock Unit Group[a] | Aquifer class[b] |
|---|---|---|---|---|---|---|
| 1 | 5.2.1.1 | Well of the White Cow Tara | Meath | Impure lst | Dinantian upper impure limestones | Lm |
| 2 | 5.2.1.2 | Lady's well Mulhuddart | Dublin | Impure lst | Dinantian upper impure limestones | Ll |
| 3 | 5.2.1.3 | Seven Blessed Wells of Killeigh | Offaly | Impure lst | Dinantian upper impure limestones | Ll |
| 4 | 5.2.1.4 | St Brigid's well Cullion | Westmeath | Impure lst | Dinantian upper impure limestones | Ll |
| 5 | 5.2.2.1 | St Fintan's well Cromogue | Laois | Impure lst | Dinantian lower impure limestones | Ll |
| 6 | 5.2.2.2 | St Hugh's well Cleighran Beg | Leitrim | Impure lst | Dinantian shales and limestones | Pl |
| 7 | 5.3.1.1 | St Fachtna's well Termon | Clare | Pure lst | Dinantian pure bedded limestones | Rkc |
| 8 | 5.3.1.1 | Poll Insheen Gleninsheen | Clare | Pure lst | Dinantian pure bedded limestones | Rkc |
| 9 | 5.3.1.2 | St Cronan's well Termon | Clare | Pure lst | Dinantian pure bedded limestones | Rkc |
| 10 | 5.3.1.3 | Tobercornan Gleninagh North | Clare | Pure lst | Dinantian pure bedded limestones | Rkc |
| 11 | 5.3.1.4 | Tober Dearg Eanty More | Clare | Pure lst | Dinantian pure bedded limestones | Rkc |
| 12 | 5.3.2.1 | Tobernalt | Sligo | Pure lst | Dinantian pure bedded limestones | Rkc |
| 13 | 5.3.2.2 | Ogulla well Tulsk | Roscommon | Pure lst | Dinantian pure bedded limestones | Rkc |
| 14 | 5.3.3.1 | Toberneeve Ballyadams | Laois | Pure lst | Dinantian pure bedded limestones | Rkd |
| 15 | 5.3.3.2 | St Kieran's well Castlekeeran | Meath | Pure lst | Dinantian pure bedded limestones | Lm |
| 16 | 5.4.1.1 | St Declan's well Ardmore | Waterford | Non-calc sed | Devonian Old Red Sandstones | Ll |
| 17 | 5.4.1.2 | Holy well at Shrone | Kerry | Non-calc sed | Devonian Old Red Sandstones | Ll |
| 18 | 5.4.1.3 | Tobar na nGealt Gleann na nGealt | Kerry | Non-calc sed | Devonian Old Red Sandstones | Ll |
| 19 | 5.4.2 | St Nicholas's well Killamery | Kilkenny | Non-calc sed | Devonian Kiltorcan-type sandstones | Rf |
| 20 | 5.4.2 | St Kieran's well Kilkieran | Kilkenny | Non-calc sed | Devonian Kiltorcan-type sandstones | Rf |
| 21 | 5.4.2 | St Brigid's well Rosenallis | Laois | Non-calc sed | Devonian Kiltorcan-type sandstones | Rf |
| 22 | 5.4.2 | St Peacaun's well Toureen | Tipperary | Non-calc sed | Devonian Kiltorcan-type sandstones | Rf |
| 23 | 5.4.3.1 | St Colmcille's well Disert | Donegal | Non-calc sed | Dinantian sandstones | Lm |
| 24 | 5.4.3.2 | St Martin's well Ballinacally | Clare | Non-calc sed | Namurian sandstones | Ll |
| 25 | 5.5.1 | St Moling's well St Mullins | Carlow | Igneous | Granites & other igneous intrusives | Pl |
| 26 | 5.5.2 | St Anna's well Gorumna Island | Galway | Igneous | Granites & other igneous intrusives | Pl |
| 27 | 5.5.3 | St Brigid's well Kilrossanty | Waterford | Igneous | Ordovician volcanics | Rf |
| 28 | 5.6.1 | St Patrick's well Cartron | Longford | Metamorphic | Ordovician metasediments | Pl |
| 29 | 5.6.2 | St Kevin's well Glendalough | Wicklow | Metamorphic | Ordovician metasediments | Ll |
| 30 | 5.6.3 | St Brigid's well Faughart | Louth | Metamorphic | Silurian metasediments and volcanics | Pl |
| 31 | 5.6.4 | St Colmcille's well Glencolmcille | Donegal | Metamorphic | Precambrian quartzites, gneisses and schists | Pl |

Table 5.1 (continued) Summary of wells described in Chapter 5

| Nr | Chapter Section | Well name | County | Lithology | Groundwater Rock Unit Group[a] | Aquifer class[b] |
|---|---|---|---|---|---|---|
| 32 | 5.7.1.1 | St Brigid's well Tully | Kildare | Sand & gravel | (Dinantian pure bedded lsts)[c] | Rg |
| 33 | 5.7.1.2 | Father Moore's well Rathbride | Kildare | Sand & gravel | (Dinantian lower impure lsts)[c] | Rg |
| 34 | 5.7.2 | St Canice's well Kilkenny | Kilkenny | Sand & gravel | (Dinantian pure bedded lsts)[c] | Rg |
| 35 | 5.7.3.1 | Holy Trinity Well Ashford | Wicklow | Sand & gravel | (Cambrian metasediments)[c] | Lg |
| 36 | 5.7.3.2 | Tobersool Balbriggan | Dublin | Sand & gravel | (Silurian metasediments and volcanics)[c] | Lg |
| 37 | 5.8.1 | St Patrick's well Trinity College Dublin | Dublin | Mixed gravel & bedrock | Gravel / Dinantian upper impure limestones | Lg/Ll? |
| 38 | 5.9.1 | Bride's well Calgath[d] | Meath | Impure lst | Dinantian upper impure limestones | Ll |
| 39 | 5.9.2 | St Brigid's well Shangarry[d] | Limerick | Impure lst / pure lst | Dinantian upper impure limestones / Dinantian pure unbedded lsts | Ll/Rkd |
| 40 | 5.9.3 | St Gorman's well Enfield[d] | Meath | Pure lst | Dinantian pure unbedded lsts | Ll |
| 41 | 5.10.1 | Shaver's well Tullaghan[e] | Leitrim | Non-calc sed | Dinantian sandstones | Lm |
| 42 | 5.10.2 | St Colman's well Salterstown[e] | Louth | Metamorphic | Silurian metasediments and volcanics | Pu |
| 43 | 5.10.3 | St Brendan's well Roskeen[e] | Mayo | Pure lst | Dinantian pure bedded limestones | Lk |
| 44 | 5.10.4 | St Begnet's well Dalkey Island[e] | Dublin | Igneous | Granites & other igneous intrusives | Pl |

Notes: [a] See Table 3.1 for list of Groundwater Rock Unit Groups (GRUGs)

[b] See Table 3.2 for details of aquifer classification

[c] This is the GRUG that underlies the sands and gravels

[d] Well in confined aquifer

[e] Well in coastal setting

## 5.2 Wells in impure limestones

This lithological grouping mainly covers those wells that tap the Dinantian upper and lower impure limestones (DUIL and DLIL, with 17 and 10 wells respectively), but also includes wells in Dinantian early sandstones, shales and limestones (DESSL, three wells), Dinantian mixed sandstones, shales and limestone (DMSSL, four wells), and Dinantian shales and limestones (DSL, one well). The main formation within the DUIL is the Lucan formation (Calp) in the east and midlands, but the DUIL also includes e.g. undifferentiated Visean limestones in Co Limerick,

whilst the DLIL includes the Ballysteen Limestone (found e.g. in counties Cavan, Longford and Westmeath) and the Malahide Formation (Co Dublin). In addition, there are five wells in the 'Mixed' category which have impure limestones as their bedrock source; one of these wells is described in Section 5.8.

The majority (27 out of 35 wells, or 77%) of wells surveyed in impure limestones are classed as being in the locally important Ll aquifer category - including all 10 wells in the DLIL and the three wells in the DESSL - whilst six of the wells (three each in the DUIL and DMSSL lithological groupings) tap aquifers categorised as locally important Lm.

### 5.2.1 Holy wells in Dinantian upper impure limestones (DUIL)

The examples described here are Well of the White Cow Tara (Co Meath), Lady's well Mulhuddart (Co Dublin), Seven Blessed Wells of Killeigh (Co Offaly) and St Brigid's well Cullion (Co Westmeath). Another prominent holy well in this Dinantian upper impure limestone grouping is Bride's well Calgath (Co Meath); this is described later within the section on wells in confined aquifers (Section 5.9).

#### 5.2.1.1 Well of the White Cow Hill of Tara, Co Meath

The Well of the White Cow is the best known of several wells in the Tara area. In addition to being known as Well of the White Cow (*Tipra bo fine*), there are several alternative names for this well – St Patrick's well (by which name it is described by French [2012]); *Caprach Cormac* (Cormac's well); *Liagh* (the Physician's well); *Deare Dubhe* (well of the dark eye); and *Poll tocair na tuiliche* ('trial by ordeal').

The entrance gate to the well site is about 270 m south along the road from the pedestrian entrance to the Hill of Tara heritage area. Although not marked on the OSI Discovery map, the well is shown on the historical 6 inch and 25 inch maps. This spring well is close to the contact between the argillaceous limestones and shales of the Dinantian Loughshinny Formation (which underlie the Hill of Tara), and the overlying shales, with limestones and sandstones, of the younger Namurian Donore Formation (see Figure 5.2). In the Groundwater Rock Unit Groupings (GRUGs), the Loughshinny Formation is classed as part of the DUIL whilst the Donore Formation

is classed as Namurian undifferentiated. Bedrock is close to the ground surface, as indicated by the X Extreme groundwater vulnerability rating.

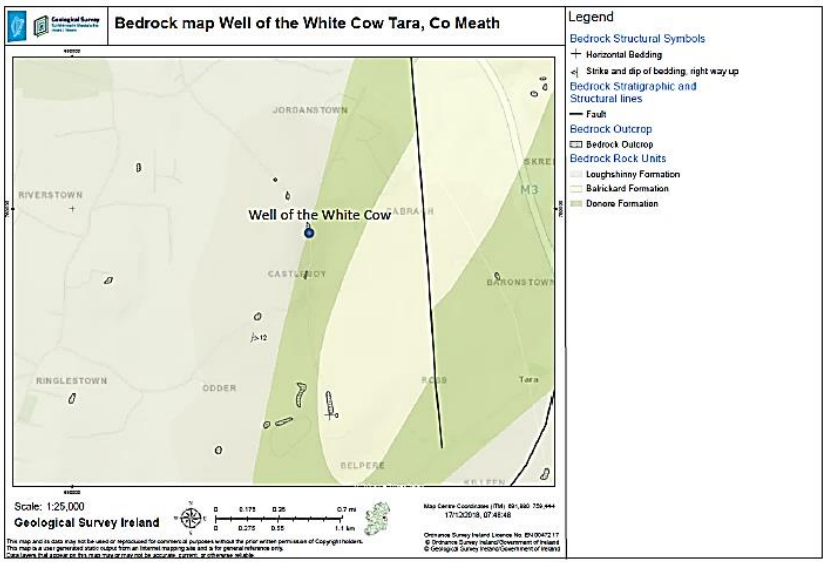



Figure 5.2 Bedrock geology map for Well of the White Cow, Hill of Tara, Co Meath. (Map prepared using GSI Groundwater Data Viewer)

The proximity of the well to the boundary between the locally important aquifer (Lm) provided by the Loughshinny Formation, with the poor aquifer (Pl) comprising the Donore Formation, suggests that it is a contact spring, with groundwater being forced to the surface where downward flow is impeded by the presence of less permeable rocks downslope to the east.

#### 5.2.1.2 Lady's well Mulhuddart, Co Dublin

Lady's well is included here as an example of a holy well which is especially susceptible to adverse human interference and pollution despite the fact that the well is of some historical importance, with a well building that may have its origins in the 14$^{th}$ century (Branigan, 2012). The well has a reputation for treating sprains, cuts, bruises and rheumatism (Branigan, 2012), whilst Logan (1980) and Healy (2001) also mention a cure for sore eyes.

The whitewashed rectangular stone well house that covers the well measures roughly 3 m x 1.6 m in its exterior dimensions. The gently pitched masonry roof is topped by two finials, one over the front entrance (containing a statue of the Blessed Virgin Mary) and the other over the rear wall and window (decorated with a cross). Entrance to the well is via an arched doorway; and there is a window at the rear. The well was virtually dry at the time of a visit in August 2016,

with just wet mud at its base. There was a lot of rubbish inside the well and in the immediate surround (see Figure 5.3). In March 2017 the well contained up to 35 cm of water – but still with lots of rubbish.



a) b)

c) d)

Figure 5.3 Lady's well Mulhuddart, Co Dublin: a) its entrance is within 1 m of a main road; the white-washed well building is topped with two finials painted in blue; b) rear view of the well building; c) the well interior, which was essentially dry on 9/8/2016; d) water and rubbish inside the well on 18/3/2017. Photos by Bruce Misstear

The bedrock in the area is dark limestone and shale belonging to the Dinantian Lucan Formation (Calp), part of the DUIL. The contact with the underlying Tober Colleen Formation is less than 300 m east of the well. Bedrock occurs close to the ground surface: Buckley (2012) refers to a shallow site investigation in the area around the well in 1983, which found that the average

depth to rock was about 2 m. The fact that the subsoils are thin suggests that this spring derives its water from the DUIL bedrock aquifer, classed as Ll. Gravels found along the Tolka valley are probably too far from the well site (400 m) to influence the well hydrogeology.

#### 5.2.1.3 Seven Blessed Wells of Killeigh, Co Offaly

This is not a well as such, but rather a spring at the head of a small stream. The well is marked on the OSI Discovery map, and is shown as the Seven Blessed Wells of Killeigh on the historical 6 inch and 25 inch maps.

It is not clear why this spring well is known as the "Seven Blessed Wells". A web entry states that there are seven natural springs in the vicinity[11], but the site seems to be based around a single spring. The same website refers to a cure for eyes. The well – or spring – is at the head of a stone-lined channel within a nicely planted garden area. There are 11 steps down into the well and the water could be seen issuing from a small gap between the bottom two steps (Figure 5.4). At the bottom step the channel is about 1.2 m wide, but then narrows to around 0.5 m; the channel discharges to a stream about 25 m from where the spring issues at the steps; the stream drains westwards, eventually joining the Clodagh River about 3 km away.

The bedrock comprises dark limestone and shale beds of the Lucan Formation, which locally dip to the north (DUIL in the GRUGs). These overlie massive Waulsortian limestones and mudstones (Dinantian pure unbedded limestones). The bedrock is overlain by cut-over raised peat and limestone till, and a Moderate vulnerability rating suggests these subsoils are more than 5 m thick at this location. The spring(s) presumably originate from the underlying locally important (Ll) Lucan Formation bedrock aquifer.

[11] http://www.thestandingstone.ie/2012/08/killeigh-holy-well-and-rag-tree-co.html (accessed 31/1/2020)



a)



b)

Figure 5.4 Seven Blessed Wells Killeigh, Co Offaly: a) the spring channel, from its source at the steps (foreground), to its outflow to the stream (beyond the wooden fence in the background); note the votives along the left bank; b) water was seen issuing from the gap between the lowermost two steps. Photos by Bruce Misstear

#### 5.2.1.4 St Brigid's well Cullion, Co Westmeath

St Brigid's well is about 3 km north of Mullingar town centre, beside a railway level crossing and the Royal Canal Supply from Lough Owel. This is a spring well that flows into a channel that joins another drain a few metres away, before flowing into the neighbouring fish farm and County Council site. The area around the well contains a circular path (with Stations of the Cross), and there is a stone chapel opposite the well. Ray (2015) cites this well as an example of where the Stations of the Cross have been recently installed at a holy well site under the patronage of an indigenous saint such as Brigid, overlaying traditional well rounding practices. The well itself is approximately oval, measuring about 0.4 x 0.5 m, and is covered by a vaulted stone canopy (Figure 5.5).

The Quaternary deposits comprise limestone tills, but these are thin in the area, with rock outcrop or subcrop nearby to the east. The bedrock is dark limestone and shale belonging to the Lucan Formation (DUIL). The Derravaragh Cherts occur a short distance to the northeast. The limestones of the Lucan Formation are classed as a locally important (Ll) aquifer whereas the nearby cherts are rated as a locally important karstified aquifer (Lk); see Figure 5.6.




a) b)

Figure 5.5 St Brigid's well Cullion, Co Westmeath: a) the well, with its vaulted stone canopy; b) the outflow channel. Photos by Bruce Misstear

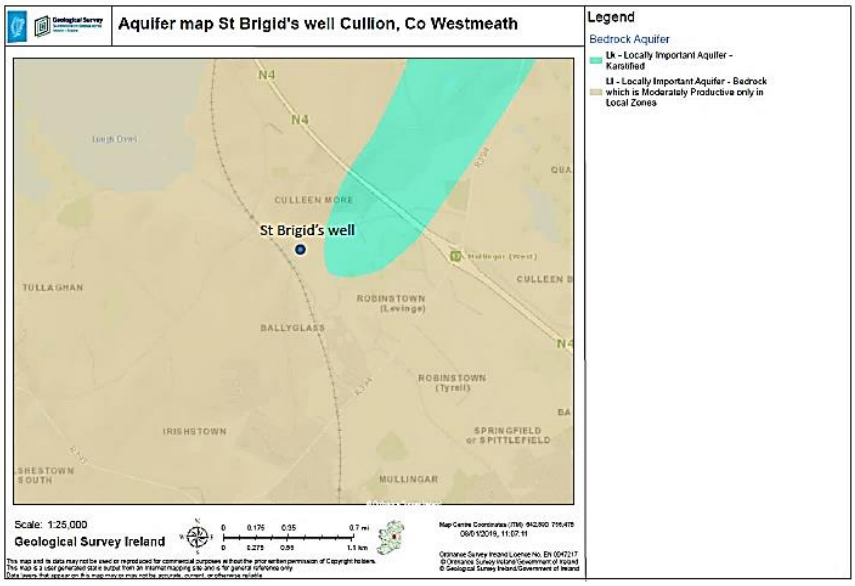



Figure 5.6 Aquifer map for St Brigid's well Cullion, Co Westmeath. (Map prepared using GSI Groundwater Data Viewer)

The location of this spring may possibly be influenced by the presence of the karstic chert aquifer, although the map shows the boundary with the Calp about 200 m to the northeast. The well was visited on a very cold day (24/11/2016) and a large contrast was observed between the air temperature (0 °C) and the water temperature in this shallow spring (11.3 °C). This might indicate a relatively long flow path and residence time, and hence possibly supports the

hypothesis that the groundwater source may be the karstic chert aquifer (or alternatively, a relatively deep source from within the Calp).

### 5.2.2 Holy wells in other impure limestones

Two wells will be described here, one in the Dinantian lower impure limestones (DLIL) and the other in Dinantian shales and limestones (DSL).

#### 5.2.2.1 St Fintan's well Cromogue, Co Laois

The well is accessed by a small road (L5658) off the R430 Mountrath to Abbeyleix road. It is in a well-tended garden, about 200 m south-southwest of a 12th century church and graveyard. In addition to a reputation for eye cures, stones from this well are traditionally taken by pilgrims to protect against shipwrecks or house fires[12]. The well is one of the holy wells described in Feehan's '*The Geology of Laois and Offaly*' (Feehan, 2013).

This well is sourced from the DLIL, more specifically from the muddy limestone and shale belonging to the Ballysteen Formation, which is classed as a locally important (Ll) aquifer. A Moderate vulnerability rating indicates that the subsoils are at least 5 m thick (and possibly more than 10 m if the sandstone till has Moderate rather than Low permeability). The holy well may therefore obtain its water at least partly from the subsoil deposits (comprising till derived from Devonian sandstones, with alluvium along the stream valley immediately to the west); there are a couple of hand dug wells in the vicinity, the presence of which might also suggest a shallow water source.

#### 5.2.2.2 St Hugh's well Cleighran Beg, Co Leitrim

This spring well is close to the eastern shore of Lough Allen. The well is partly covered by a 'half-beehive' shaped building. There is a flat stone at the entrance, over which the spring well was overflowing when visited in May 2018. The most striking feature is the bright orange iron-rich (ochre) deposits that cover the base of the well, and the iron staining and deposits where it

[12] http://www.askaboutireland.ie/reading-room/history-heritage/folklore-of-ireland/tales-customs-and-beliefs/saint-fintans-wells/; accessed 31/1/2020

overflows the stone at the well entrance and in the small channel/ditch where it discharges to the nearby stream (Figure 5.7).



Figure 5.7 The striking orange colour produced by iron staining and ochre deposits in St Hugh's well Cleighran Beg, Co Leitrim. Photo by Bruce Misstear

The groundwater source is the Carraun Shale Formation (shales with minor limestones), classed as Dinantian shales and limestones (DSL). This iron-rich (chalybeate) spring water is much more mineralised than the water in the nearby stream (EC values of 687 and 85 µS $cm^{-1}$, respectively, measured on 10/5/2018).

## 5.3 Wells in pure limestones

In an analysis of the distribution of karst landforms according to GRUGs, Drew (2018) found that 83% of the landforms are in the pure bedded limestone unit, including 71% of the springs, with 8% of landforms and 11% of springs in the pure unbedded limestone unit. Interestingly, 9% of the landforms and 17% of the springs are located in impure limestones: this highlights that karst features can occur in all carbonate rocks, albeit they are most abundant in the pure bedded limestones. In relation to aquifer category, Drew's analysis showed that karst landforms can occur in all categories (except Pu); springs are most common in the Rkc category (accounting for almost 60% of the total).

The survey of holy wells in the present research covered 49 wells in the pure limestones lithological grouping, comprising Dinantian pure bedded limestones (30 wells), Dinantian pure

unbedded limestones (17 wells) and Dinantian dolomitised limestones (two wells). The DPBL includes the Burren Formation in Clare, the Rickardstown Formation in Kildare, the Ballyshannon Formation in Donegal, the Ballyadams Formation in Laois and Kilkenny, the Oakport Limestone Formation in Mayo and the Dartry Limestone Formation in Monaghan and Sligo, plus undifferentiated Visean in Roscommon (note that the Visean also includes impure limestones), whilst the main DPUL formation is the Waulsortian.

The pure limestones lithological grouping contains several prominent karst wells, including spring wells issuing from conduit karst: the survey involved 20 holy wells in the Rkc aquifer category, plus 11 wells in Rkd, three wells in the Rk and six wells in the Lk classes (the remaining nine wells fall mainly in the non-karstic Ll category). Nevertheless, karst features may be found in aquifers not designated as karst e.g. St Kieran's well Castlekeeran in Co Meath (Lm; see Section 5.3.3.2) and, as noted above by Drew (2018), even in limestones that are not classed as pure. The classic karst areas occur in the west on the Burren Plateau in Co Clare and in the Western Lowlands of Galway, Mayo and Roscommon, but karst wells are found elsewhere including in the Eastern Lowlands (Meath, Westmeath, Laois, Kilkenny and North Tipperary), the Plateaux of the Northwest in Sligo / Leitrim and in the South (Cork, Waterford and South Tipperary).

### 5.3.1 Holy wells on the Burren karst plateau, Co Clare

The Burren Plateau in northwest Co Clare covers an area of 400 km$^2$ and contains numerous karst landforms including springs (Drew, 2018). Many of these have been designated as holy wells, and these include St Fachtna's well Termon, Poll Insheen Gleninsheen, St Cronan's well Termon, Tobercornan Gleninagh North, and Tobar Dearg Eanty More. All are located in regionally important conduit karst (Rkc) aquifers formed by Dinantian pure bedded limestones (especially the Burren Formation). These beds generally dip gently to the south-southwest, and Drew (2018) notes that this has influenced the development of the groundwater flow paths along bedding planes. Other influences on karstification on the Burren Plateau include east-west joints and north-south mineral veining, and the presence of clay or shale wayboards between limestone beds (Bunce and Drew, 2019; Walsh *et al.*, 2019). The locations of the five wells discussed here in relation to the bedrock geology of the Burren Plateau are shown in Figure 5.8.

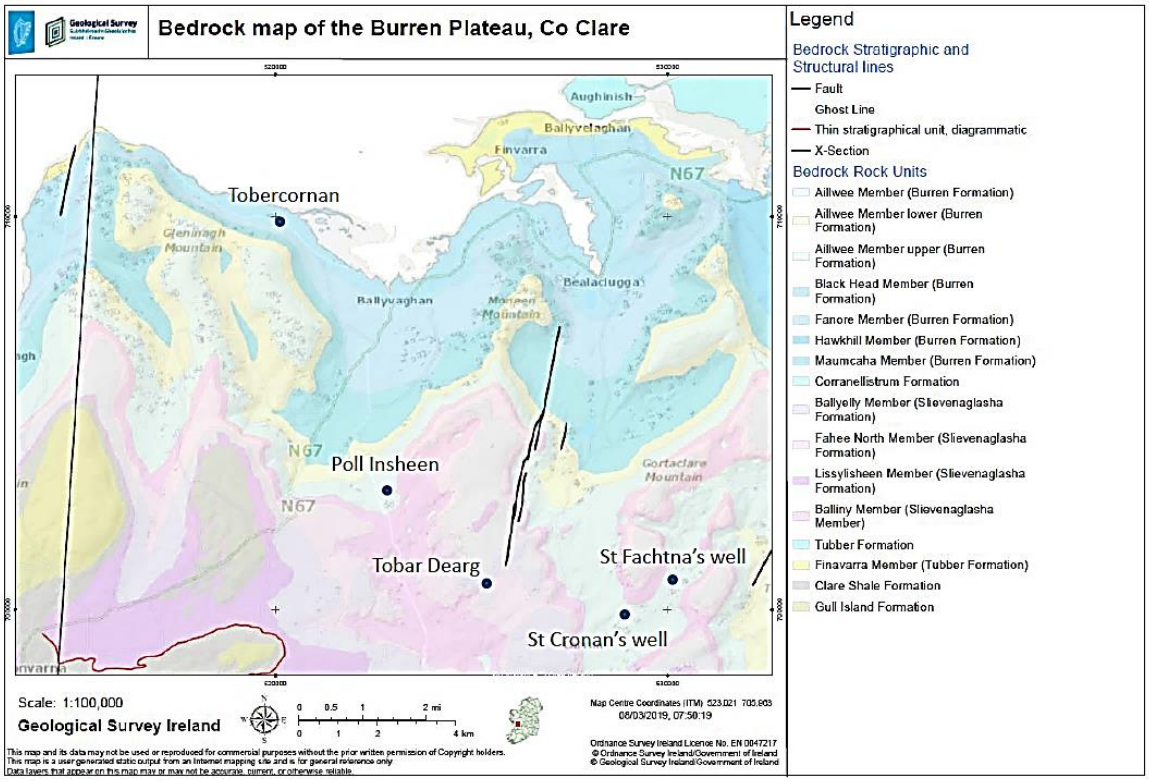



Figure 5.8 Bedrock geology map of the Burren Plateau showing the locations of the holy wells described in the text. (Map prepared using GSI Groundwater Data Viewer)

#### 5.3.1.1 St Fachtna's well Termon and Poll Insheen Gleninsheen, Co Clare

These are two examples of wells formed within a solution-enhanced hollow (known as a kamenitza) in epikarst (Figure 5.9). Kamenitzas are common in karst limestone areas such as the Burren. The karstified limestone bedrock at both sites belongs to the Aillwe member (Upper) of the Burren Formation (part of the DPBL unit). Despite their similar geologies and hydrogeological settings, the wells have different reputations as regards cures: eye ailments in the case of St Fachtna's well (Kirby, 2014) and toothache for Poll Insheen (Rackard and O'Callaghan, 2001; Doolan, 2002).



a) b)

Figure 5.9 Holy wells formed in solution-enhanced hollows (kamenitzas) in karst limestone: a) St Fachtna's well Termon: the bedding joint that presumably supplies the well is just visible below the water surface; b) Poll Insheen Gleninsheen, with its stone cairn above (note the toothbrushes – this well has a reputation for curing toothache). Photos by Bruce Misstear

St Factna's well (Tobar Fachtna) is on the Carran Loop path, close to the roadside where it is signposted (the townland is sometimes given as Coskeam, although the well appears to be in Termon). Behind the well there is a square stone cairn (leacht?), which is one of several similar cairns in the area that presumably mark stations for the pilgrimage route or *turas*. The well (kamenitza) is oval shaped, measuring 0.5 m front to back, and 0.33 m in width and is fed by an open bedding plane joint visible in the well at a depth of 0.36m. There could possibly also be a deeper inflow zone as the well extends to a depth of 0.75 m, but the base of the well was not visible. The well contained 0.48 m of water when visited in August 2018. Drew (2014) noted that, according to local people, the well never dries up. The well is not shown as a karst feature on the GSI Groundwater Viewer.

Poll Insheen is about 5 km south of Ballyvaughan, accessed by a farm track heading north off the east side of the R480. The well is associated with treating toothache (Rackard and O'Callaghan, 2001; Doolan, 2002), and indeed is referred to in the book by Brenneman and Brenneman (1995) simply as 'Tooth Well'. A stone cairn between 0.5 and 0.6 m high covers the small circular hollow in the limestone pavement that is Poll Insheen. The well is only 0.25 m in

diameter and contained about 0.1 m of water when measured in May 2017, August 2018 and April 2019. The well area is surrounded by a simple two-bar metal fence. Nearby, but outside the fence, there is another circular water-filled kamenitza similar to Poll Insheen, but without a cairn over it. This well is 0.2 m in diameter, and contained 0.2 m of water on 2/8/2018.

In contrast to St Fachtna's well, the source of water inflow at Poll Insheen is not so evident. The stone cairn above the well would shelter it from receiving direct rainfall, and there is no surface furrow or channel (karren) on the rock surface leading to the well (unlike the second small well outside the fence, where such a furrow is visible – see Figure 5.10). Again, there is no bedding joint or other structural feature visible in the well apart from a small opening on the south (low) side of the well, above the water level. There is a small piece of vegetation a few cm above the high water mark on the left (southwest) wall of the well, from which water could be seen dripping (very slowly – one drop every few seconds) into the well; this, at least, indicates one source of inflow from the epikarst, albeit a small one. However, the water level in the well appears to be higher than the base of surrounding grikes, which appear to be dry (although some contain vegetation at their base). Poll Insheen seems to be in a relatively isolated block of limestone.



a) b)

Figure 5.10 Poll Insheen Gleninsheen, Co Clare: a) a deep north-south joint (grike) runs past the well (top right of photo); the water level in the well appeared to be higher than the elevation of the dry base of the grike; b) the second kamenitza, just outside the metal fence that protects Poll Insheen: a channel (karren) can be seen leading to this 'well', unlike at the main Poll Insheen in a) or at St Fachtna's well in Figure 5.8a. Photos by Bruce Misstear

A karst spring (referred to as a holy well) is shown a few metres west of Poll Insheen on the GSI Groundwater Viewer and is presumably the same well (or possibly the second kamenitza noted here); the townland is given as Berneens, but Poll Insheen appears to be located just inside the boundary of Gleninsheen townland.

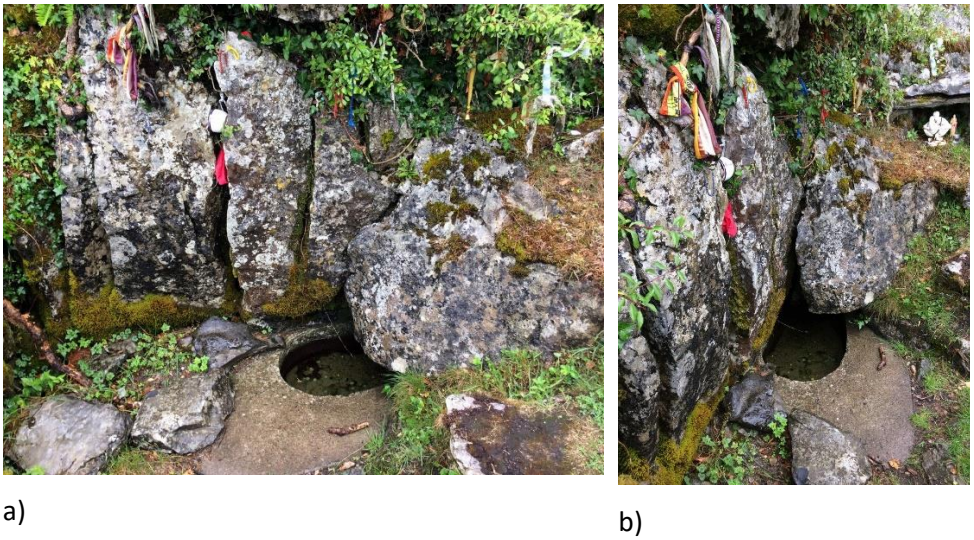
#### 5.3.1.2 St Cronan's well Termon, Co Clare

Like St Fachtna's well, St Cronan's well (Tobar Cronan) is on the Carran Loop path, close to the ruins of Templecronan church. There are two 'gable shrines' (flat flagstones arranged in a tent shape) near the church ruins that may date from the 7th or 8th century[13], suggesting a long history for the pilgrimage at this site, possibly including the well. The well is associated with a cure for eye problems (Kirby, 2014).

It is an oval shaped well (with maximum dimensions 0.82 m x 0.48 m) set in concrete, located at the base of fractured limestone outcrop (Figure 5.11). There is an outflow from the well which runs underground to the outside of the walled enclosure, where it discharges into a long narrow rectangular concrete trough; the outflow from the trough appeared to be of the order of 1 to 2 l $s^{-1}$ in August 2018.

The spring well is located along an east-west open fracture, where it is intersected by NNE-SSW fractures. Its source catchment is the higher ground to the north and east. It is shown as a karst spring on the GSI Groundwater Viewer. Drew (2014) noted that the spring occurs near the boundary of the Burren Formation (Aillwe member [Upper]) and the overlying Slievenaglasha Formation, and that this boundary is marked by the presence of shale and chert. This low permeability horizon impedes the downward movement of groundwater, leading to its emergence at springs such as that at St Cronan's well. There are rushes in the field beyond the well enclosure, consistent with the presence of a low permeability shale bed restricting the downward percolation of water. As elsewhere in the Burren, the DPBL is classed as a regionally important karstified aquifer (RKc) by the GSI.

[13] https://pilgrimagemedievalireland.com/2016/08/14/templecronan-and-the-relics-of-st-cronan-co-clare/; accessed 31/1/2020



a) b)

Figure 5.11 St Cronan's well Termon, Co Clare: a) the concrete-lined well is at the base of a jointed limestone escarpment; b) the spring issues from the base of an open east-west fracture, which is intersected by NNE-SSW fractures. Photos by Bruce Misstear

#### 5.3.1.3 Tobercornan Gleninagh North, Co Clare

Tobercornan is a karst spring that issues from the northern base of Cappanawalla Mountain, along the coast road 3 km northwest of Ballyvaughan. The bedrock comprises thickly bedded limestones belonging to the Black Head Member of the DPBL.

The well is within a grey limestone well house, 3 m high, with small pointed turrets at its corners, which are supported by stone buttresses (hence it is known as the 'Pinnacle well'). There is a tall arched entrance, with four steps down into the well. The well has a keyhole shape, with a width of 1.2 m and a length from front to rear of 1.4 m, and contained about 0.2 m of water when visited in May 2017 and August 2018. There is limestone outcrop and gravel in the base of the well. Water can be seen entering through a crack in the limestone at the back, right corner of the well (Figure 5.12). There is a Clare County Council sign on the inside rear wall saying 'Drinking Water. Please Keep Clean'.



a) b)

Figure 5.12 Tobercornan Gleninagh North, Co Clare: a) the well house with its distinctive pinnacles; b) water (which is very clear) enters the well through the crack in limestone at the rear corner of the well. Photos by Bruce Misstear

#### 5.3.1.4 Tobar Dearg Eanty More, Co Clare

This is not a well, but rather a series of springs (Figure 5.13). Its name 'Red well' derives from the presence of *Rhodophyta* red algae; there are also green algae. There were no signs of any votives or other indications of pilgrimage at the site during a visit to the site in August 2018. Nevertheless, Tobar Dearg has a reputation for treating rheumatism (Doolin, 2002) and it is marked on the OSI Discovery Map, and also on the historical 6 inch and 25 inch maps (as Toberderg).

The springs are at the top of a dry valley that runs southwest towards the Caherconnell visitor centre. This spring line issues from shallow epikarst with limestones belonging to the Ballyelly Member of the Dinantian Slievnaglasha Formation, part of the DPBL lithological unit. The well is shown as a karst spring on the GSI Groundwater Viewer.

The source catchment is the higher ground to the east. Drew (*pers comm*, 2018) indicates that the flow is variable, but that this spring is a reliable water source. The spring flow disappears underground a short distance below the spring line. The local farmer pipes some of the spring flow for watering animals.



a) b)

Figure 5.13 Tobar Dearg Eanty Mor, Co Clare: a) and b) water flowing across a bedding plane; some of the reddish (algal) staining which gives the 'well' its name can be seen. Photos by Bruce Misstear

### 5.3.2 Large karst springs in the Western Lowlands

Two prominent examples of karst springs with large flows that are also holy wells are Tobernalt in Co Sligo and Ogulla well at Tulsk in Co Roscommon. Both are sourced from regionally important karst aquifers with conduit flow (Rkc). Both fall into the area referred to by Drew (2018) as the Western Lowlands, which mainly covers lowland areas of counties Mayo, Roscommon, Galway and Clare, but also includes the part of Sligo where Tobernalt is located.

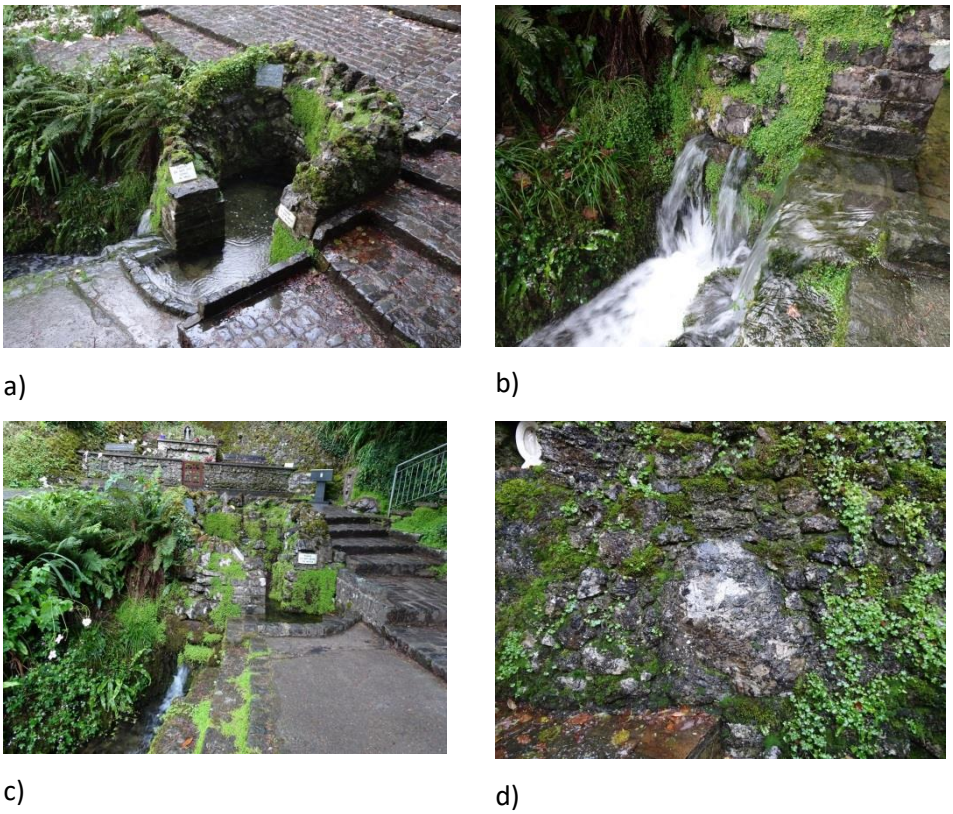
#### 5.3.2.1 Tobernalt, Co Sligo

Tobernalt is near the western shore of Lough Gill (near Carraroe). O Giollain (2005) refers to *Tober an Ailt* as meaning 'well of the joint', perhaps indicating a reputation for curing body aches, but an alternative translation of the name would be 'well of the cliff', reflecting its physical setting at the base of an escarpment. Another possible meaning is 'Well of Angels' (B O'Kelly, *pers comm*, 2018). Ray (2013) mentions Tobernalt as a holy well that, although associated with St Patrick, is not dedicated to a particular saint. According to one web report[14], Tobernalt is an ancient site, reported as pre-dating the arrival of Christianity in the 5th century CE, but it is especially associated with being a place of prayer during Penal times.

This is an oval-shaped well more than 2 m long and about 1.6 m wide, with a limestone wall surround (Figure 5.14a). The well is part of a karst spring that issues at the base of the cliff

[14] http://www.holywellsligo.com/about.html; accessed 3/2/2020

(probably from a karst conduit). In summer, a large discharge (several litres per second) could be observed coming from an opening in the cliff below and to the left of the well, which forms a river channel downstream. In winter, in addition to this outlet, water could be seen flowing into the channel from the well itself, both via a stone weir at the front of the well and via two holes in the stone wall of the well (Figure 5.14b).



a) b)

c) d)

Figure 5.14 Tobernalt Co Sligo: a) the oval-shaped well in winter, with flow over the stone weir at the front of the well; b) in winter, discharge is from the well via the stone weir at the front and a strong flow from two holes in the stone wall (8/12/2017): compare with the next photo taken in summer; c) in summer, the spring issues from an opening at the base of the cliff below the well (15/8/2017); d) outcrop of Dartry limestone in the cliff face to the right of the altar behind the well. Photos by Bruce Misstear

The bedrock is dark fine-grained cherty limestone belonging to the Dinantian Dartry Limestone Formation, with beds locally dipping gently to the northwest. The Dartry Limestone is a DPBL and, as noted above, is classed as an Rkc aquifer. The spring is marked as a karst feature on the GSI Groundwater Viewer, and the flow is given as 5000 $m^3$ $d^{-1}$ (58 l $s^{-1}$), the data coming from Chance (2005). It is interesting that the temperature of the spring water on a very cold day in

winter (10.3 °C, 8/1/2/2017) was only slightly below that in summer (11.1 °C, 15/8/2017), suggesting a relatively long groundwater flow path and residence time.

#### 5.3.2.2 Ogulla well Tulsk, Co Roscommon

The well is named after the 6th century CE saint Oigh-Ghiolla and is also reported to be the place where St Patrick baptised Etna and Fidelma, the daughters of the High King of Ireland (Healy, 2001). The site, which is about 1 km west of Tulsk, is well cared for and frequently used, as evidenced by the presence of a chapel (an octagonal, glass-faced, structure) and the votives at and around the well. According to Healy (2001), the well has a reputation for curing cancer, arthritis, aching limbs and eye problems. Moreover, a bottle of Mestinon tablets was spotted at the site on 24/11/2016, which suggests a looked-for cure for a muscle ailment (these tablets are used to treat neuromuscular disease).

The well is on the right bank of a stream fed by at least two large springs at this site. The springs join together and form a channel about 1.5 m wide and 0.4 m deep at the bridge across to the octagonal chapel on the left bank of the stream. The stream channel then widens out to about 2-3 m before flowing through a 1.2 m wide weir. The well itself is horseshoe-shaped, with stone walls and a (modern) Celtic stone cross (Figure 5.15). The well has a maximum width of approximately 0.9 m, and it measures about 0.9 m from the step to the rear of the well.



a) b)

Figure 5.15 Ogulla well Tulsk, Co Roscommon: a) the horseshoe-shaped well with the stream and octagonal chapel behind; b) the springs that issue upstream of the well. Photos by Bruce Misstear

There are glacial tills and peat deposits in the vicinity of the spring, but the subsoils are probably only 3-5 m in thickness (Meehan *et al*., 2015). There is an esker 400-500 m southeast of the source, which runs from southwest to northeast. The bedrock is undifferentiated Visean limestones (DPBL), classed as an Rkc aquifer.

This is a major karstic spring site which is part of the Mid Roscommon Group Water Scheme, and has been subjected to several studies into its zone of contribution (ZOC), as described by Meehan *et al*., 2015; Duncan *et al*., 2017; Drew, 2018). The 2015 report by Meehan *et al*. established a ZOC of 32 $km^2$, based on a desk study and hydrogeological mapping methods, and this was followed by dye tracing experiments in 2016 which led to a revision of the ZOC down to 17 $km^2$ (Duncan *et al*., 2017). An aquifer map showing traced underground connections is given in Figure 5.16 (based on the mapping in the GSI Groundwater Viewer) and a conceptual model for the spring, with one of the flow traces, is illustrated in Figure 5.17.

The group water scheme began operating in 1977 and has a typical abstraction rate of about 200 $m^3\ d^{-1}$ (Meehan *et al*., 2015). However, at the time of their study Meehan *et al*. noted that the spring was contaminated and so was not being used by the GWS (which instead was relying on a second spring source at Carnalasson to the south). Meehan *et al*. (based on earlier work by Hickey, 2009) report a range of flows from 625 (summer) to 9500 $m^3\ d^{-1}$ (winter), with a mean flow of 3400 $m^3\ d^{-1}$, equivalent to 7 to 110 l $s^{-1}$ and mean flow of 39 l $s^{-1}$. At the time of this researcher's first visit in November 2016, the flow appeared to be several 10s of litres per second.

Based on monitoring data for the period 2010 to 2012, the EC varied between 306 and 949 µS $cm^{-1}$, with an average of 562 µS $cm^{-1}$ (n = 83 samples; Meehan *et al*., 2015). The large variations are consistent with a mixed conduit flow and diffuse karst aquifer system, with a higher proportion of rapid throughflow of lower EC water occurring during winter months. Whilst the chemical quality of the water appears to be generally good, with only one value of ammonium reported as exceeding the drinking water limit, there were 38 exceedances (out of 88 raw water samples) for faecal coliforms. Meehan *et al*. (2015) noted that the spring is fed by at least one swallow hole and sinking stream, making it susceptible to pollution.

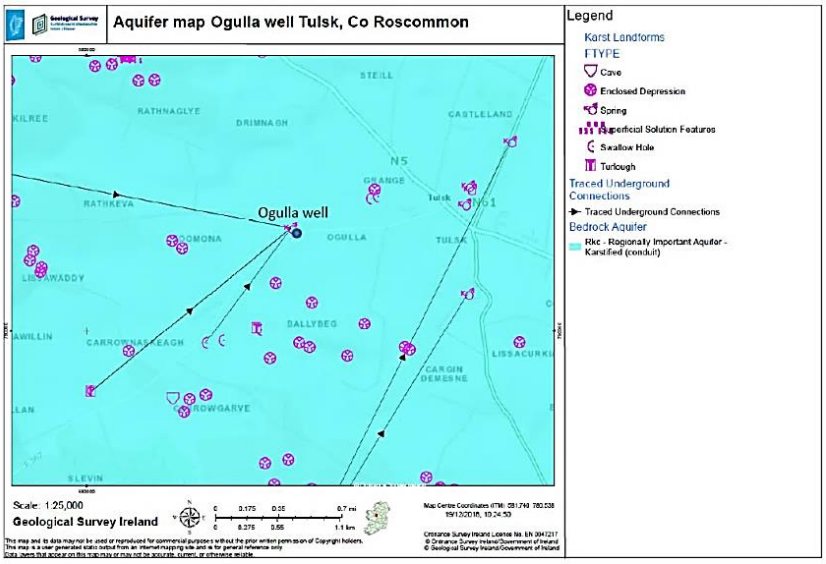



Figure 5.16 Aquifer map for Ogulla Spring, Co Roscommon, showing the traced underground connections. (Map prepared using GSI Groundwater Data Viewer)

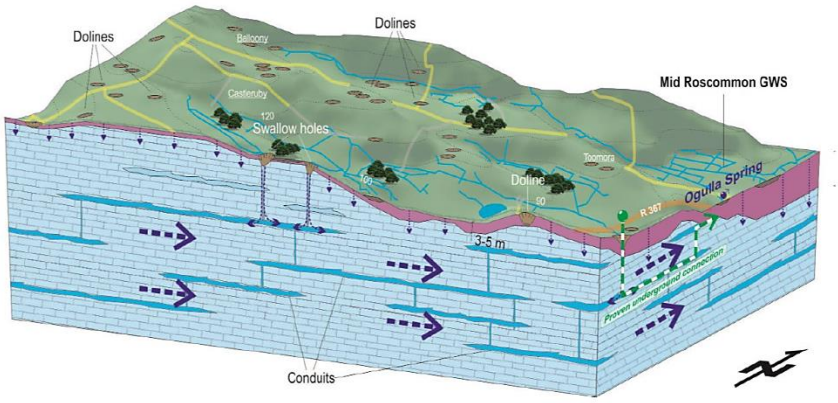



Figure 5.17 Conceptual model of Ogulla spring showing one of the flow traces (from Duncan *et al*., 2017)

This researcher recorded near identical values for the EC, pH and temperature between the well water and stream water during visits in November 2016 and August 2017, thereby indicating a common source. On 24/11/2016, for example, the values of EC, temperature and pH were 660 µS $cm^{-1}$ (well) and 657 µS $cm^{-1}$ (stream); 9.5 °C (well) and 9.4 °C (stream); and 6.95 (well) and 6.87 (stream), respectively. Consistent with earlier findings, the water chemistry the following summer was slightly more mineralised (709 and 708 µS $cm^{-1}$ for the well and stream, respectively), indicating a higher proportion of diffuse karst flow and less conduit flow in summer.

### 5.3.3 Holy wells in karst in the Eastern Lowlands

Drew defines the Eastern Lowlands as covering Meath, Westmeath, Offaly, Laois and North Tipperary, and indicates that this is the limestone region where least is known about karstification. Here, two holy wells will be described, Toberneeve at Ballyadams in Co Laois and St Kieran's well in Castlekeeran, Co Meath. Unlike the wells on the Burren Plateau, which are all characterised by conduit flow karst, the aquifers at Toberneeve and St Kieran's well are classed as regionally important diffuse karst (Rkd) and locally important (Lm), respectively.

#### 5.3.3.1 Toberneeve Ballyadams, Co Laois

The well is within a low, pitted karst limestone mound in a large field, which is 100 m southwest of the old Ballyadams graveyard. The mound rises perhaps 1 m above the field, is oval shaped, with dimensions 9 m by 7 m (approximate). The well is covered by a flat metal sheet held in place by two blocks of limestone. There is a heavy metal object (a doorscraper?) by the well with statuettes of Jesus and Mary (Figure 5.18). The well comprises a roughly circular hole in the limestone (kamenitza). The hole is 0.29 m in diameter and about 0.6 m deep: it contained about 0.15 m of brown, muddy water when visited in June 2018 and 0.18-0.2 m in April and June 2019. The OSI Discovery map and the historical 6 inch and 25 inch maps show two wells in this field – Toberneeve and Tobernasool. Only one well is now visible, and its location coincides (approximately) with that of Toberneeve. The name Toberneeve may be an Anglicisation of *Tobar na Naomh*, 'well of the saints'[15].

In addition to the pitted and partly grass covered outcrop containing the well, limestone outcrop can sometimes be seen along the base of the access track south from Ballyadams, near the gate into the field containing the well. This low, smooth limestone is cut by north-south joints. The bedrock geology map shows limestones of the Dinantian Ballyadams Formation (DPBL). These beds strike northwest-southeast, dip gently to the southwest, and pass up into the Clogrenan Formation southwest of the well.

[15] https://www.logainm.ie/en/28133; accessed 3/2/2020



a) b)



c) d)

Figure 5.18 Toberneeve Ballyadams, Co Laois: a) the low, partly grass-covered mound containing the well is clearly visible in the rear centre of the picture; b) and c) the solution-enhanced hollow (kamenitza) in limestone outcrop that is Toberneeve; d) a conduit and open joint inside the well, just above the water surface. Photos by Bruce Misstear

This is a curious well. Despite being a small hole in an isolated rocky mound, the well has clearly been in existence for at least two centuries (it is marked on the 1830s OS map). Moreover, it contained water (albeit brown, and relatively stagnant, with an EC value of 1113 µS $cm^{-1}$) when visited in June 2018, which coincided with a comparatively long dry spell. During a later visit (in March 2020), a small conduit and open bedding plane joint were observed inside the well at the level of the water surface (Figure 5.18d). These observations suggest that it has a groundwater source – shallow epikarst, perhaps - rather than being merely a receptacle for surface water run-in. The metal cover would probably preclude direct run-in from the very small area of outcrop above, and there was no sign of staining on the side wall of the well above the water level (some discolouration would be expected if water occasionally ran down the sides of the well). Toberneeve is mentioned in the 2004 Groundwater Protection Scheme report for Co Laois (Deakin and Wright, 2004), where it is listed as a karst spring (along with Tobernasool – the 6

inch map numbers for these and other features are included, but it is not clear if the springs were visited when the report was prepared). A search by this writer of the large field containing Toberneeve did not reveal a second outcrop or well, although there were some shallow depressions consistent with a karstic landscape. If the outcrop containing the second well was relatively low and flat, then it may have been grassed over since the time of the 19th century mapping.

In an historical account of Ballyadams church in Daniel O'Byrne's '*History of The Queen's County*' (1856, page 36), he mentioned that 'Near the ruins of the church are three cavities in a very strangely formed part of the hill. The cavities contain water accounted sacred to Saint Patrick, likely derived from the name of the hermit [Carrageen, the hill where a hermit lived]; - they are not more than two feet to two and half in depth, and about from twelve to ten inches in diameter; they are perfectly circular; and at the bottom of the concave there is no apparent passage for water to enter the wells or cavities; yet, not withstanding, the situation of the rock precludes any supposition that under water springs up into the cavities. It is asserted that, if the waters be taken out of the cavities, on the next morning the same quantity of water will be found in each well; and it matters not how great the drought of a season may be, the waters are found in the wells'.

Feehan, in his '*Geology of Laois and Offaly*' (2013), includes a similar extract from O'Byrne's book and links it to the holy well Tobernasool; however, his accompanying photo is clearly the same well as that shown in Figure 5.18 which, as mentioned earlier, is closest to the position of Toberneeve on the historical maps and hence is referred to here as Toberneeve. The depth and diameter of the wells in O'Byrne's account are consistent with the well reported here (0.6 m deep and 0.29 m in diameter), albeit that the rocky outcrop contains only one well of such dimensions. It is possible that two of the cavities referred to by O'Byrne are obscured by the soil and grass that now partly covers this rocky mound.

#### 5.3.3.2 St Kieran's well Castlekeeran, Co Meath

St Kieran (or Ciaran) was an 8th century CE saint who founded a monastery at Castlekeeran, near Kells. The well is a popular place of pilgrimage. In 1917, about 10,000 people attended the pattern celebrations to listen to a speech by the prominent republican, Countess Markievicz (French, 2012); a stone plaque commemorating this event was erected near the entrance to the

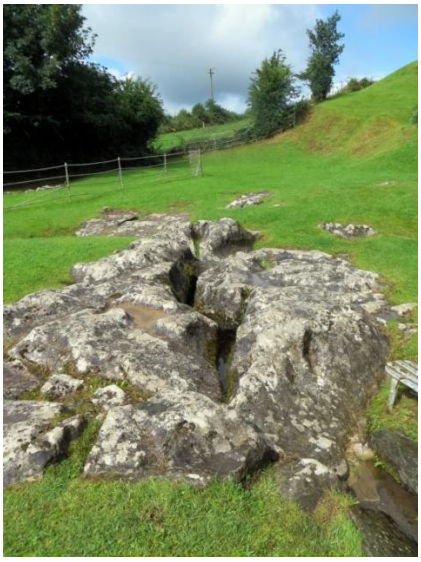
site in 2016. Ray (2015) refers to a legend about an immortal trout in the well, mentioning that pilgrims gather at midnight on the eve of the pattern hoping to the see the trout. If it appears, then this is a sign that prayers will be answered. There is an old graveyard with Celtic high crosses in a field east of the holy well.



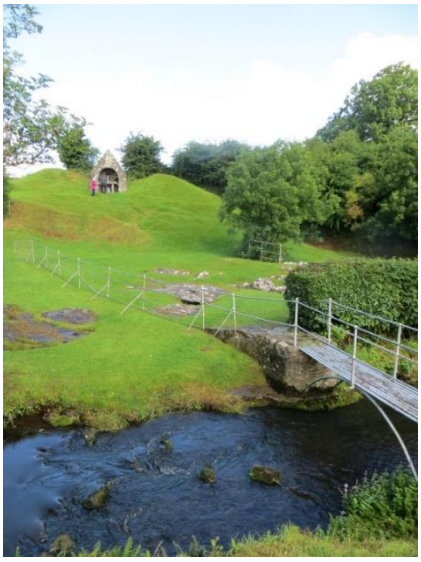
a)



b)



c)



d)

Figure 5.19 St Kieran's well Castlekeeran, Co Meath: a) the springs issue from limestone pavement, including St Kieran's well beside the tree behind the railing; the stone oratory on the hill behind the well was built in the early 20$^{th}$ century; b) two of the springs that issue from the karstified limestone at the Castlekeeran holy well site: the main St Kieran's well is on the right, below the tree; the third spring is between the fence and the trees in the (left) background; c) this section of limestone pavement is believed to cure backache if the sufferer sits in the hollowed rock; the outcrop is cut by a fracture (running 110$^{o}$ ESE), to form clint and grike topography typical of karst landscapes; d) view of the well site from road; the springs discharge into the stream in the foreground, which is a tributary of the Blackwater. Photos by Bruce Misstear

Three small springs issue from the base of a limestone hill at this site. The main well (with a sign) is the one furthest to the northeast (Figure 5.19). This spring well is between 0.8 and 0.9 m wide, and about 0.3 m deep, and has shallow steps down to it.

The different parts of the spring system have reputations for curing headaches, toothaches, foot ailments and warts. The low weathered limestone outcrop (with a fracture running through it at 110$^{o}$) apparently cures backache if the sufferer sits down in the rock hollow (this unlucky back sufferer actually slipped and fell on this wet rock!) – Saint Kieran is reputed to have sat in this hollow (Rackard and O'Callaghan, 2001). The healing powers are reportedly most effective at midnight before the pattern, which is held on the first Sunday in August (Logan, 1980; Healy, 2001).

The spring system is at the base of a hill (which rises about 7 m above the springs), on top of which a small oratory has been constructed (Figure 5.19a). The outflow from the springs discharges into the stream beside the road (but a few metres downstream), which joins the River Blackwater about 500 m to the northeast. The limestone pavement at the spring site includes classic karst features such as clints and grikes (Figure 5.19c). Owing to the rarity of such karst features in Co Meath, St Kieran's well has been designated as a County Geological Site[16] (see Section 8.3.3 for an explanation of geological heritage sites).

The Carboniferous limestones at the well site belong to the Stackallen Member (comprising micrite and mudstone) of the Meath Formation (Figure 5.20). The Meath Formation overlies the Liscarton Formation (which comprises mainly laminated beds of siltstones and mudstones, and muddy limestones). The Liscarton Formation unconformably overlies Silurian metasediments and volcanics belonging to the Clontail Formation. Using the GRUG terminology, the bedrock at the site is Dinantian pure bedded limestone (DPBL) overlain and underlain by Dinantian sandstones, shales and limestones (DESSL). The Dinantian rocks occur within a synclinal fold, which plunges to the south-southwest. The spring site is near the northern limit of the syncline, and close to the synclinal axis – raising the possibility that fracturing along the fold axis has some bearing on the occurrence of the spring. On the geology map, the fold structure can be seen to

[16] https://secure.dccae.gov.ie/GSI_DOWNLOAD/Geoheritage/Reports/MH002_St_Keerans_Well.pdf (accessed 17/7/2020)

be cross-cut by west-southwest to east-northeast trending faults. At the spring site, a joint striking at 110° ESE cuts through the main limestone outcrop.

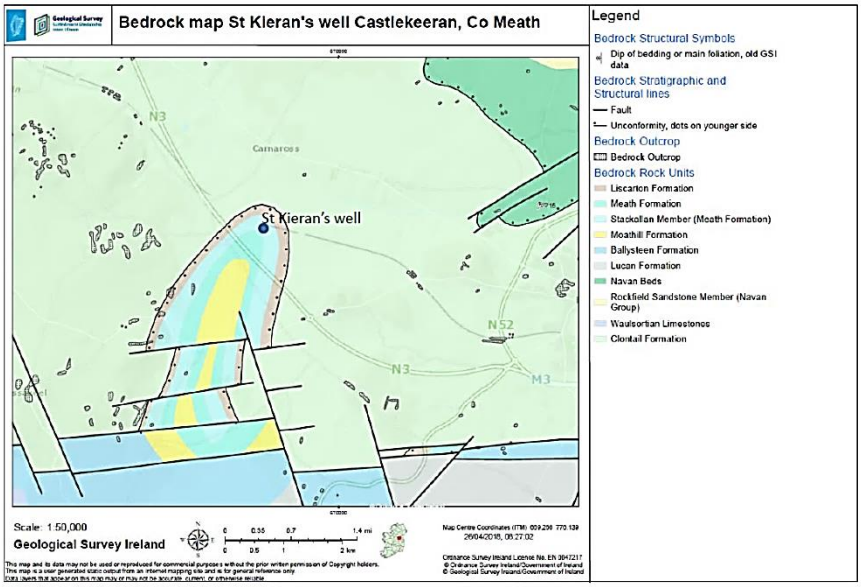



Figure 5.20 Bedrock geology map for St Kieran's well Castlekeeran, Co Meath. (Map prepared using GSI Groundwater Data Viewer)

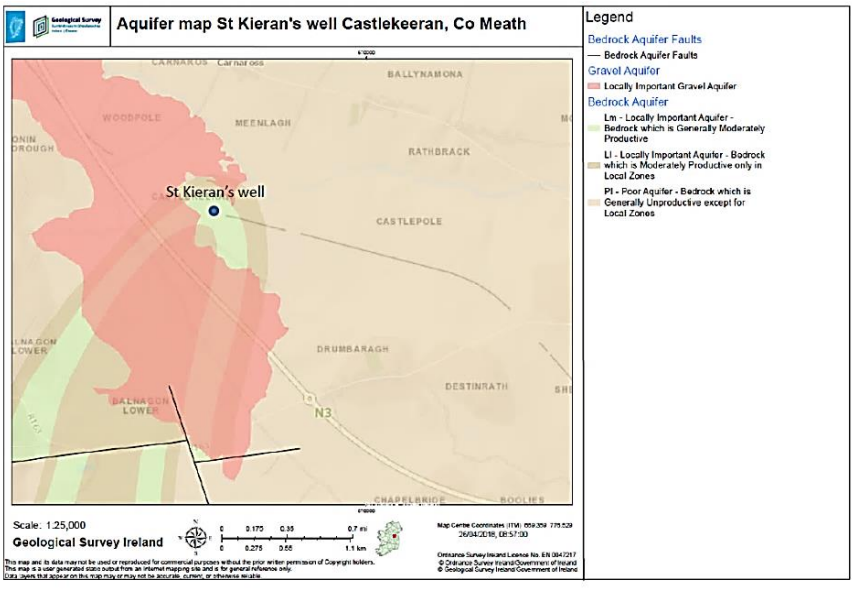



Figure 5.21 Aquifer map for St Kieran's well Castlekeeran, Co Meath, showing the locally important bedrock aquifer that supplies the well and the locally important gravel aquifer nearby. (Map prepared using GSI Groundwater Data Viewer)

St Kieran's well is shown as a karst spring on the GSI Groundwater Viewer. Meehan (2012) noted that although the groundwater source is unknown, the recharge area is probably the higher ground to the northwest, part of which is covered by fluvioglacial sands and gravels, and part by till (Figure 5.21). There is an embankment from a (now dismantled) railway line which passes east of the well, but this probably does not affect the site hydrogeology. The limestone is classified as a locally important bedrock aquifer (Lm), whilst the sands and gravels nearby are classed as a locally important gravel aquifer (Lg). When measured during a prolonged dry period in the summer of 2018, the springs were found to have a lower water EC than the nearby stream (about 580 µS $cm^{-1}$ compared to 700 µS $cm^{-1}$ on 18/7/2018), suggesting the latter may have a different (or partly different) groundwater source e.g. from the gravels.

St Kieran's well at Castlekeeran was one of the four wells chosen for monitoring during this research (Section 4.1.4). The depth to water at the spring outlet was measured periodically over a 2-year period from July 2016 to July 2018, and the data are summarised in Figure 5.22. The monthly rainfall data for Dublin airport are also included. The water level (really the 'stage' of the spring) varied by only 6 cm over this period, with a highest value recorded in April 2018 (after a particularly wet March, with 100 mm of rainfall), and lowest in July 2018 (following a very dry June, with only 5 mm of rainfall)

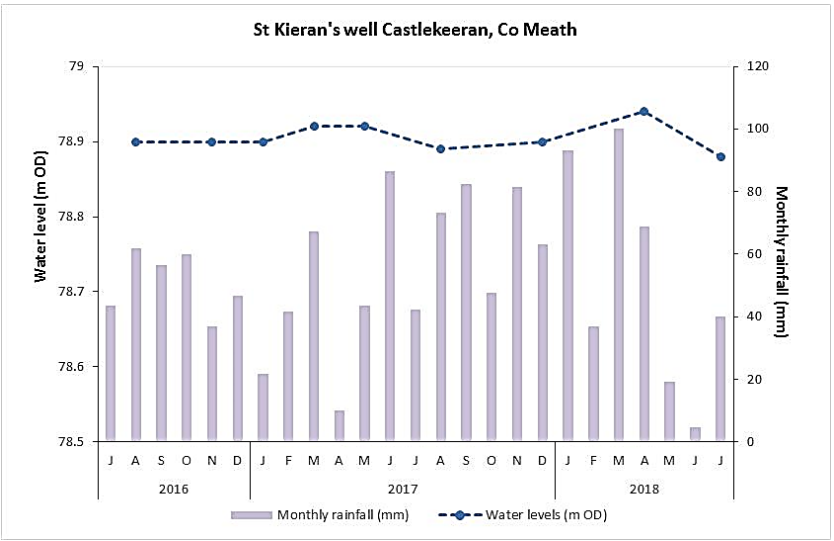



Figure 5.22 Water levels at St Kieran's well Castlekeeran, Co Meath; monthly rainfall data are for Dublin airport and were obtained from Met Éireann

## 5.4 Wells in non-calcareous sediments

Forty-seven holy wells were surveyed within the non-calcareous sedimentary grouping, including 18 wells located in Devonian Old Red Sandstones (DORS), which are mainly found in Cork and Kerry. There were also non-calcareous sedimentary wells surveyed in Upper Devonian Kiltorcan-type sandstones (DKS, four wells) and in Dinantian and Namurian sandstones and shales (25 wells).

Not only is there a large diversity of lithologies within this non-calcareous sedimentary grouping, there is also a large range of aquifer classes, from regionally important Rf aquifers to poor Pu aquifers. For the DORS, 13 of the 18 wells (72%) fall within the locally important Ll aquifer class, while the remainder are categorised as Pl. The four DKS wells are all in the Rf aquifer category. All but one of the seven wells in the Dinantian sandstones grouping are classed as being in a locally important Lm aquifer (the exception, Planxty well in Co Monaghan, probably taps an Rf aquifer), whilst the five wells in the Dinantian mudstones and sandstones (Cork Group) are classed as being in an Ll aquifer. The Namurian sandstones and Namurian undifferentiated groups are rated as Ll (and contain 10 wells), whereas the Namurian shales (with three wells) are classed as either Pl or Pu.

### 5.4.1 Holy wells in Devonian Old Red Sandstones

Of the 18 ORS wells, three examples are described here: St Declan's well Ardmore Co Waterford, the holy well at Shrone Co Kerry, and Tobar na nGealt in Gleann na nGealt, also Co Kerry.

#### 5.4.1.1 St Declan's well Ardmore, Co Waterford

St Declan founded a monastery in Ardmore in about the year 416 CE and thus reportedly pre-dates St Patrick as the person who first brought Christianity to Ireland, albeit his travels and influence were not as widespread[17]. Foley (2010) and Broderick (2016) describe the traditions surrounding the well and other sites associated with St Declan in Ardmore, including at St Declan's stone (a conglomerate erratic) on the foreshore, which is said to have travelled across the sea to Ardmore carrying St Declan's bell. The rituals included drinking water from the well.

[17] http://www.ardmorewaterford.com/st-declans-well-ardmore/; accessed 3/2/2020)

Various cures are reputedly linked to this well, including for eye problems, sprains, wounds and rheumatism (Logan, 1980; Foley, 2010; Broderick, 2016).

St Declan's well is on the cliff pathway south of Ardmore, beside the ruins of an old church, and about 25 m above the shoreline. The well is within a sandstone and mortar block well house, which has two rectangular portals (Figure 5.23). The well house is topped with a couple of old carved stones showing the crucifixion (there was apparently formerly a third cross, which is now missing). The well dimensions are 1.95 m wide and 0.6 m from front to rear, and it typically contained about 0.05 to 0.1 m of water when observed during six visits between April 2017 and March 2019. The well discharges via a rough channel, 0.3 m wide, which drains towards the church ruins and then to the sea. There was only a trickle of water at the times of the various visits in 2017, 2018 and 2019. The water in St Declan's well is slightly brackish, with an EC around 1000 µS $cm^{-1}$.



a) b)

Figure 5.23 St Declan's well Ardmore, Co Waterford: a) the sandstone well house has two portals and is topped by two carved crucifixion scenes; b) outcrops of Old Red Sandstone in the cliffs near the well. Photos by Bruce Misstear

Outcrops of Old Red Sandstone are visible along the shoreline below the well, and around the headland (Figure 5.23b). These appear to strike approximately east-west, consistent with the main Hercynian structural trend. At the well, the rock formation is the Ardmore Member of the Old Red Sandstone, described as grey to red sandstone and grey siltstone. The sandstones on the cliff south of Ardmore, where St Declan's well is located, represent the southern limb of an east-west trending syncline, with the town of Ardmore being underlain by younger Dinantian strata (Figure 5.24).

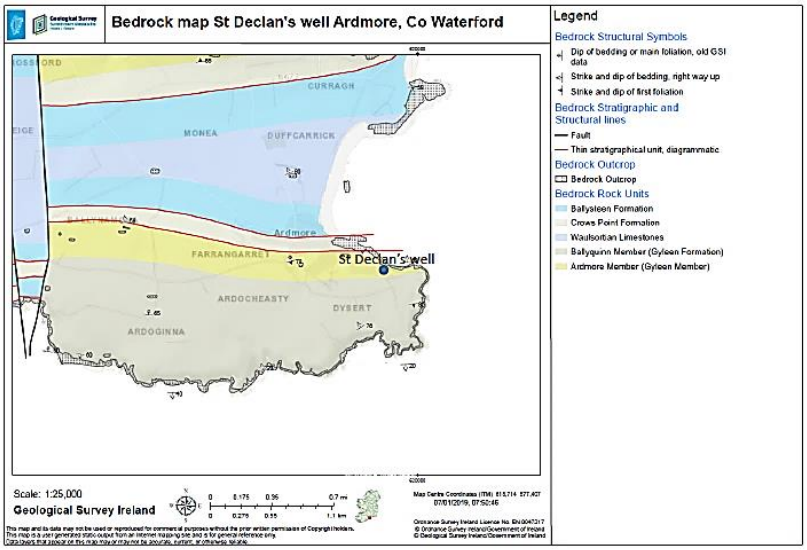



Figure 5.24 Bedrock map for St Declan's well Ardmore Co Waterford. (Map prepared using GSI Groundwater Data Viewer)

The ORS is a locally important (Ll) aquifer in this area. The rocks along the coastline are highly fractured and the occurrence of the spring well at this location might be related to a north-south fault that results in an indentation in the shoreline below the well site.

There were formerly two mine workings in the vicinity, one of which, known as the 'Putty Hole', was in the cliff directly below the well site. The mine was worked in the 17th and 18th centuries for iron, copper, lead and silver (Parkes *et al*., 2013). The name Putty Hole relates to the 'heavy mud' that occurs in the cave/mine adit (Suipéil, 2019); the presence of such weathered material would be consistent with faulting here (although this is just speculation on the part of this researcher).

#### 5.4.1.2 Holy well at Shrone, Co Kerry

The holy well at Shrone is at the side of ring fort (*cathair*) known locally as 'The City'. The well is marked as an unnamed holy well on the 6 inch and 25 inch historical maps (which show the ring fort as a cromlech). Some people believe that this site has been a place of pilgrimage since pre-Christian times, with the site being linked to St Craobh Dearg, a sister of St Gobnait[18]. The well is surrounded by a semi-circular dry stone wall (sandstone) at the edge of the ring fort. The well is a circular concrete pipe/caisson, 0.6 m in diameter, the rim of which stands about 0.2 m proud

[18] http://liminalentwinings.com/the-city-shrone-may-day-2013/; accessed 3/2/2020)

of the surrounding steps (Figure 5.25). The well contained 0.36 m of water when visited in August 2017. Water from the well is reportedly used to treat sick cattle, and it is also sprinkled on cattle or the land.



a) b)

Figure 5.25 Holy well at Shrone Co Kerry: a) the concrete caisson that now forms the well; note that the water level in August 2017 was about 10 cm higher than the stepped area outside the caisson; b) view from the well looking SSW towards the hills known as the Paps. Photos by Bruce Misstear

The well site is on the lower slopes of two rounded hills known locally as the Paps, which reach heights of 690 m about 3 km SSW of The City. The bedrock map describes the local geology as green sandstone and purple siltstone of the Upper Devonian Glenflesk Chloritic Sandstone Formation. There is a covering of sandstone till. The water level in the well caisson was roughly 10 cm higher than the base of the stepped area immediately outside the pipe, suggesting slightly artesian conditions for this locally important sandstone aquifer. The water level also appeared to be higher (by > 1 m?) than that in the stream a few metres away. The water temperature was somewhat elevated at 14.7 $^{o}$C, similar to the air temperature at the time of measurement (4/8/2017). A High vulnerability rating indicates that the subsoils are at least 3 m thick at this location. The ORS aquifer outcrops on the high ground to the south, and then falls below the subsoils northwards, suggesting the subsoils may be acting as a local confining layer.

#### 5.4.1.3 Tobar na nGealt Gleann na nGealt, Co Kerry

Tobar na nGealt is located in a valley known as Gleann na nGealt, about 3 km WSW of Camp on the Dingle peninsula. There are many stories concerning the well and its reputed cures for madness and mental health ailments (Tobar na nGealt can be translated as ‘well of the mad’). These include cures for Mis, the crazed woman who gave her name to the Slieve Mish

mountains, for King Bolcan of France (following the battle of Ventry), and the well also features in more recent stories, include one by Peig Sayers (of the Blasket Islands)[19].

The site marked by a sign to the well is located in the stream on the west side of a minor road, where it is joined at a Y-junction by an even smaller road (Figure 5.26). The 19th century OS map, however, shows the location of the well/spring to be upstream of the road Y-junction (perhaps 50 m or so upstream of it, on the east side of the main road; Figure 5.27). The current 'well' appears to be the outlet of this stream from the culvert under the west side of the road. According to Brigid O'Connor (who lives close to the site), this is the well site known for the cure, and which was sampled for the TG4 television featuring the well (see below); BOC was aware of the spring site shown on the historical map, but told this researcher that that site is overgrown, inaccessible and had a reputation in the past for drying up (O'Connor, *pers comm*, 2018).




Figure 5.26 OSI Digital Globe image showing the location of the current Tobar na nGealt, and the original location. (Map prepared using GSI Groundwater Data Viewer)

[19] https://hubpages.com/education/Gleann-na-nGealt-Valley-of-the-Mad; blog by Jones, accessed 3/2/2020; https://www.irishtimes.com/news/health/recovering-well-1.556572 by O'Connell, accessed 3/2/2020; http://westkerry.com/blog/?cat=3; accessed 3/2/2020)

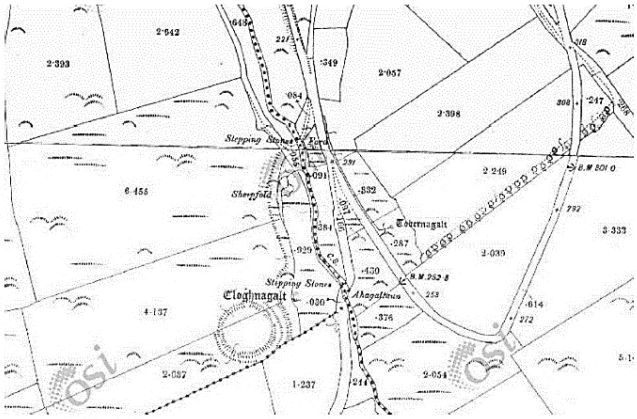



Figure 5.27 Part of the 19th century OSI 6 inch map sheet showing the original location of Tobar na nGealt, east of the stream. (Map prepared using GSI Groundwater Data Viewer)

There was a metal cup/tankard in the bank above the well/culvert, and quartz stones placed across the outflow (Figure 5.28). The river channel is about 1.4 m wide and was 10 cm deep at the point where water leaves the well/culvert in August 2017, and 21 cm deep in November 2018. A tree (hazel?) on the right bank was adorned with beads and ribbons. There was also a small statue on the stream bank. This stream enters a larger stream a few metres to the west. The larger stream runs north-south along the main valley.



a) b)

Figure 5.28 Tobar na nGealt Gleann na nGealt, Co Kerry: a) the overgrown path to the well (August 2017); the sign to the well can be seen in the trees on the right (although it is partly obscured); b) the "well" in the stream bed coincides with the outlet from the culvert beneath the road; note the white stones at the outlet and the tankard in the alcove above. Photos by Bruce Misstear

The Quaternary map shows a strip of alluvium along the stream valley, with till derived from Lower Palaeozoic sandstones and shales on either side. The bedrock comprises sandstones of the Silurian-Devonian Ballymore Sandstone Formation. The Ballymore sandstones are included in the Old Red Sandstone lithological grouping. The beds dip northwards, where they are overlain unconformably by sandstones of the Upper Devonian Cappagh Sandstone Formation (the contact is about 300 m north of the well site). The bedding strike is northeast to southwest. A High vulnerability rating suggests that the alluvium is perhaps 3 to 5 m thick along the base of the valley (assuming the subsoils to possess low permeability), so the spring/stream flow is likely to be influenced by baseflow from this alluvium as well as from the underlying locally important ORS bedrock aquifer.

This well achieved some fame owing to the TG4 documentary broadcast on 28th October 2012 that reported a finding of relatively high lithium in the water (55.6 µg $L^{-1}$ – see Section 6.2.2 for a general discussion of lithium levels in groundwater, and the links between lithium and mental health, and Section 8.2.3 for an account of the results of the lithium testing in the current research, which gave much lower values).

### 5.4.2 Holy wells in Kiltorcan and Kiltorcan-type sandstones

As noted in Section 3.2, the Kiltorcan-type sandstones are one of the few bedrock aquifer units to exhibit some primary, intergranular permeability in addition to secondary, fracture permeability (Hunter Williams *et al*., 2019). Four of the surveyed wells in the non-calcareous sedimentary grouping are located in Upper Devonian formations classed as Kiltorcan-type sandstones (DKS). These are St Nicholas well Killamery and St Kieran's well Kilkieran, both located in ancient graveyard sites in Co Kilkenny; St Brigid's well Rosenallis, in Co Laois; and St Peacaun’s well at Toureen in the Glen of Aherlow in Co Tipperary. In addition, a fifth well (St Kavan's well Annatrim, Co Laois) may tap a mixed DKS and gravel aquifer.

The two Kilkenny wells tap the Kiltorcan Formation itself, whereas St Brigid’s well in Laois is in the Upper Devonian Cadamstown Formation. According to the bedrock geology map, St Peacaun’s well in Co Tipperary is located close to the contact between the Dinantian Lower Limestone Shale (LLS), and the underlying Upper Devonian Kiltorcan Formation, and may represent a contact spring, where flow from the Kiltorcan-type sandstones (which occupy the

higher ground to the south) comes to the surface, where it encounters the lower permeability shale beds of the LLS. As noted in the introduction to Section 5.4, the Kiltorcan-type sandstones are classed as regionally important fractured rock aquifers (Rf), and they represent the most productive sandstone aquifers in the country.

Photos of four wells of these wells are included in Figure 5.29.



a) b)

c) d)

Figure 5.29 Wells tapping Kiltorcan or Kiltorcan-type sandstones: a) St Nicholas's well Killamery is a spring beside a standing stone, which has a rectangular opening cut into its base; b) St Kieran's well at Kilkieran Co Kilkenny; c) the keyhole shaped St Peacaun's well Toureen Co Tipperary; d) The 'chapel like' stone well house of St Brigid's well beside the main street in Rosenallis, Co Laois. Photos by Bruce Misstear

### 5.4.3 Wells in Dinantian and Namurian sandstones and shales

Two examples from the 25 wells surveyed in these lithologies will be described here. These are: St Colmcille's well Disert Co Donegal (Dinantian sandstones) and St Martin's well Ballinacally in Co Clare (Namurian sandstones). Other surveyed wells that tap non-calcareous Dinantian or Namurian strata include St Bridget's well Mountbridget near Buttevant, Co Cork (Namurian shales); St Patrick's well Dromard, Co Sligo (Dinantian sandstones); St John's well at Johnswell, Co Kilkenny (Namurian shales); St Patrick's well Knockpatrick, Co Limerick (Namurian sandstones); and St Brigid's well Liscannor, Co Clare (Namurian undifferentiated).

#### 5.4.3.1 St Colmcille's well Disert, Co Donegal

The well is in a field on the lower slopes of the Blue Stack Mountains. It is reached by minor roads and tracks leading northeast from the village of Frosses. The well is close to an old graveyard (cillin) which is marked on the OSI Discovery map; although the well is not shown on that map, it is marked on the 6 inch Cassini map. The townland name Disert apparently originates from the Latin word for desert (*desertum*), and is associated with hermitage sites at several locations in Ireland.

Archaeological investigations are currently being carried out at the site by Dr Fiona Beltane of Sligo IT, with the support of the Disert Heritage Group (Beglane *et al*., 2016; Beglane, 2018; Beglane *et al*., 2018). These have included a drone survey and earth resistance surveys (the geophysical surveys were carried out in two phases by Dr James Bonsall and the reports are available as appendices to the 2016 and 2018 Disert Heritage Project reports). The oval ecclesiastical enclosures detected at the site are characteristic of the early medieval period. Available archaeological evidence at the site 'spans at least 1500 years', although folklore associations in the area 'hint at a prehistoric element to the site' (Beglane *et al*., 2016). Physical excavations commenced in 2019 and provided some prehistoric stone tools, evidence of pre-Christian activities at the site[20].

This is an irregular, approximately oval-shaped stone-lined well located at the base of an old willow tree (Figure 5.30). The well measures about 0.8 m from front to rear and has a maximum width of 1.1 m. There is a square wooden cover, with handle, that partly covers the well. The

[20] https://ifrglobal.org/program/ireland-disert/ (accessed 4/6/2020)

well contained 0.46 m of water at time of a visit in August 2018. There are stone cairns near the well – these acted as stations during the pilgrim's *turas* (Beglane *et al*., 2018). The surrounding fields also contain the old graveyard, a stone altar and a megalith (a stone arch). The well has a reputation for curing toothache, whereas a healing stone near the megalith has a reputation for curing backache (Beglane *et al*., 2016).

McClure (in Beglane *et al*., 2016) refers to the Disert site as being on a rock-cored drumlin, one of several such features in the area. The GSI bedrock map describes the bedrock geology as comprising coarse feldspathic sandstone and conglomerates of the Dinantian Killin Formation. Some exposures along the track to the graveyard include heavily weathered sandstone and conglomerate (Figure 5.30c). Dalradian metamorphic rocks occur 200-300 m to the north of the well; the faulted contact runs ENE to WSW.




a)



b)



c)



d)

Figure 5.30 St Colmcille's well Disert Co Donegal: a) the well is beside the willow tree; b) a square wooden cover over the well; c) weathered conglomerate forming a low hill alongside the approach track to the graveyard; d) weathered conglomerate and till – possibly including a transition zone for groundwater flow. Photos by Bruce Misstear

The subsoils (tills derived from metamorphic rocks and blanket peat) are less than 3 m thick at this site, and the spring well is sourced from the locally important (Lm) Dinantian sandstone aquifer. Judging by the exposures nearby, the upper layers of sandstone and conglomerate are highly weathered, and so the main groundwater flow to the spring may be through the transition zone. High-resolution air photographs - produced from drone surveys as part of the Disert Heritage Project - suggest that a fault runs through the site of this spring well: the evidence is 'a discontinuity in the ground level….. dog-legging at the well' (Beglane *et al*., 2016).

#### 5.4.3.2 St Martin's well Ballinacally, Co Clare

St Martin's well is in the village of Ballynacally, about 2-3 m above the right bank of Ballynacally River, which drains into the nearby estuary of the River Fergus. There are a series of shrines at this well-tended site, with several statues. The dedication of the well to the French saint may owe its origins to a visit by St Senan to the town of Tours (Houlihan, 2015). The well reputedly provides cures for sore eyes and feet, and rheumatism[21].

The blue and white concrete block well house has several alcoves, the largest containing a statue of St Martin (Figure 5.31). There is an arched portal with a wooden door providing access to the well chamber, which has a vaulted wooden roof. The well is approximately 1 m square and contained about 10 cm of water at time of visit in May 2017.

Outcrops of thinly cleaved beds of shale and siltstone, with occasional thicker beds of sandstone, occur at the site (Figures 5.31c and 5.31d). The shale beds dip steeply to the south near the well, but are folded and become sub-horizontal with a gentle westerly dip a few metres down along the path towards a shrine of Our Lady of Lourdes. The geology map shows that the siltstones and sandstones belong to the Namurian Gull Island formation (part of the Namurian sandstones GRUG), which overlies the Clare Shale Formation. The presence of the spring at this location may be influenced by the local faulting that has disturbed the Carboniferous strata. The Namurian sandstones are classed as a locally important aquifer (Ll) in this area.

[21] http://www.clarelibrary.ie/eolas/coclare/history/holy_wells_ballynacally_lisseycasey.htm, accessed 3/2/2020; the website quotes the Irish Folklore Commission Schools' Collection of 1937.



a) b)



c) d)

Figure 5.31 St Martin's well Ballinacally Co Clare: a) the well house over St Martin's well, with its arched wooden door; b) the interior of the well house, with water entering below the concrete rear wall; c) the highly cleaved shale bedrock; d) a massive bed of sandstone below the statue. Photos by Bruce Misstear

## 5.5 Wells in igneous rocks

These comprise 13 surveyed wells in the granites and other igneous intrusives unit, and three wells in Ordovician volcanics; there were no wells surveyed in the basalts and other volcanics unit. The granite wells are located in counties Carlow, Dublin, Galway, Kilkenny, Mayo and Wicklow, whilst the wells in Ordovician volcanics are in counties Dublin, Waterford and Wexford. The granites are classed as Pl or Ll aquifers, whereas the Ordovician volcanics are classed as Lm aquifers for the well in Dublin (Lady's well Flemington) and as Rf for the two wells in Wexford (St Mogue's well Ferns) and Waterford (St Brigid's well Kilrossanty).

### 5.5.1 St Moling's well St Mullins, Co Carlow

St Moling was born in 614 CE and founded a monastery at St Mullins. Apart from many miracles being attributed to him during his lifetime, one of his more earthly achievements was the

construction of a millrace that led to the tradition of 'wading the waters' during the pilgrimage (a map showing the course of the millrace is provided by Nugent, 2020). There is still an annual pilgrimage at the well that attracts large crowds (on the Sunday that precedes the 25th July, the latter date being the feast of St James). Ray (2013) cites St Moling's well as an example of a site where 'dispersed natives' of County Carlow make their holiday plans around the pattern day in July, as an opportunity for family reunions.

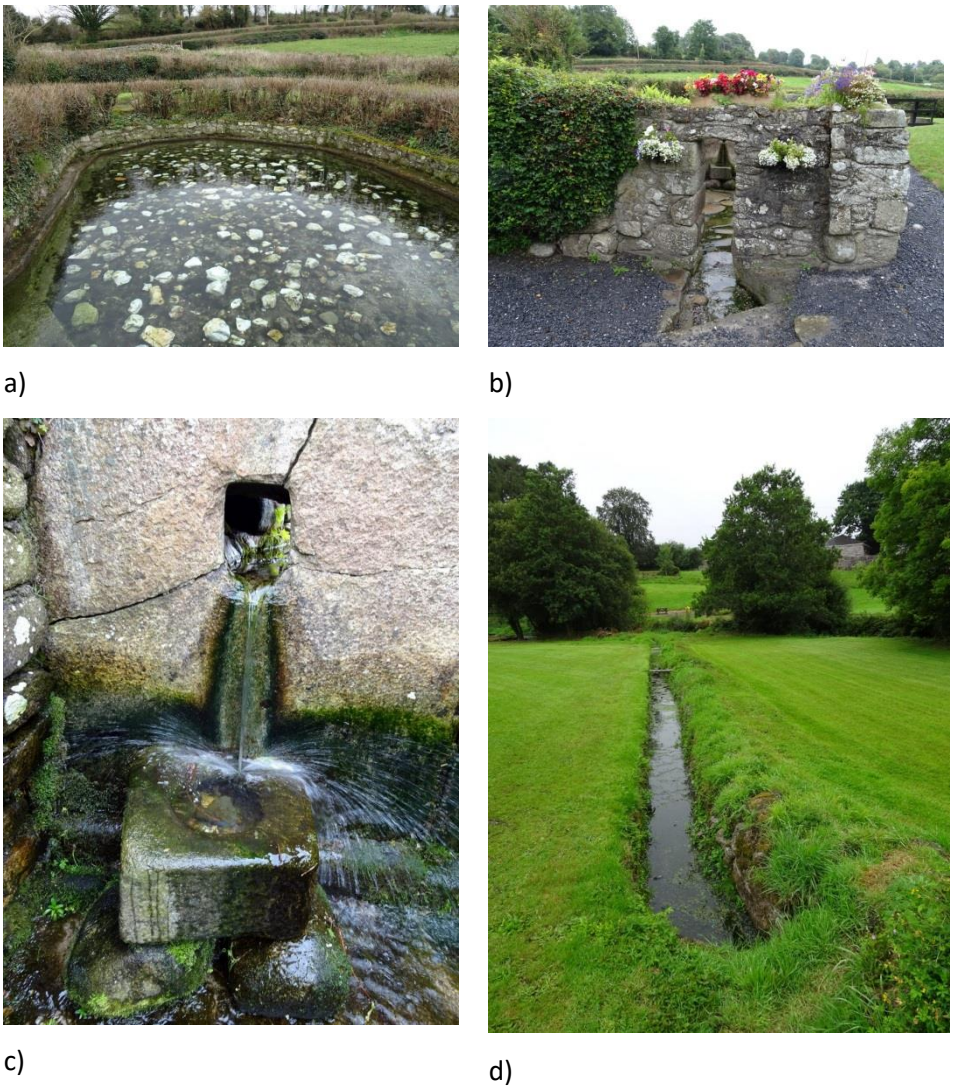
Many cures are associated with this well. The local St Mullin's heritage trail booklet mentions cures for blindness, headaches and ulcers. Rackard and O'Callaghan (2001) mention the protection of children against influenza (by dousing the child's head three times in flow of water), and also associate the well with a cure for warts. Ray (2013) refers to sufferers from toothache packing their teeth with soil from Father Kavanagh's grave nearby, before washing their mouth at the well. In the 14th century, the well was visited by many thousands of pilgrims during the plague year of 1348 (Clyn, 2007).

St Moling's well was one of the four monitoring wells chosen for this project (Section 4.1.4). The spring forms a pond approximately 4 m by 6 m in area, and about 0.4 to 0.5 m deep. Rackard and O'Callaghan (2001) report that this pond is said to contain seven springs. The pond overflows through two small openings (in the stone work) into an adjacent well house (Figure 5.32); from one of the openings, the water trickles down into a small hollowed stone reservoir (perhaps a type of bullaun stone or baptismal font) which overflows onto the floor of the chamber, whereas from the other opening water trickles directly onto the floor of the chamber. The water then flows across the flagged floor of the well house, exiting through a portal. The well house, or oratory, is the remains of an early medieval baptismal chapel, with a roof (now gone) reputedly made from the wood of a sacred yew tree[22]. From the well house, the water discharges to the Aughavaud River via a narrow, overgrown channel.

The bedrock comprises granite belonging to the Blackstairs Granite. The overlying granite tills are thin, as indicated by the E Extreme vulnerability rating. The spring site seems to correspond to a change in slope, with steeper gradients to the east and northeast above the spring. The flow into the well house from the pond in summer was estimated at c. 0.3 - 0.5 litres per second (2/8/2016). On 7/4/2018 a very strong flow was observed, with the water splashing strongly from the 'bullaun stone' (Figure 5.32c). The fact that the spring continues to flow during the

[22] https://holywellsofcork.com/category/cures/warts/; accessed 3/2/2020

summer and that the superficial deposits are thin in this area, both indicate that the spring has a bedrock source, probably the transition zone between the superficial deposits and the weathered granite bedrock (but see comment below in relation to water EC values). The granite is classed as a poor (Pl) aquifer.



a) b) c) d)

Figure 5.32 St Moling's well St Mullins, Co Carlow: a) the pond which is the spring source for the well (reputedly 7 springs discharge into the pond); b) the exterior of the well house (oratory) – the main inflow is visible through the portal on the back wall above the "bullaun" stone or baptismal font, whilst the outflow channel can be seen in the foreground, outside the portal; c) a strong flow of water into the well chamber was observed on 7/4/2018; d) the overflow channel, looking downstream towards the Aughavaud River. Photos by Bruce Misstear

Water level measurements for the pond that is St Moling's well are shown in Figure 5.33, along with monthly rainfall data for the Oak Park climate station in Co Carlow. When looking at the figure, the reader should note that that there was a change in datum from August 2017 (the wall previously used had been partly removed), and also that the well had been pumped shortly before the measurement in July 2018. (On 18/7/2018, there was no overflow from the pond into the well chamber, and discussions with the local landowner established that he had partly drained the pond earlier that morning, and that this was done every three weeks or so during summer to clean out the pond weed; he added that the water level in the pond recovers overnight).

Interestingly, whereas the EC of the well water had varied very little in seven measurements taken between August 2016 and April 2018 (values ranging from 192 to 208 µS $cm^{-1}$), a much higher EC value of 312 µS $cm^{-1}$ was recorded on 18/7/2018 after the pond had been partially drained (see Section 7.7.1). This suggests that the inflows may derive from more than one depth – perhaps, a less mineralised inflow from the transition zone and a more mineralised inflow from the deeper bedrock – or that the water remaining in the pond after the partial cleaning out was relatively stagnant.

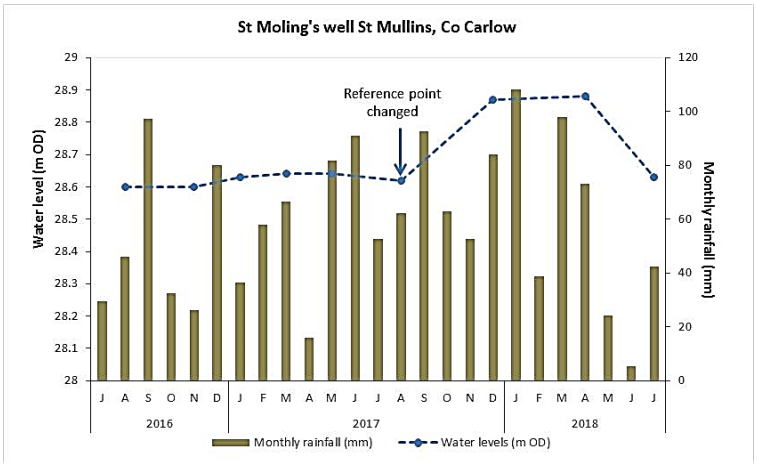



Figure 5.33 Water levels at St Moling's well St Mullins, Co Carlow; monthly rainfall data are for Oak Park in Co Carlow and were obtained from Met Éireann

### 5.5.2 St Anna's well Gorumna Island, Co Galway

St Anna's well (Figure 5.34) is located beside Lough Tan on Gorumna Island, and is accessed by a recently laid concrete pathway. The granite here forms low, smooth rock pavement; there are

small areas of boggy land with blanket peat in between the outcrops. The well is less than a metre above the shore of Lough Tan – also known as Lough Nafiddaun - and only a few metres from it. There is a stone altar built on a low granite outcrop. At the entrance to the altar there is a small triangular opening (0.25 x 0.28 x 0.35 m) that contained about 0.22 m of water on 30/3/2017. The sides of the triangular opening coincide with joints in the granite outcrop; these align at 20° NNE, 305° WNW and 75° ENE. The granite belongs to the Errisbeg Townland Granite Formation, part of the Galway Granites. The lithology is described on the GSI map legend as megacrystic pink/grey monzogranite.



a) b)

c) d)

Figure 5.34 St Anna's well Gorumna Island, Co Galway: a) view of the well beside the southeastern shore of Lough Tan; b) the well enclosure (centre), with flower beds (left) and grotto (right); c) the triangular well: the influence of jointing on the well shape can be clearly seen; d) the position of the well in relation to the lake. Photos by Bruce Misstear

The water level in the well appears to be slightly higher than that in the nearby lake (by 0.5 m or so). Also, the EC and pH of the well water and lake are slightly different, with the well water being somewhat more mineralised, all suggesting that the well water is groundwater (albeit very

shallow), although the possibility that it is mainly from rain water run-in, which has become slightly mineralised, cannot be ruled out. Curiously, the water in the font was the most mineralised.

### 5.5.3 St Brigid's well Kilrossanty, Co Waterford

This is one of two surveyed wells in Ordovician volcanics – specifically rhyolitic volcanics, with grey and brown slates, of the Campile Formation. In fact, there are three wells at this site: aligned roughly north-south from St Brigid's well (Tobar Bride) to Our Lady's well (Tobar Mhuire), to the Well of Jesus (Tobar Iosa, Figure 5.35). Each well is about 20 m from the next one. The main well here appears to be the one dedicated to St Brigid, since this is the well signposted from the main road. Broderick (2016) confirms that St Brigid's well is considered the most important ('most efficacious') well; Broderick, and also Keane (2018), note that the Ordnance Survey Letters of 1841 record only two wells at this site, St Brigid's well (Tobar Bride) and Our Lady's well (Tobar Mhuire).




Figure 5.35 OSI Digital Globe image showing the locations of the three wells at Kilrossanty, Co Waterford. Note the scale bar at the bottom left of the image. (The image was prepared using the GSI Groundwater Data Viewer)

The wells are all finished in a similar manner. They are approximately keyhole-shaped and lined with stones and mortar; they have a concrete surround and are partly protected by wooden fencing (Figure 5.36). St Brigid's well is 1.5 m long and has a maximum width of about 1 m; it contained 0.4 m of water when visited in April 2017, and some coins were observed in the well. There is a (buried) drainage line visible downgradient (east) of the well. Tobar Mhuire is 1.4 m

long with a maximum width of about 0.75 m; it had 0.35 m of water on 14/4/2017. There were beads beside the well and some coins in the well. The well of Jesus has more of an eggcup than keyhole shape, with the visible part 0.9 m long and 0.8 m wide, and it contained 0.22 m of water on 14/4/2017; there is a 1.2 m square concrete manhole cover obscuring part of the well. This well, which is located in the southeast corner of the field, drains eastwards through an open channel into the neighbouring field – the channel is 0.25 m wide and had a very small flow (probably less than 0.1 l $s^{-1}$) in April 2017; and possibly even smaller flow during a return visit in May 2017. There is a statue of Jesus beside the well.

The Campile Formation is classed as a regionally important fissured rock aquifer. An east-west trending fault passes through the volcanic bedrock within 250 m north of the well site, and terminates at the unconformable contact with younger Old Red Sandstone (Coumshingaun Conglomerate Formation) about 500 m northwest of the site. The vulnerability rating is Moderate, suggesting that the local sandstone tills are at least 5 m thick (and possibly greater than 10 m if they are of moderate rather than low permeability), so they may contribute to the flow of these shallow springs. In terms of physiography, the springs issue from the base of a low bank below the nearby graveyard wall; the location of the spring line coincides approximately with the boundary between the mountain ice-sculpted ridge and the rolling to gently undulating glacial sediments units shown on the physiographic unit map.



a) b)

Figure 5.36 The holy wells at Kilrossanty, Co Waterford: a) the 3 wells, with St Brigid's well in the foreground, Tobar Mhuire in the middle and the Well of Jesus (Tobar Iosa) at the far corner of the field; b) St Brigid's well (note the buried drain leading away from the well). Photos by Bruce Misstear

## 5.6 Wells in metamorphic rocks

Within the metamorphic rock lithological grouping, wells were surveyed in Cambrian metasediments (six wells), Ordovician metasediments (14 wells) and Silurian metasediments and volcanics (15 wells), plus wells in older Precambrian quartzites, gneisses and schists (11 wells); there were no wells surveyed in the Precambrian marbles rock unit. The surveyed wells in the Lower Palaeozoic metasediments are widely distributed (including in counties Carlow, Cavan, Dublin, Kilkenny, Longford, Louth, Meath, Tipperary, Waterford, Wexford and Wicklow), whilst the wells surveyed in Precambrian metamorphics are found in counties Donegal, Galway, Mayo and Wexford.

The metamorphic bedrock aquifers at all of these wells are classed as poorly productive (i.e. in either Ll, Pl or Pu categories). The Precambrian quartzites, gneisses and schists and the Cambrian metasediments are classed as Pl for all the wells in these groupings, whereas the aquifer ratings for Ordovician and Silurian metasediments are a mixture of Pl and Ll, except for two of the well sites which are classed as Pu.

### 5.6.1 St Patrick's well Cartron, Co Longford

The well is on the western side of a hill known as Corn hill, which rises eastwards to an elevation of 278 m OD. It is a square well (0.5 x 0.5 m) inside a large whitewashed concrete well house (Figure 5.37). The front of the well house is about 5 m wide, and rises in a triangular shape to a height of 2 m; it is topped by an alcove with a near life-size statue of St Patrick. The well contained 0.33 m of water in August 2017. It is a spring well which discharges into a marshy area in the field below (and ultimately to a drain/stream that flows under the road and to the northwest).

The geology map shows bedrock outcrop or subcrop in the vicinity of the well. The bedrock comprises greywackes, shales and minor volcanics of the Ordovician Coronea Formation, which is part of the Longford-Down inlier (Tract 2), bounded to the north by Carboniferous strata and to the south by a fault (the Carrickateane fault). The bedding strike is northeast to southwest, with some of the beds locally overturned.



a) b)

Figure 5.37 St Patrick's well Cartron, Co Longford: a) the entrance to the field containing St Patrick's well (note the rushes at the bottom of the field, indicating poor drainage in the area where this spring well discharges); b) the white-washed well building is inside a wooden fenced enclosure (note the well is at the base of an embankment). Photos by Bruce Misstear

The change in slope in the field likely has an influence on the location of the spring (Figure 5.37b). No outflow was observed on 15/8/2017 (just a marshy area in the field below the well), but some outflow was observed previously in November 2015. The X Extreme vulnerability rating indicates that the subsoils are very thin in this area, so the spring most likely issues from the transition zone at the top of the metasedimentary bedrock, which is classed as a Pl aquifer.

### 5.6.2 St Kevin's well Glendalough, Co Wicklow

Glendalough was an important monastic site in the medieval period, and is a popular tourist attraction today. St Kevin's well is located in the Glendasan River valley, at the foot of Derrybawn Mountain, close to the right bank of the river and near the Glendalough visitor centre. This is a circular stone-lined well, about 1.2 m in diameter, with its base about 1.3 m below ground level (from the south side). There are steps (of mica schist) down into the well from the river (north) side. The well was almost dry at the time of the first visit in September 2016 (Figure 5.38a), but it contained about 0.24 m of water in January 2017. The well was again virtually dry on 19/5/2017, but contained water when visited in January 2018 and March 2019. The well site is about 1 m to 2 m above the river, so the water level is perhaps close to river level.



a)



b)

Figure 5.38 St Kevin's well Glendalough, Co Wicklow: a) the well was almost dry at the time of this photo (September 2016); b) looking from the well to the fast-flowing Glendasan River in January 2018. Photos by Bruce Misstear

The bedrock comprises dark blue-grey slate, phyllite and schist belonging to the Ordovician Maulin Formation. Several mica schist boulders are visible nearby. The Glendasan valley in the vicinity of the well follows a northwest-southeast fault. The general strike of the Ordovician beds is NNE-SSW, with dips to the ESE. The Quaternary deposits along the Glendasan River valley consist of alluvium and gravels derived from granite. In terms of groundwater vulnerability, the well is near the boundary between X and E Extreme (covering the mountain to the south) with High for the river valley. As the well is close to the edge of the high ground to the south, and as the water is more mineralised than the nearby river (EC of 45 µS $cm^{-1}$ for the well water compared to 28 µS $cm^{-1}$ for the river in September 2016), the source may be the metamorphic bedrock aquifer rather than the superficial deposits.

### 5.6.3 St Brigid's well Faughart, Co Louth

Lying on a small hill north of Dundalk, Faughart is a site of historic importance, both as the birthplace of St Brigid in 643 CE and as the scene of a battle in 1318 when Edward Bruce, brother of Robert, was killed (part of his remains are reputedly buried in this graveyard). St Brigid lived in this area before moving to Kildare where she became an abbess[23]. Isaac Butler (botanist) visited this well in 1744 and commented 'At a small distance from the [old] church [of Faughart] northward there is a well of good spring water which lathers very well, it is covered with a stone arch in bad repair' (Conlon, 1999). The fact that the water lathered well suggests low hardness.

[23] http://irelandsholywells.blogspot.ie/2011/10/saint-brigids-shrine-and-well-faughart.html (accessed 4/2/2020)

The well is on the east side of the medieval graveyard on Faughart Hill. The maximum elevation of Faughart Hill is 113 m, whereas the valley below to the east has an elevation of around 50 m OD. The well is inside a beehive-shaped stone and mortar well building (Figure 5.39), close to top of Faughart Hill. There are about a dozen steps leading down to the entrance to the well house (the entrance is about 1.7 m below ground level). The well is rectangular, measuring approximately 0.82 m in width and 0.68 m from front to rear.



a) b)

Figure 5.39 St Brigid's well Faughart, Co Louth: a) the stone and mortar beehive well house; b) view eastwards from well, towards a valley and the Carlingford peninsula beyond. Photos by Bruce Misstear

The Quaternary map shows till derived from granites (TGr), with rock outcrop or subcrop within 50 m or so to the east and south of the well. The bedrock consists of calcareous greywackes of the Silurian Clontail Formation. These metasediments are unconformably overlain by Dinantian sandstones and limestones about 600 m or so southeast of the well. The location of this well so close to the top of a hill is surprising, as it must have a very limited recharge area - the zone of contribution is unlikely to exceed 2 ha, and is probably less. The E Extreme vulnerability rating indicates that bedrock is within 3 m of the land surface here, and the probable source of groundwater is the transition zone / upper weathered metamorphic bedrock, which is classed as a Pl aquifer. Meehan (*pers comm*, 2019) mentioned that, elsewhere in Louth, the transition zone in Lower Palaeozoic metasediments is sometimes 2-3 m thick, but on the high ground here on Faughart Hill it is unlikely to exceed 1 m.

### 5.6.4 St Colmcille's well Glencolmcille, Co Donegal

The well is about 1.5 km north of the centre of Glencolmcille. St Colmcille's well is marked at this location on the 6 inch Cassini map (dating from the 1940s), but the 19th century 6 inch OS map shows the well to be at a different location, 250-300 m to the SSE (Figure 5.40). The stone cairn at the current well site is marked on the current OSI Discovery map.

This is a very well-known holy well, and forms part of the three to four hour long *turas* that includes a megalithic court tomb as one of its stations (Ray, 2013). Archaeologist Michael Herity has suggested that cross-inscribed stones found at several of the Glencolmcille turas sites may date as far back as the 6th to 8th centuries CE (Ray, 2015). That the well has been popular with pilgrims for many years is evident from the size of the cairn formed by stones left by the pilgrims. However, if the well location has moved since the original 6 inch mapping of the 1830s and 1840s, then the cairn likely dates from only the last 150 years or so. Rackard and O'Callaghan (2001) recount a story that there were formerly two stones at the well, one which cured headaches and the other for sore eyes.

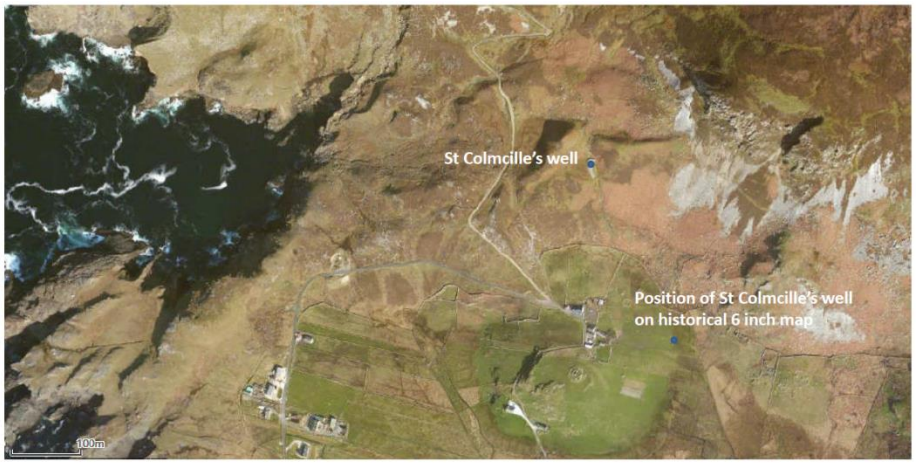
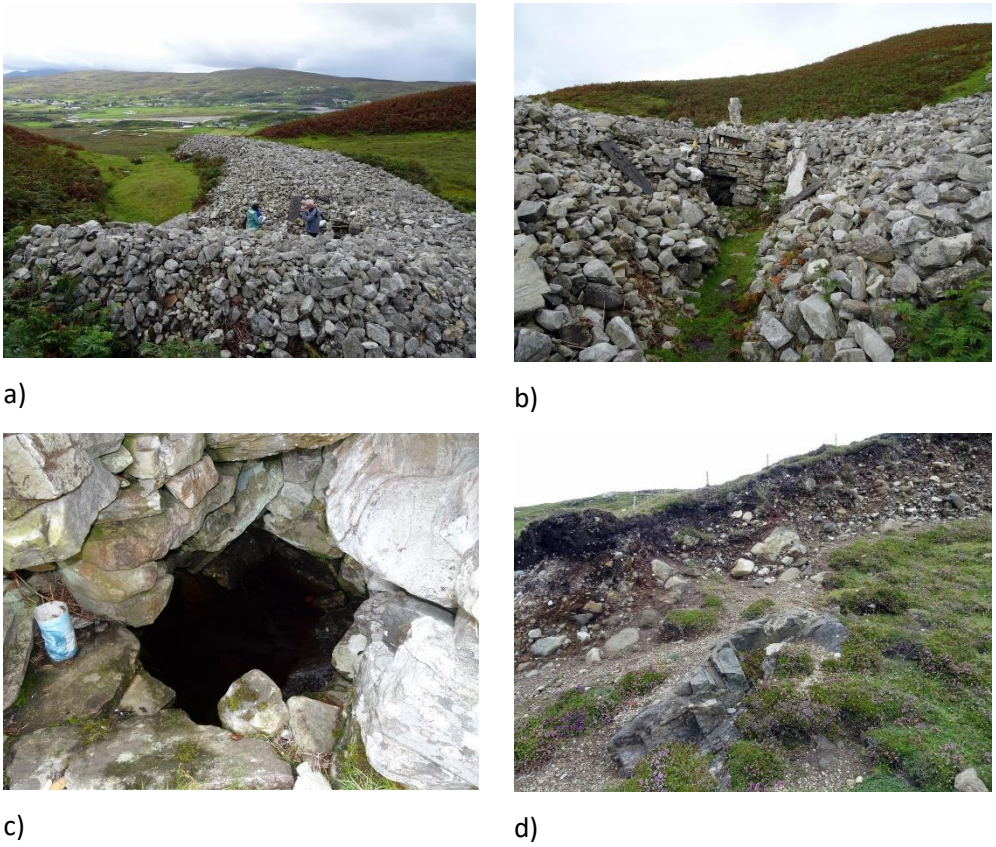



Figure 5.40 OSI Digital Globe image showing position of current St Colmcille's well and position of well as shown on the 19th century 6 inch OSI map. Note that the current well may lie on a NNW-SSE structural lineament. (Image prepared using GSI Groundwater Data Viewer)

The well is within a side opening into a large cairn of stones (Figure 5.41). The cairn probably results from the tradition in which each pilgrim carries three stones to the well as part of their

pilgrimage (Harbison, 1991; Ray, 2015). The well is lined with grey quartzite blocks. The well measures 0.8 m from front to back and it contained 0.2 m of water when visited in August 2017.



a) b) c) d)

Figure 5.41 St Colmcille's well Glencolmcille, Co Donegal: a) the curved mound formed by the stone cairn that surrounds the well; b) the entrance amongst the stones to the well; c) the well; d) exposure of possible transition zone (1-2 m thick) alongside minor road near a signpost to St Colmcille's well. Photos by Bruce and David Misstear

The GSI bedrock map describes the local rock as 'whitish quartzite with pebble beds' belonging to the Dalradian Slieve Tooey Quartzite Formation. The map legend notes that this is possibly the most persistent formation of the Dalradian Supergroup, extending from Connemara through Donegal to Banffshire in Scotland. South of the well, the Slieve Tooey Formation is in faulted contact with the Port Askaig Formation (also Dalradian), which comprises diamictites, schists and quartzites (Figure 5.42). The faulted contact between the Slieve Tooey and Port Askaig Formations south of the well follows the regional NE-SW structural trend, whilst fold axes in the area (as mapped in the Port Askaig Formation) generally follow an ESE to WNW direction. The regional NE-SW structural trend is evident in the alignment of the coastline west of the well (and

the north side of Skelpoonagh Bay is influenced by a NW-SW structural trend). Schist and grey quartzite stones are plentiful in the area. The Quaternary map shows outcrop or subcrop in the vicinity of the well. There are tills derived from metamorphic rocks to the south, and blanket peat to the south and north.

The water source for the (current) well is obscured by the large stone cairn. The cairn appears to impound a small stream that flows down the hill behind the well, creating marshy ground. The well was probably a spring, which possibly contributed to the flow in this small stream. Exposures of weathered/transition zone material are visible along the roadside near the path to the well (Figure 5.41d), and it is likely that this spring issues from the transition zone. The location of this spring well may also be influenced by the geological structure: the detailed topography highlighted by the OSI Digital Globe image suggests the well may fall on a NNW-SSE structural feature, which cuts the low hills immediately to the north (see Figure 5.40).

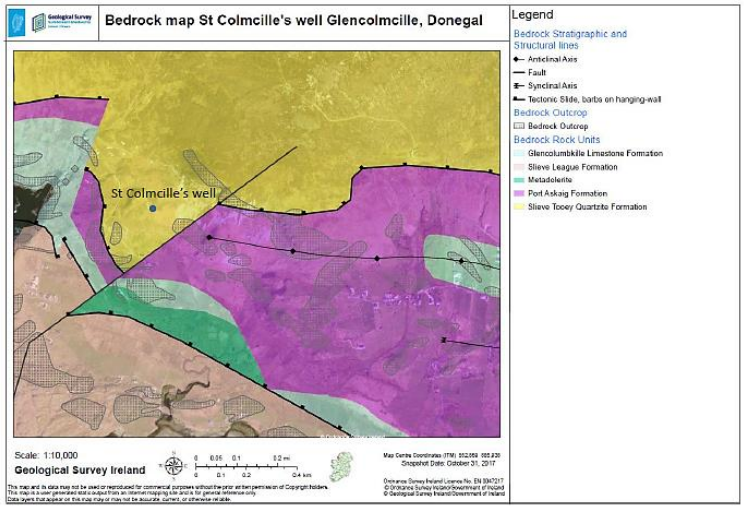



Figure 5.42 Bedrock geology map for St Colmcille's well Glencolmcille, Co Donegal. (Map prepared using the GSI Groundwater Data Viewer)

## 5.7 Wells in sands and gravels

Eight wells were surveyed within sand and gravel aquifers (not including those wells that are believed to have a mixed bedrock and gravel source; see Section 5.8 below). These include three wells in Ireland's most extensive sand and gravel aquifer, the Mid Kildare Curragh aquifer, which is classed as a regionally important Rg aquifer; St Canice's well in the sand and gravel aquifer in Kilkenny (also Rg); and the Holy Trinity well at Ashford in Co Wicklow and Tobersool in Co Dublin, both of which are in locally important (Lg) sand and gravel aquifers.

### 5.7.1 Holy wells in the mid-Kildare (Curragh) regionally important sand and gravel aquifer

The mid-Kildare sand and gravel aquifer (commonly known as the Curragh aquifer) covers an area of 202 km$^2$ and represents the most extensive sand and gravel aquifer in the country. The Physiographic unit description (Level 2) is flat to gently undulating ice-moulded topography. The Curragh aquifer consists of glaciofluvial deposits, which were laid down in a trough in the underlying Carboniferous limestone bedrock. In the centre of the Curragh, these deposits have an estimated maximum thickness of 65 m and they thin towards the aquifer margins (Daly 1981; Hayes *et al*. 2001). The sediments exhibit extensive lateral variability, typical of glaciofluvial deposits (Misstear *et al*., 2009b). The Curragh aquifer is generally unconfined, although the presence of clay layers may act locally as confining or semi-confining layers. Pumping tests have indicated hydraulic conductivity values for the gravels of up to 200 m d$^{-1}$, but more typically lie in the range 5 to 30 m d$^{-1}$ (and 0.1 to 1 m d$^{-1}$ where the gravels are clayey; Misstear *et al*., 2009b). Three holy wells were surveyed in the Curragh sand and gravel aquifer (Figure 5.43), two of which are described below: St Brigid's well at Tully and Father Moore's well.

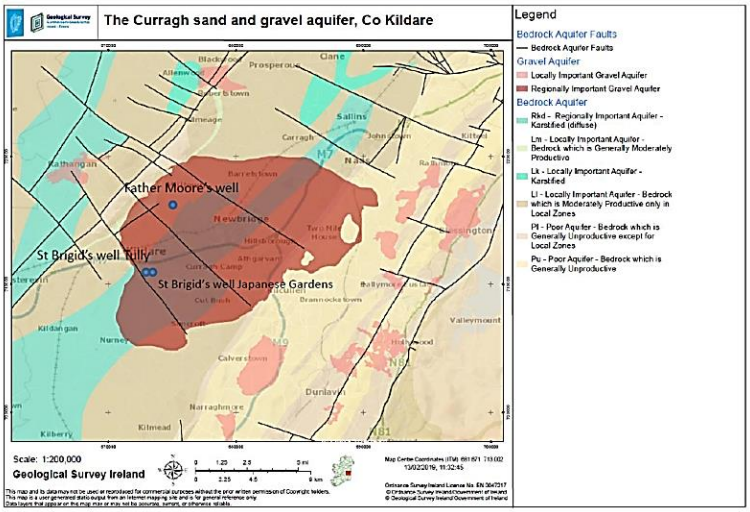



Figure 5.43 Map showing the extent of the Curragh sand and gravel aquifer, and the locations of holy wells. (Map prepared using GSI Groundwater Data Viewer)

#### 5.7.1.1 St Brigid's well Tully, Co Kildare

St Brigid's well at Tully is located about 2 km south of Kildare town and is possibly the best-known sacred well in County Kildare. The 1.25 m diameter, 0.6 m deep well is surrounded by a

low walled parapet, and is partly overshadowed by branches of a large conifer tree that (usually) contains many rags and other votive offerings (Figure 5.44 and see also Figure 2.6 in Chapter 2). Between the well and its outflow point 35 m away (a small rectangular opening, from which water flows through two hollowed stones under a stone arch decorated with a St Brigid's cross), there are several small standing stones used in performances of the Stations of the Cross.



a)



b)



c)



d)

Figure 5.44 St Brigid's well Tully, Co Kildare: a) the circular stone-lined well with rag tree behind; b) view from the well past the stations to the stone arch pictured in c); c) the stone arch under which the water from the spring well discharges (the water issues from the small opening just visible behind the two hollowed stones); d) downstream of the arch, the discharge of the well enters the Tully stream. Photos by Bruce Misstear

This spring well issues from the Curragh sand and gravel aquifer and drains southwards into the Tully stream. Although this researcher could not find an up to date aquifer thickness map (one

that includes data from the groundwater investigations that accompanied the Kildare Bypass project in the early 2000s), it is likely that the saturated thickness of the gravel aquifer at this location is at least 5 m and possibly exceeds 10 m. As noted above, the sand and gravel aquifer is classed as Rg, whilst the underlying pure bedded limestone (belonging to the Dinantian Rickardstown Formation) is classed as a regionally important diffuse karst aquifer (Rkd). The GSI Groundwater Data Viewer shows that one of the monitoring boreholes for the Kildare Bypass Project was drilled beside the access laneway to the holy well; it was drilled (in June 1998) by light percussion to 15 m – suggesting that the bedrock may have been encountered around this depth.

St Brigid's well was one of the four wells selected for monitoring (Section 4.1.4), and water levels recorded over the period July 2016 to July 2018 are shown in Figure 5.45, together with monthly rainfall values for Casement aerodrome, about 45 km northeast of Kildare. Water levels varied by only 6 cm over this period. The levels are partially controlled by the outlet from the well that feeds the opening beside the stone arch shown in Figure 5.44c. The highest water level was observed in December 2017 and the minimum in August of that year.

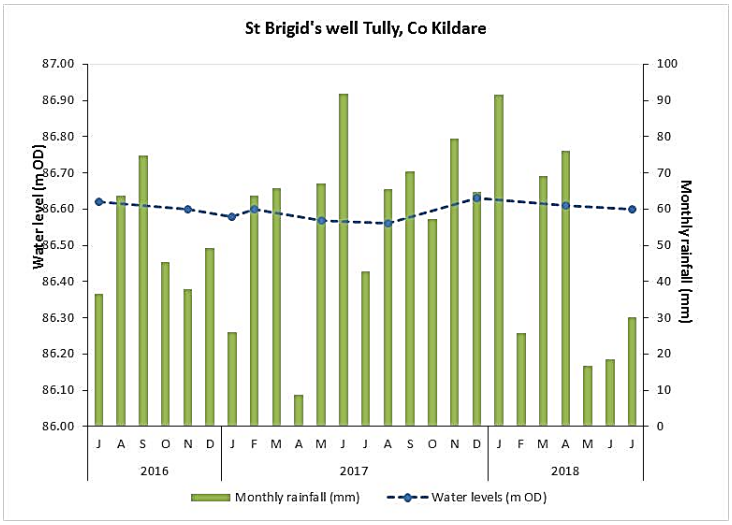



Figure 5.45 Water level hydrograph for St Brigid's well Tully, Co Kildare; monthly rainfall data are for Casement aerodrome and were obtained from Met Éireann

### 5.7.1.2 Father Moore's well Rathbride, Co Kildare

This is an example of a holy well named after a so-called 'healing priest', Father John Moore (1779-1826). Ray (2013) describes how priests, who were believed to have healing powers, but

who could not pass these onto children, would bless a well or spring with their healing ability. This practice was most common in the 19th century. Before the time of Father Moore, the well was known as the Black well and had links to St Brigid (Buckley, 2012). The well has a reputation for various cures including headaches (Logan, 1980), backaches and mental health (Foley, 2010). A silk hat that belonged to the priest is brought out each August, to be worn by pilgrims seeking a cure.

Father Moore's well is located in Rathbride townland about 4 km northeast of Kildare town. The well is not shown on the OSI Discovery map, nor on the historical 6 inch map, but is marked on the 25 inch map. The current well is 1.8 m in diameter and is set inside a hexagonal walled enclosure, which also contains a shrine and commemorative plaques (Figure 5.46). There is an overflow pipe from the well that leads to a drain. The spring source for the well appears to be in an overgrown area directly behind (east) of the walled enclosure (Figure 5.46c). It is likely that the saturated thickness of the gravel aquifer at this location is at least 5 m and could be 10 m.



a)




b)



c)

Figure 5.46 Father Moore's well, Co Kildare: a) the circular well (with stepping stones), which is located inside a hexagonal walled enclosure; b) memorial plaque to Father Moore; c) the spring source behind the current well enclosure. Photos by Bruce Misstear

### 5.7.2 St Canice's well Kilkenny City

St Canice's well is in Kilkenny city, within a steeply sloping garden that leads down to the right bank of the Breagagh River. The 6th century CE Saint Canice (*Cainnech*) is the patron saint of Kilkenny and its famous cathedral.

The well is inside a small stone chapel-shaped building, with a vaulted roof (Figure 5.47). Water flows into a stone basin in the floor of the building from a 7 cm diameter stone pipe set in the rear wall. The flow rate was estimated by the researcher as about 0.5 l $s^{-1}$ on 22/3/2017. The interior of the well house is approximately 1.5 wide and 2 m long; the height of the vaulted ceiling is about 2.7 m above the stone floor and there are stone benches along the two side walls. The current building reportedly dates at least as far back as the 17$^{th}$ century[24]. Outside the well, water flows through a stone-lined channel about 20 cm wide and 25 cm deep, containing a few cm of water, which discharges towards the nearby Breagagh River.



a)



b)



c)



d)

Figure 5.47 St Canice's well Kilkenny: a) view down the steep (frosty) slope towards the well house and Breaghagh River; b) the Chapel-like well house; c) water flowing from a small diameter stone pipe in the rear wall into the rectangular stone basin below; d) the narrow channel leading from the spring well towards the river. Photos by Bruce Misstear

The well site lies within the glaciofluvial sands and gravels that occur along the valley of the River Nore in Kilkenny. These are classed as a regionally important sand and gravel (Rg) aquifer

[24] https://www.stcanicesparish.ie/st-canices-church/kennys-well/; accessed 4/2/2020)

(see Figure 5.48); the underlying Dinantian pure bedded limestone (Ballyadams Formation) is classed as a regionally important diffuse karst aquifer (Rkd). A High vulnerability rating indicates the sands and gravels are more than 3 m thick at this site (and a Low vulnerability rating along the Breagagh valley suggests that there are more than 10 m of low permeability subsoils here). A large contrast between the well water temperature and the air temperature was observed during the visit on 8/2/2017 (11.3 °C and -1 °C, respectively – a difference of about 12 degrees). This may indicate that the groundwater source for the spring is partly from the deeper limestone aquifer as well as from the overlying shallow sands and gravels.

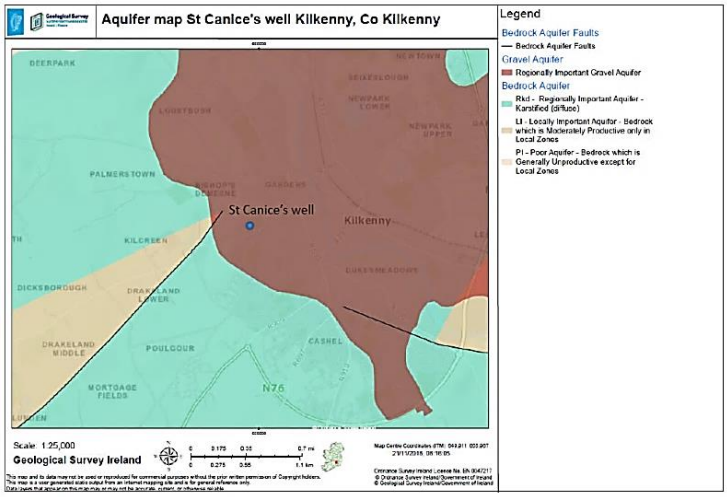



Figure 5.48 Aquifer map showing the location of St Canice's well within the Rg gravel aquifer. (Map prepared using GSI Groundwater Data Viewer)

The GSI Groundwater Viewer shows a small 'stagnant' spring called Lacken well, less than 50 m east of St Canice's well, on the same (right) bank of the Breagagh River. The yield is given as 30 $m^3\ d^{-1}$. The Viewer indicates St Canice's well itself to be on the north (left) bank of Breagagh (but this does not accord with the actual location, nor other descriptions of the well location), and to have a yield of 10 $m^3\ d^{-1}$ (about 0.1 l $s^{-1}$), much less than the flow rate observed during the visit by this researcher in February 2017.

### 5.7.3 Holy wells in locally important sand and gravel aquifers

In some situations where local sand and gravel deposits are relatively extensive, they are classed as a locally important Lg aquifer on the aquifer map, whereas in other cases the aquifer map shows only the underlying bedrock aquifer. One example of each situation is described below.

#### 5.7.3.1 Holy Trinity Well Ashford, Co Wicklow

Holy Trinity well near Ashford in Co Wicklow is an example of a spring well that taps sands and gravels that are sufficiently extensive to be mapped as an Lg aquifer. The well is located 1.5 km north of Ashford, 20-25 m west of main road towards Roundwood. There is a relatively new sign and plaque (erected by Wicklow Wells and Ashford Tidy Towns) at the entrance to the well site. The well is marked on the OSI Discovery map and on the historical 6 inch and 25 inch maps.

The well comprises an approximately circular shallow pool (circa 0.7 m in diameter and about 7 cm deep) at the base of an embankment, which rises about 3-4 m up to the field behind (west of) the well. The well is fed by small springs from the north and south; these presumably issue from the embankment (the site was very overgrown when visited, so the spring sources were difficult to see). The outflow at the time of first visit (7/9/2016) was probably in the region 0.1-0.2 l $s^{-1}$. The aquifer map shows the well near the eastern edge of a 4.5 $km^2$ area of locally important sand and gravel aquifer (Figure 5.49). The underlying Cambrian metasedimentary bedrock (comprising greywacke and shale of the Devil's Glen Formation) is classed as a poor (Pl) aquifer.

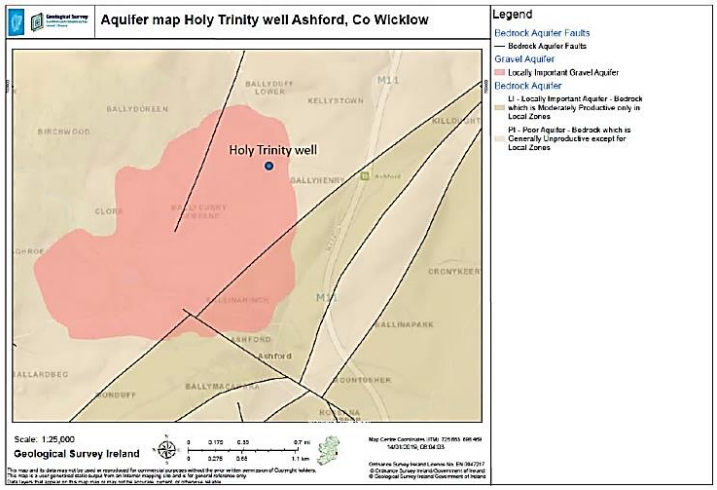
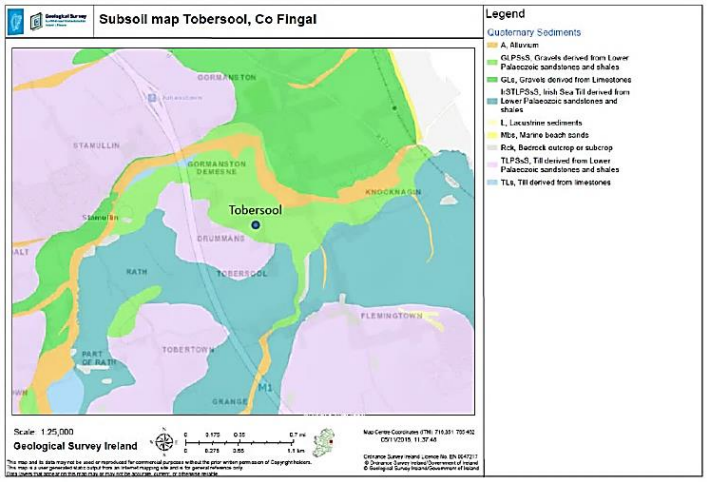


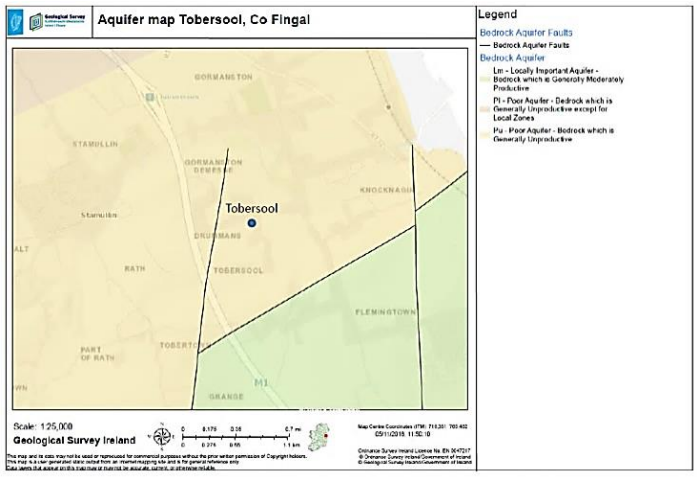

Figure 5.49 Map showing the location of Holy Trinity well Ashford, Co Wicklow, within a locally important gravel aquifer. (Map prepared using GSI Groundwater Data Viewer)

### 5.7.3.2 Tobersool Balbriggan, Co Dublin (Fingal)

Tobersool is an example of a holy well in a sand and gravel deposit that is not sufficiently extensive to be mapped as an Lg aquifer. The well is located within a private farm about 3 km northwest of Balbriggan. (It is shown on the OSI Discovery map and on the historical 6 inch and 25 inch maps.) This is a shallow stone-lined rectangular well (0.6 m x 0.9 m), and it contained about 0.3 m of water when visited in August 2016. As the name suggests, Tobersool has a reputation for curing eye ailments (Branigan, 2012). It is also known as St Brigid's well.




a)




b)

Figure 5.50 Tobersool, Co Dublin: a) Quaternary map; b) aquifer map. (Maps prepared using GSI Groundwater Data Viewer)

The Quaternary map indicates the well to be located in glaciofluvial sands and gravels derived from Lower Palaeozoic sandstones and shales (see Figure 5.50). However, the aquifer map does

not show these sands and gravels, but is based rather on the underlying bedrock (greywacke sandstone and siltstone belonging to the Silurian Denhamstown Formation; Silurian metasediments and volcanics [SMV] in the GRUG classification), which is classed as a poor (Pu) aquifer. Despite not being shown on the GSI aquifer map, the fluvioglacial sands and gravels are the more likely groundwater source for this shallow well, rather than the metasedimentary bedrock, although the latter may also contribute.

## 5.8 Wells in mixed gravel and bedrock aquifers

In addition to the eight wells which tap sand and gravel aquifer, there were 13 wells surveyed where the groundwater source was considered to be a likely combination of sands and gravels and underlying bedrock. Of course, and as explained in Section 4.2.5, this categorisation of a 'mixed' aquifer source is only an interpretation, one that would generally require invasive borehole investigations at the sites to verify. In most cases the interpretation is based on the presence of alluvium or glaciofluvial sands and gravels at or very close to the well site, but where these superficial deposits are insufficiently extensive to be mapped as an Lg aquifer. Examples include St Catherine's well Fieldstown, St Sylvester's well Malahide and St Werburgh's well in Swords, all in Co Dublin (these wells all possibly tap sands and gravels in combination with impure limestones); St Brigid's well in Kilcullen in Co Kildare (close to the River Liffey, about 3 m above the river level, the groundwater source may be the valley alluvium or gravel, in combination with the transition zone of the underlying Silurian metasediments); Ladywell Ballinakill, on the boundary between Kilkenny and Laois (pure bedded limestones with sand and gravel); and St Brigid's well at Drum in Co Roscommon (pure unbedded [Waulsortian] limestones with glaciofluvial gravels). One example will be discussed here: St Patrick's well at Trinity College Dublin.

### 5.8.1 St Patrick's well Trinity College Dublin

The well is described in Sweeney's 1991 book '*The Rivers of Dublin*'; he mentions that the well was originally located behind Number 9 Nassau Street. Neither this location nor the present one is shown on the 19$^{th}$ century 6 inch OS map (although the current well is marked on the early 20$^{th}$ century 25 inch map). Sweeney reports Dr Rutty as writing in 1757 that the water from St Patrick's well was 'saltish and laxative', which may have been associated with some health

benefits. Branigan (2012) remarks that St Patrick reputedly first baptised the pagans of Dublin at this well.

The well is accessed via a gate into the Provost's garden from the basement level of the Arts Building. This is a brick and stone-lined chamber (Figure 5.51) under the footpath that runs along the north side of Nassau Street; the top of the well is about 2-3 m below street level. The well diameter is 1.4 m. The well is full of silt and stones up to within 0.8 m of the well surface, and was dry when visited in January 2017. A year later (on 30/1/2018), the well contained about 0.65 m of water (the water reportedly reappeared in the well in early January, after being dry for most of 2017). Branigan (2012) indicates that this well was 40 feet deep (12 m) but is 'now only 4ft deep' (1.2 m) – suggesting that some further silting up had occurred by the time of this researcher's inspections in 2017/2018.



a) b)

Figure 5.51 St Patrick's well Trinity College Dublin: a) the brick and stone lined well chamber and dry well in January 2017; b) the well with water in January 2018. Photos by Bruce Misstear

The well is close to the likely old channel of the River Stein (see Figure 5.52) and so may tap a sand and gravel aquifer within this buried channel, possibly in combination with the underlying limestone and shale bedrock belonging to the Lucan Formation (Calp rock). The sand and gravel deposit is not included on the GSI Quaternary map (which shows made ground ['Urban'] and limestone till in this area), whilst the Calp bedrock is classed as a locally important aquifer (Ll). The sand and gravel aquifer formed within this old river channel has been exploited in the past

as a source of low enthalpy heating for the College, by wells in the northeast corner of the campus.

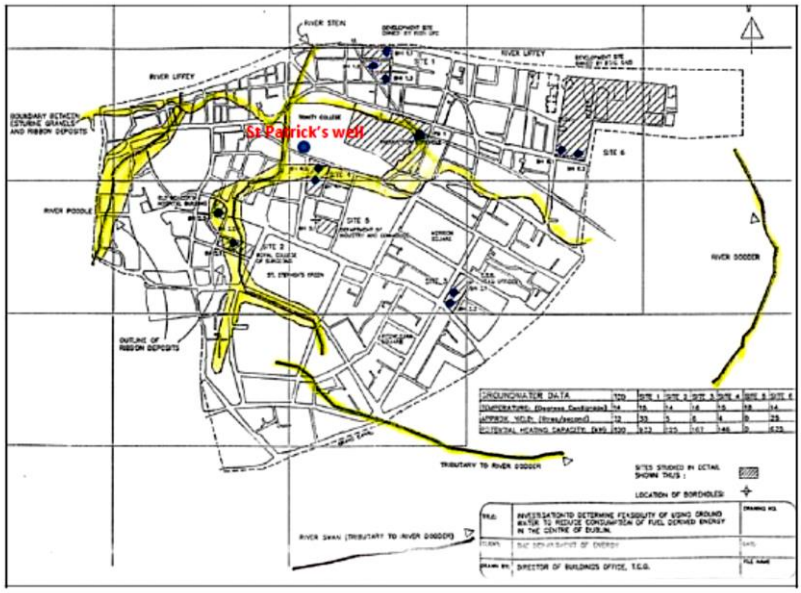



Figure 5.52 Map showing buried valleys associated with tributaries of the River Liffey in south-central Dublin (in yellow); St Patrick's well is at the edge of the Trinity College campus, near the Nassau street entrance (map obtained from the Estates Office, TCD; St Patrick's well location added by the author)

## 5.9 Wells in confined aquifers

The vast majority of wells described thus far are shallow springs that issue from unconfined superficial or bedrock aquifers (and sometimes both). In a small number of cases there is evidence that the aquifer is confined. Three wells in confined aquifers will be described here: Bride's well at Calgath, Co Meath; St Brigid's well at Shangarry, Co Limerick; and St Gorman's well near Enfield in Co Meath. The latter two wells have been the subject of previous hydrogeological investigations.

### 5.9.1 Bride's well Calgath, Co Meath

Bride's well is located 2 km north of Kilcock, on the west side of R125. Buckley (2012) refers to the well as Bride's well Mulhussay, whereas French (2012) calls it St Brigid's well Kilcloon. However, according to the GSI Map Viewer and some websites, the well lies in the townland of Calgath. Strikingly, the well is at a high point in a field (the mound is marked on the historical 6

inch and 25 inch maps); indeed, Aldwell and Burdon (1980) remarked that several of the warm springs in Leinster are on small rises or mounds, including Bride's well (which they refer to as Bride's River or Breda's well). It was chosen for monitoring (Section 4.1.4) as an example of a holy well in a confined aquifer.

The well is protected by an octagonal wooden fenced enclosure with a wooden gate (Figure 5.53). The well is keyhole-shaped, with four steps leading down into it. The 'keyhole' is 2.7 m long, its stepped entrance section is 0.6 m wide, and the well itself is approximately circular, with a diameter of 0.8 m and typical water depth during monitoring of 0.9 m (see below). The well is lined with stone (limestone) and mortar, and is partly covered by a coarse, circular steel grid. It has a reputation for curing deafness and ear troubles (French, 2012).



a)



b)



c)




d)

Figure 5.53 Bride's well Calgath, Co Meath: a) the well is on a small mound; b) the octagonal wooden fenced enclosure surrounding the well; c) the metal grill partly protecting the water surface; d) a plaque indicting that Bride's well is a chalybeate well and that water temperatures in winter are up to 70 $^{o}$F. Photos by Bruce Misstear

The plaque at the well notes that it is a chalybeate well with water that is warm in winter (70 $^{o}$F – or 21 $^{o}$C) and cool in summer (Figure 5.53d); however, water temperatures recorded over a 2-year period in this research were in the range 12.3 to 14.6 $^{o}$C (the mean of 11 measurements was 13.0 $^{o}$C), much lower than the 70 $^{o}$F (21 $^{o}$C) mentioned on the plaque (see Section 7.7.1). These measurements were all made on samples collected from near the surface of this 0.9 m deep well: to check if temperatures were higher where the water probably enters at the base of the well, an EC meter with a probe at the end of a 1 m cable was used to record the temperature on 9/4/2019, and found the water temperature at the bottom of the well to be the same as that near the surface. Water can be heard leaving the well through an overflow pipe that probably drains to the ditch at the (western) edge of the field, about 30 m away. The water levels were monitored periodically over a 2-year period and were relatively stable (see Figure 5.54), albeit the levels were controlled at least to some extent by the outlet pipe. It is interesting that the well level was maintained even during the prolonged dry spell of summer 2018. There is iron-staining visible on the well lining below the water surface (and iron-coloured leaves on the water surface), confirming the chalybeate description of the well.

The bedrock geology comprises dark limestones and shales (Calp) of the Lucan Formation. These Dinantian upper impure limestones are classed as a locally important aquifer (Ll). A NE-SW fault is shown on the geology map about 500 m east of the well (which, together with a second fault further east, bounds Dinantian lower impure limestones [Ballysteen Formation]). This fault is intersected by a NW-SE fault to the south.

The groundwater vulnerability is classed as Low, indicating that the site is underlain by more than 10 m of low permeability subsoils (tills derived from Namurian sandstones and shales). However, Meehan (*pers comm*, 2019) mentioned that some bedrock mounds covered by thinner subsoils have been encountered elsewhere in this area of Meath, where the vulnerability had also been mapped as Low; hence, it is possible that the vulnerability rating is not accurate. Nevertheless, the (current) Low vulnerability class, together with the elevated topographic setting, the relatively high reported water temperature and fairly constant water EC (which varied only between 626 and 636 µS cm$^{-1}$ in 9 measurements over the monitoring period – see Section 7.7.1) all suggest a confined aquifer with a bedrock source that may be relatively deep. The likely recharge area is to the north, where the land rises to over 120 m OD about 2 km north of the well.

The GSI Groundwater Viewer shows Bride's well as a spring (actually, the spring is shown twice), with a yield of 20 $m^3$ $d^{-1}$ in one entry and 155 $m^3$ $d^{-1}$ in the second entry, the latter flow record from January 1982.

Water level data for the 2-year monitoring period from July 2016 to July 2018 are shown in Figure 5.54, along with monthly rainfall values for Dublin airport. The total water level variation over this period was only 6 cm and, somewhat surprisingly, the highest water level was recorded during the summer of 2017. It should be remembered that the outlet pipe in the well acts a partial control of water levels, with only the level measured in August 2017 being above the pipe obvert.

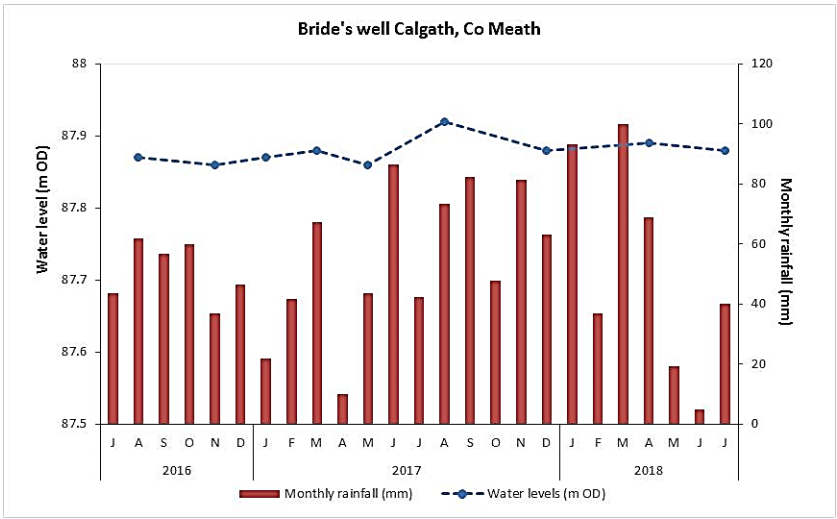



Figure 5.54 Water level hydrograph for Bride's well Calgath, Co Meath; monthly rainfall data are for Dublin airport and were obtained from Met Éireann

### 5.9.2 St Brigid's well Shangarry, Co Limerick

Ó Danachair (1955) refers to a legend that this well sprang up for the baptism by St Brigid of a pagan chieftain who lived in the ring fort at this site. He also mentions that the well has a reputation for treating eyes and other ailments. The well is located within a large garden area on the south side of the N21 road, about 1.5 km southwest of Newcastle West. The site includes a small building (pump house?), a shrine to St Brigid, a tap, bench, lighting, flower pots and several trees – hawthorn, ash and chestnut. The well is a circular modern structure, with a diameter of 1.1 m; the alignment of the walls along the path approaching the well give it a keyhole like appearance (Figure 5.55). Water enters the well up through a vertical pipe with an

internal diameter of 12 cm (outside diameter = 25 cm); the signboard at the site refers to this being an artesian well. The well contained 0.3 m of water when visited in August 2017. The well discharges into a concrete lined channel (0.92 m wide; water depth of 3 cm); the flow rate was difficult to estimate, but was certainly less than 0.5 l $s^{-1}$.



a) b)

Figure 5.55 St Brigid's well Shangarry, Co Limerick: a) The wall arrangement leading to the well gives a keyhole appearance; b) water enters the well through the circular stone pipe at its centre, and discharges into the concrete channel to the left. Photos by Bruce Misstear

The signboard says that 'St Brigid's well is an artesian spring coming up from deep fissures in the underlying limestone'. The temperature of this water is reportedly 'remarkably' constant, consistent with a deep groundwater source. The GSI Groundwater Viewer records a dug well at this approximate location (which is referred to as St Bridget's well). The well depth is given as 0.6 m and its use stated as a Group Scheme, with an abstraction of 110 $m^3$ $d^{-1}$. The general comments section refers to 'overflow warm'. (The Geological Heritage website – see Section 8.3.3 - refers to it as a warm spring, but that it is an 'Unaudited site').

The geology comprises undifferentiated Visean limestones (Dinantian upper impure limestones) overlying Waulsortian limestones (Dinantian pure unbedded limestones, Figure 5.56). The subsoil cover is limestone till, which is probably more than 10 m thick (based on the Low vulnerability classification). The undifferentiated Visean limestones are classed as a locally important (Ll) aquifer, whereas the underlying Waulsortian limestones are classed as a regionally important diffuse karst aquifer (Rkd). Given the possibility that this spring has a deep source, then it may originate from the Waulsortian.

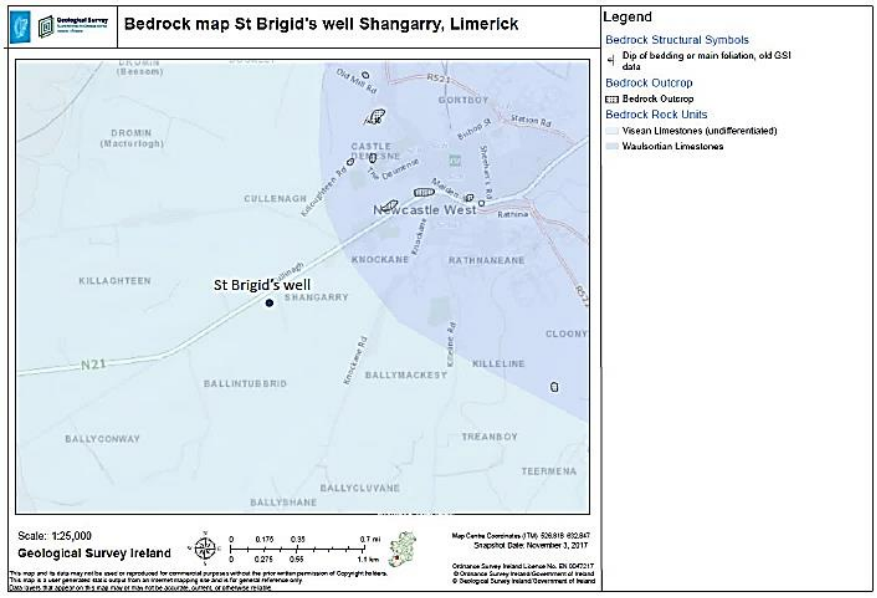



Figure 5.56 Aquifer map for St Brigid's well Shangarry, Co Limerick. (Map prepared using GSI Groundwater Data Viewer)

This well is referred to in an article by Brück *et al*. (1986) concerned with the warm springs of Munster. The site is described as being close to the 'shattered' contact between Calp limestone (i.e. Dinantian upper impure limestone) and a well-jointed reef limestone (the Waulsortian). Based on a geophysical survey, the superficial deposits were found to be thinnest at this locality, perhaps facilitating this artesian water reaching the ground surface. The average water temperature over a one-year period was 13.1 $^{o}$C – about 2.5 $^{o}$C warmer than that in a control well 4 km away. The mean groundwater EC at St Brigid's well for the 1981-82 monitoring period was 414 µS cm$^{-1}$, somewhat lower than the value of 483 µS cm$^{-1}$ recorded in the 2017 visit by this researcher (see Section 6.4.2 and Section 7.9).

### 5.9.3 St Gorman's well Enfield, Co Meath

St Gorman came from Wales, and reputedly was a pupil of St Finian at nearby Clonard; pilgrimages were made to the well on the first Sunday in May (French, 2012). St Gorman's well is in the grounds of the aptly named Hotwell House near Enfield. St Gorman's well is a large shallow depression which was dry when visited in January 2017 (Figure 5.57a) and, according to the well owner, Nicholas Wilkinson, it had been dry since May the previous year. The well contained water during a return visit on 31/1/2018 (Figure 5.57b: there was perhaps a metre of so of water in the centre of the depression, but it was not possible to measure the depth); a few bubbles could be seen rising up from near the centre of the pool. The (undated) GSI County Site

Geological Report for St Gorman's well (it is listed as a County Geological Site; see Section 8.3.3) mentions that it has an area of 40 $m^2$. The shallow depression appears to be an irregular circle measuring about 8 x 6 m, flanked by ash and willow trees. There was also an elm rag tree previously. French (2012) mentions that pilgrims used to bathe the afflicted part of the body in the well water and then tie a cloth to this elm; the cure would take effect as the cloth rotted. There is a boulder at the edge of the depression which, according to Mr Wilkinson, reputedly contains imprints of St Gorman's knees.



a) b)

Figure 5.57 St Gorman's well Enfield, Co Meath: a) the dry well in January 2017; b) the well with water in January 2018. Photos by Bruce Misstear

The subsoil comprises limestone till, with gravels immediately to the west. The depth to rock is 3 m at this site (Burdon, 1983), The bedrock geology map (Figure 5.58) shows the well to lie on massive unbedded lime-mudstones of the Waulsortian (Dinantian pure unbedded limestones in the GRUG), close to the faulted contact with limestones and shales of the younger Lucan Formation (Dinantian upper impure limestones) which passes about 200 m south of the well. The Waulsortian is classed as a locally important aquifer (Ll) in this locality.

St Gorman's well is one of several warm springs in Leinster and so has been much studied (Aldwell and Burdon [1980] remarked that the well was examined by a geologist – Du Noyer - as long ago as 1859), and most recently by Blake (Blake, 2016; Blake *et al*., 2016). As the spring itself was prone to drying up, Blake installed her groundwater temperature and quality instrumentation in a nearby observation borehole (20 m west of St Gorman's well), which is one of three boreholes drilled for geothermal investigations by the Geological Survey of Ireland in the 1980s. During the visit by the present researcher on 31/1/2018, the two observation wells closest to St Gorman's well were both flowing. The artesian head was above the well cap but

not up to the overflow pipe set in the top of the cap, so the potentiometric surface was about 0.2 m above ground level. Interestingly, the borehole water (as measured in the artesian borehole nearest St Gorman's well) was warmer and slightly less mineralised (i.e. lower EC) than the water in the holy well (675 and 718 µS $cm^{-1}$ for the borehole and holy well, respectively), consistent with a complex temperature and flow profile, as discussed by Blake (2016), and summarised below.

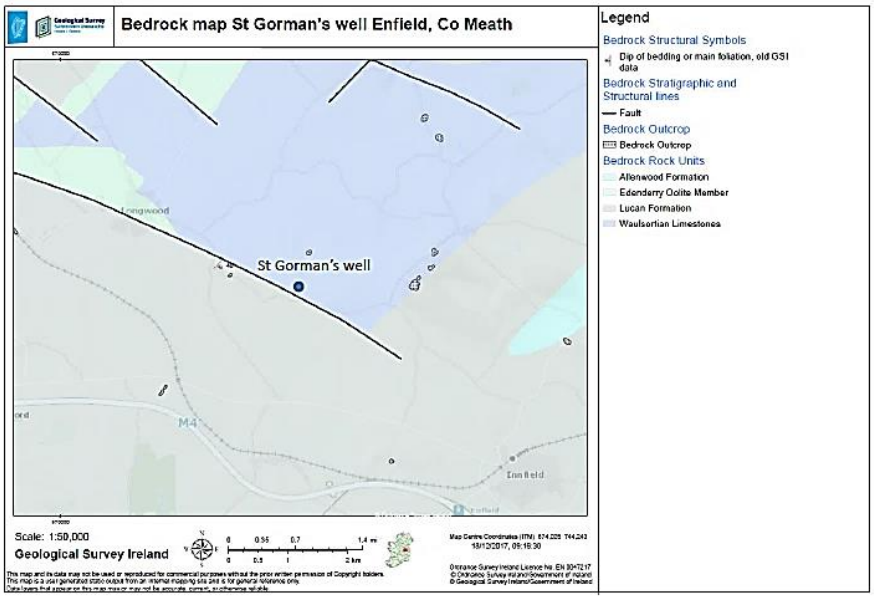



Figure 5.58 Bedrock geology map for St Gorman's well near Enfield, Co Meath. (Map prepared using GSI Groundwater Data Viewer)

Blake notes that St Gorman's well is located close to the faulted contact between the Waulsortian Limestone and the younger Lucan Formation (see Figure 5.58). During monitoring from the summer of 2013 to early 2015, the temperature varied from 10.5 to 21.8 °C (mean = 17.2 °C), with the maximum occurring in winter. Blake *et al*. (2016) describe the well as having a very complex temperature and EC profile, which they attribute to a conduit fracture flow system and a non-linear response to recharge. The observation borehole in which temperature and EC measurements were taken is artesian during periods when St Gorman's well contains water (see also Section 6.4.2).

Blake's research did not include measurements of flows from St Gorman's spring. However, in an earlier study in the 1980s, Burdon (1983) reported that the mean discharge from St Gorman's well was 398 $m^3$ $d^{-1}$, whilst the maximum was 1018 $m^3$ $d^{-1}$ which occurred in winter (for a 12-month monitoring period in 1982). That year, September was the only month where zero

outflow was recorded (although the average flows in August and October were only 5 $m^3$ $d^{-1}$). The GSI Groundwater Viewer includes St Gorman's well as a warm spring, with temperatures in the range 17 to 23 °C, and gives a maximum winter flow output of 1244 $m^3$ $d^{-1}$ for January 1982 (slightly higher than the value quoted above from the Burdon report).

## 5.10 Wells in coastal settings

The focus in this section is on wells close to shorelines. Thus coastal wells on cliffs are not included: one such well, St Declan's well at Ardmore Co Waterford, has already been described (under non-calcareous sedimentary wells – the well is in Devonian Old Red Sandstone) in Section 5.4; a second example would be St Kee's well at Foohagh in Co Clare, which is located on near-horizontal beds of non-calcareous Namurian sediments close to sea cliffs. The coastal wells described here are generally located close to the high tidal water level, and are characterised by elevated EC. The physiographic unit classification (see Section 4.2.3) does not always reflect the coastal setting: whereas some of the shoreline wells are classed as belonging to the coastal plain unit, others have designations reflecting the influence of glaciation e.g. drumlin and ribbed moraine topography for St Denis's well near Clogher in Co Louth and St Finian's well Kenmare, Co Kerry.

The wells described in this section are: Shaver's well Tullaghan, Co Leitrim, St Colman's well Salterstown, Co Louth, St Brendan's well Roskeen Mayo and St Begnet's well Dalkey Island, Co Dublin. The latter is the only shoreline holy well surveyed which is located on an island (another island well, on Gorumna Island in Co Galway – described in Section 5.5.2 - is close to the shoreline of a lake rather than the sea).

### 5.10.1 Shaver's well Tullaghan, Co Leitrim

This is one of two holy wells surveyed along the narrow coastal strip of Leitrim, the other being nearby St Patrick's well. Located off a minor road to Tullaghan, Shaver's well is accessed through a gate and by a grassy track through a pasture field towards the coast, passing St Patrick's well on the way. Shaver's well is less than 50 m from the shoreline, and has an elevation of less than 10 m OD. (It is therefore somewhat further from the shoreline than the other wells described in this section, but can still be considered a low-lying coastal well). According to a web blog posted

by local historian Joe McGowan in 2011[25], shaver's well got its name because St Patrick and his followers shaved here.

Like the nearby St Patrick's well, Shaver's well comprises a large oval cairn of rocks that has a small well in an opening at one side (Figure 5.59). The well measures approximately 0.7 m from front to back and 0.4 m in width. It contained 0.55 m of water when visited in August 2017, and 0.46 m of water in May 2018; during the 2018 visit, when the water level was lower, a plastic pipe was observed in the well, which drains towards a ditch and to the sea. Above one side of the cairn, there is a statue of St Patrick inside a shrine set on a concrete base.



a)



b)

Figure 5.59 Shaver's well Tullaghan, Co Leitrim: a) the stone cairn surrounding the well, with the sea in the background; b) the well, with a flat sandstone 'capstone' across its top. Photos by Bruce Misstear

Bedrock of sandstones, siltstones and shales of the Dinantian Mullaghmore Sandstone Formation (Dinantian Sandstones in the GRUG) outcrops in the vicinity of the well, notably along the shore. The Mullaghmore Sandstone Formation is overlain by the Benbulben Shales to the south (which are then in faulted contact with older Bundoran Shales), and is underlain by the Bundoran Shale Formation to the northeast (around Bundoran). The beds along the beach appear to dip gently to the south.

The Mullaghmore Sandstone Formation is classed as a locally important aquifer (Lm). An X Extreme vulnerability rating indicates that the overlying subsoils are less than 1 m thick at the well. It was observed that Shaver's well contained more water than St Patrick's well located 240 m further inland: this is consistent with the more coastal location of Shaver's well since, in

[25] http://www.irishcultureandcustoms.com/ACalend/StPatWell.html; accessed 5/2/2020)

general, groundwater levels tend to be both shallower and have smaller fluctuations near the shoreline than water levels in wells further inland.

### 5.10.2 St Colman's well Salterstown, Co Louth

The well is located along the shoreline between Annagassan and Dunany Point (about 3 km east of Annagassan). The well is shown on the historical 25 inch map, but it is not marked on the 19th century 6 inch map. Conlon (2000) refers to the well by the name of Toberhullamag (the name marked on the 25 inch map), although he points out that there has been confusion locally regarding to whom the well is dedicated. The well has a reputation for curing sore eyes: Conlon (2000) says that this may be linked to its use for bathing sore eyes by miners from the former copper and lead mines nearby.

The well consists of a small shallow, rectangular depression (0.25 x 0.2 m) in beach gravel, with a stone plaque dedicated to St Colman at its rear (Figure 5.60). The well had a maximum depth of only 4 cm of water when first visited by this researcher on 9/3/2017 but, by the time of return visits two years later (9/4/2019 and 11/6/2019), the well had been deepened to about 0.3 m by removing some of the beach gravel and placing a boulder of weathered concrete to create a rim on its north (seawards) side. However, a year later (10/3/2020), the boulder had been removed and the well was again only a few cm deep.



a) b) c)

Figure 5.60 St Colman's well Salterstown, Co Louth: a) the small beach well with the stone plaque behind (note the compass clinometer for scale); b) view inland, with the well on the left of this cleft (the cleft may represent a fracture zone); c) the broken rock forming the transition zone (in the embankment opposite the well). Photos by Bruce Misstear

The well is perhaps 3 m below the level of the nearby road, and only about 1 m above the normal high tide level; in April 2019, there was some sea weed in the well and around it, and the water was much more brackish (see below), suggesting that the well had been inundated during a recent spring tide. On the bank above the well there is an old rusted iron plaque where the name of St Colman is still just about visible.

The superficial deposits in the embankment behind the well comprise Glacio-marine sediments, including beach sands and gravels (the physiographic unit is hummocky glaciofluvial sediments topography), but there is rock outcrop along the beach below the well. The exposures are of hard sandstones and mudstones belonging to the Silurian Salterstown Formation. The metasediments strike at about 60$^{o}$ northeast and dip steeply (again 60$^{o}$) northwest near the well, but the strike and dip of the metasediments vary.

With thin subsoils and rock outcrop at the site, this spring issues from the thin transition zone observed in the embankment near the well (see Figure 5.60c), and its location could also be influenced by faulting (the path down to the well from the road probably coincides with a fracture zone – see Figure 5.60b). The EC of the well water is somewhat elevated (e.g. 715 µS cm$^{-1}$ on 9/3/2017; and 1500 µS cm$^{-1}$ after a spring tide on 9/4/2019), but it does indicate fresh groundwater as opposed to seawater (or surface runoff). It is likely that the well becomes inundated by seawater at spring tides and during storms. A notable feature of the water chemistry is the exceptionally high nitrate: a sample collected in April 2019 gave a nitrate value of 81.5 mg l$^{-1}$ (as N, or 361 mg l$^{-1}$ as $NO_3$), whilst a 2017 sample, collected when the water was less brackish, gave a less elevated nitrate value of 19.3 mg l$^{-1}$ (as N). These results are discussed further in Section 7.5.2.

### 5.10.3 St Brendan's well Roskeen, Co Mayo

St Brendan was born in the 6$^{th}$ century CE at Fenit in Co Kerry, and gained fame as a navigator. The well is beside Roskeen graveyard (where there is a statue of St Brendan). This shoreline well is surrounded by a dry stone wall. There are crude, shallow stone steps leading down to the well, which measures 0.9 m from front to rear and is about 1 m wide (Figure 5.61). The well contained 0.43 m of water at time of visit in May 2018. The well is at or close to the high tide mark. A small river (with fresh water) enters the sea close to the well. There is a stone altar (leacht) beside the well, with a sign beside it indicating the prayers to be said at the well.



a)



b)

Figure 5.61 St Brendan's well Roskeen, Co Mayo: a) looking from the well towards the stream (which discharges through twin culverts beneath the road); b) the well is in front of the stone altar (leacht). The (fresh water) stream is in the foreground, with the graveyard behind. Photos by Bruce Misstear

The bedrock geology consists of dark limestone and calcareous shale belonging to the Rockfleet Bay Limestone Formation (Dinantian pure bedded limestones). The beds dip at 10 to 15 degrees to the SSW; the Rockfleet Bay Limestone Formation overlies sandstones and siltstones of the Capnagower Formation – the contact is a short distance north of the well. There are limestone boulders in the dry stone wall around the well. The superficial deposits comprise tills derived from Devonian and Carboniferous sandstones; a Moderate vulnerability rating suggests these are at least 5 m thick. As the well is close to the contact between the Rockfleet Bay limestone and shales (a locally important karstified, Lk, aquifer), with the underlying sandstones and siltstones of the Capnagower Formation (Lm aquifer), the well may represent a contact spring (Figure 5.62).

This was the only well encountered in the surveys that contained salt water (see Section 7.5.5). The well is clearly inundated by the sea at high tides: the well water EC of about 61,150 µS $cm^{-1}$ (measured, after dilution, in the lab) is similar to that of sea water, in contrast to the fresh water in the stream that enters the sea beside the well (where the EC was measured as 540 µS $cm^{-1}$ in May 2018).

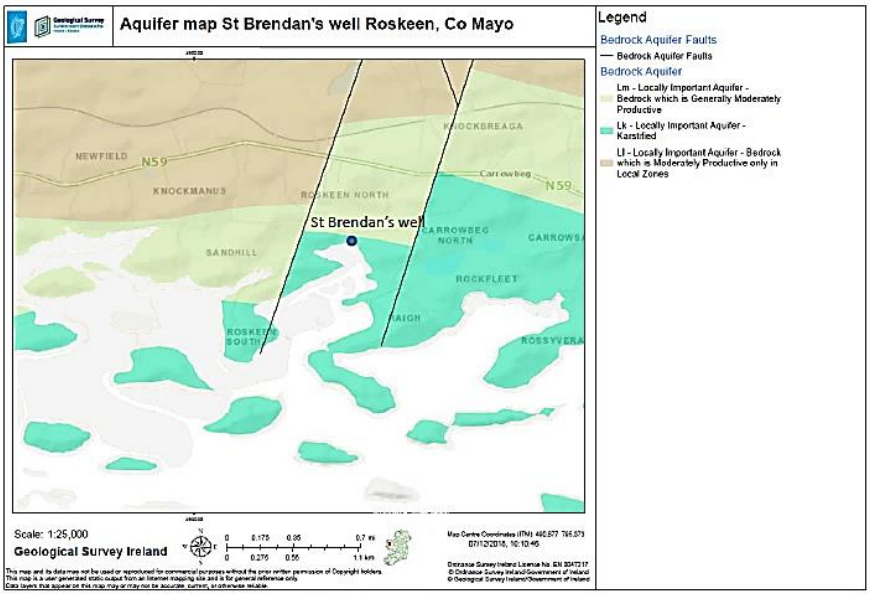



Figure 5.62 Aquifer map for St Brendan's well Roskeen Co Mayo; the well is close to the contact between the Lk limestone and Lm sandstone aquifers. (Map prepared using GSI Groundwater Data Viewer)

### 5.10.4 St Begnet's well Dalkey Island, Co Dublin

Dalkey Island is located a few hundred metres offshore from the town of Dalkey, Co Dublin. The 7th century St Begnet is the patron saint of Dalkey, and she reputedly baptised pilgrims at the well on the island[26]. St Begnet's well is referred to as the Scurvy well on the 19th century 6 inch OSI map. It presumably supplied the garrison of the Martello tower and gun battery during the 19th century and, before then, the monks of the 10th century church nearby. Indeed, Mesolithic and Neolithic remains have been found on the island, so the well may have a very long history. It now provides a source of water for the island's goats. It is reportedly the only well on the island nowadays, although Branigan (2012) noted that 'some believe there were two separate wells…..one called St Begnet's Well and one called Scurvy Well'.

The whitewashed well structure (Figure 5.63) is clearly visible from the sea when approaching the island by boat, but less visible from the island itself. The well is along the shoreline south of the boat landing strip, and it is accessible by a narrow grassy path. The rectangular well is inside a whitewashed stone well building, most of which looks modern (there is some older stonework on the left [north] side of the well). There is an old rusty hinge at the well entrance, indicating

[26] http://irelandsholywells.blogspot.ie/2011/08/saint-begnets-well-dalkey-island.html; accessed 5/2/2020)

that there was once a door or grill (this writer vaguely recalls an iron gate, from the time he first visited the island in the 1970s). The well measures 0.56 m from front to back, and is 0.65 m wide. It contained a maximum depth of 0.13 m of water (although its base was uneven) in August 2017. The well is located about 2 m or so above the high tide mark (Figure 5.63a). The well overflows through an old iron pipe, but this was not flowing at the time of visit in August 2017.



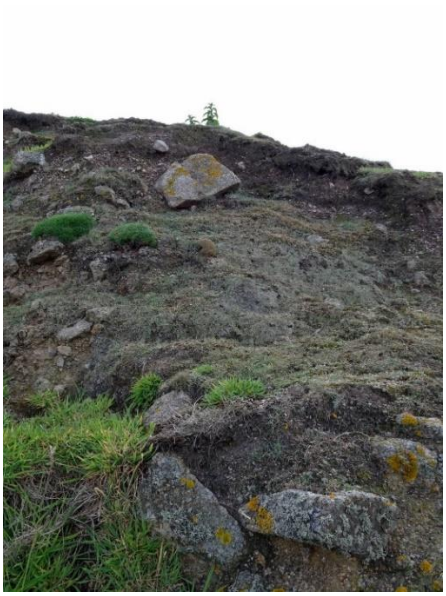
a)



b)



c)



d)

Figure 5.63 St Begnet's well Dalkey Island, Co Dublin: a) the well appears to be at the base of a transition zone, above massive granite outcrop; b) the entrance to St Begnet's well; c) the overflow pipe is just visible below the white-washed well structure; d) the embankment above the well, which appears to be a transition zone between subsoil and shallow bedrock. Photos by Bruce Misstear

The well is on granite outcrop covered by broken blocks of granite in a weathered rock and subsoil matrix – probably representing the transition zone (Figure 5.63a and 5.63d). There are

several joint sets visible in the granite outcrop: major sub-vertical joints trend at 320° NW and 45° NE. The island has the asymmetrical shape of a Rôche Moutonnée, with a gentle slope rising from the north, in the direction of the ice transport. The transition zone is the likely source of groundwater for this well, with recharge via the thin overlying till. Given its usage in historic times for e.g. supplying the fort and Martello tower garrison, the flow is probably quite reliable. The water quality (at least from the chemical viewpoint) must also remain potable. The EC of the water in August 2017 was 589 µS $cm^{-1}$: although this is somewhat elevated compared to granite wells in non-coastal settings (see Chapter 7.5), it does represent fresh groundwater.

## 5.11 Spa wells

Five spa wells at four former spa sites were sampled during the research, primarily to compare the water quality of these wells with that of holy wells, since both types of wells are often associated with health cures. The four spa sites visited were Lisdoonvarna (Co Clare); Drumod spa Swanlinbar (Co Cavan), Louisa Bridge (Leixlip, Co Kildare) and Mallow (Co Cork); see Figure 5.64. The hydrogeology of these sites is described here, whilst the groundwater quality results are discussed in Section 7.8.

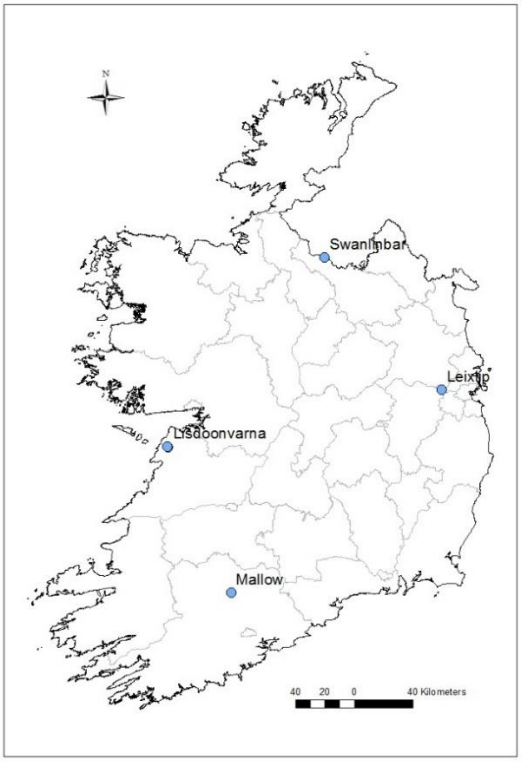



Figure 5.64 Location of spa towns where spa wells were surveyed

### 5.11.1 Lisdoonvarna spa wells, Co Clare

Lisdoonvarna developed as a spa town in the middle of the 19th century, and reached its peak popularity in the period from the 1880s to the 1920s (Foley, 2010). The first pump room was built in 1867 and baths were added in 1875; a new pump room was constructed in 1892 and the current bath house was built in the 1930s and 1940s. The Sulphur well in the pump room is still operational and the spa centre is open for visitors during summer months.

The main spa centre is on the south side of the town, at the junction of the R476 and the R478 and at the confluence of the Gowlaun and Aille rivers (Figure 5.65). There were originally six spa wells in Lisdoonvarna, of which the Sulphur well at the main spa centre is the only one in use. This Sulphur well source dates from the 18th century and the well is located inside the pump room (Figure 5.66a and Figure 5.66b). It is approximately 0.6 m in diameter and lined with brick. It is covered with a glass see-through top, and the interior of the well is lit. The well is reportedly about 3 m deep, with silt at its base. The water level appeared to be about 2 m below the floor of the pump room in August 2018. There is a tap in the pump room; the spa site also includes a bath house (fed from this well) and a visitor centre containing an exhibition about the history of the spa and of the town more generally.




Figure 5.65 OSI Digital Globe image showing locations of the extant spa wells in Lisdoonvarna



a)



b)



c)



d)



e)



f)

Figure 5.66 Lisdoonvarna spa wells, Co Clare: a) the spa centre, with the pump room to the right, the bath house behind, and the Gowlaun River in the foreground; b) the Sulphur well inside the Pump room; c) the old pump house near the Double wells, which is now a library (note the two external taps in the alcoves on the tower like entrance to the building); d) the Double well closest to the pump house: iron staining was visible on the ground near the well, so this may be the chalybeate well; e) the 'Twin wells': the sulphur 'well' to the left (note the white precipitate) and the iron 'well' to the right (with the ochre deposit); these two seepages are only 0.6 m apart and appear to issue from beneath the same hard bed; f) outcrop of highly weathered shales alongside the path leading to the Twin wells. Photos by Bruce Misstear

The so-called Double wells are located on the left bank of the Kilmoon river, just upstream of where it crosses below the R67 (Figure 5.65). The old pump house here is now used as a library (Figure 5.66c). The two wells are 30 m apart and are inside stone arched well buildings with iron gates that were locked at the times when visited and therefore inaccessible (Figure 5.66d). Both wells have wooden covers. The well houses were partly overgrown and there was no sign of recent activity. There are two outside taps in alcoves on the exterior wall of the library (i.e. the old pump house); these are presumably fed by the two wells, but neither was working. The Double wells are known as the magnesia and chalybeate (i.e. iron) wells; iron staining was visible around the well closest to the library, so this is likely the chalybeate well, whilst that beside the road is probably the magnesia well.

The Twin wells (known for sulphur and iron) are located about half a km downstream of the main town, near the confluence of the Killoon Stream with the Aille River (the wells are about 5 m from the right bank of the Aille River), at the west end of Town Park (Figure 5.65). The Twin wells are, in fact, two small seepages from rock outcrop (Figure 5.66e), about 0.6 m apart, one of which (with the larger 'flow') collects in a small circular 'well', 0.2 to 0.3 m in diameter, which was covered by leaves and a white precipitate (probably calcium sulphate). The seepage to its right (really just an intermittent dripping) has given rise to an ochre deposit, after which the water trickles towards the first 'well' (the presence of a distinct 'twin well', below the iron-rich seepage was not evident). The rock face with the seepages is covered by a concrete shelter and by a wooden railing making access for sampling difficult. Both the sulphur-rich and the iron-rich seepages seem to originate from below the same hard bed (which occurs within a mainly shale sequence). This hard bed looks like a sandstone and is probably part of the hard, compact Phosphate Shale referred to in the geology description below.

In addition to the main Sulphur well, the Double wells and the Twin wells, there was formerly also a copper-rich (copperas) well behind Tivoli terrace, on the west side of the main street, but this is reportedly covered over. Only the Double wells are shown on the historical 6 inch map. However, the Pump house containing the Sulphur well plus the Twin wells are included on the 25 inch historical map.

The main Sulphur well and the Twin wells (sulphur and iron) were considered effective against gout, rheumatism, consumption and liver problems (Foley, 2010). The magnesia and iron-rich

Double wells were used 'as blood tonics and for weak stomachs', whilst the copperas well was used for treating diseases.

The geology and hydrogeology of the Lisdoonvarna Spa wells has been described by Drew (2001). The town lies on the Namurian Clare Shale Formation, comprising shale, sandstone and siltstone beds with a total thickness of about 20 m. The Clare Shales have been dissected by the rivers that run through the town (the Gowlaun, Aille and Killoon Rivers), and beds of the underlying Visean Burren Limestone Formation are exposed along the river beds. According to Drew's account, the bedrock geological sequence in Lisdoonvarna, from youngest to oldest, consists of: a) ribbed beds of sandy black shales; b) Goniatite Shale (8-14 m of black shale); c) Phosphate Shale (0-3 m of hard dark grey black shale with calcite and dolomite); d) Cahermacon Shale (0-3.5 m of black shale with phosphate and pyrites – where this latter unit is absent, the Phosphate Shale lies directly on the Burren Limestone. Soft, highly weathered shale outcrops can be seen along the access path down to the Twin wells (Figure 5.66f).

On the bedrock geology map, the sediments along the river valley are described as cyclical crinoidal limestones belonging to the Lissylisheen Member of the Slievenaglasha Formation, which has a thickness of 4 m. These Dinantian beds pass up into Namurian mudstones belonging to the Clare Shale Formation (12-15 m thick). The beds dip gently to the south. To the south of the town (just south of the Sulphur well) the geology map shows siltstones and sandstones of the Namurian Gull Island Formation (Figure 5.67). The Slievenaglasha beds are included in the Dinantian pure bedded limestones GRUG, whilst the overlying Clare Shales are classed as Namurian shales; the Gull Island rocks are classed as Namurian sandstones.

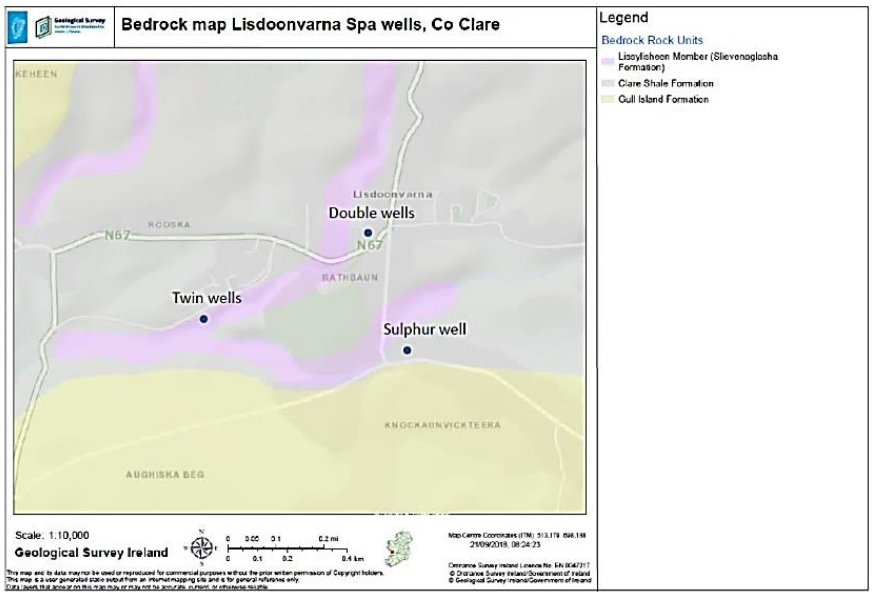



Figure 5.67 Bedrock geology map of Lisdoonvarna showing the spa wells. (Map prepared using GSI Groundwater Data Viewer)

The springs and seeps that give rise to the various spa waters issue from near the base of the Clare Shales, especially at the hard Phosphate Shale bed (Drew, 2001). Drew reported that the outflows from each of the wells are modest: 400 L hour$^{-1}$ (Sulphur well); 80 L hour$^{-1}$ (chalybeate well of the Double wells); 40 L hour$^{-1}$ (magnesia well). The flows from the Twin wells, as mentioned above, and observed by this author, only amount to a very small trickle. With such small outflows, Drew does not infer a recharge source area beyond the shales formation (Drew, *pers comm*, 2018), as has been speculated elsewhere, where the water origin is given as the limestones of Slieve Elva, north of Lisdoonvarna[27]. The Clare Shales are classed as a Pu aquifer.

Regarding the water chemistry, Drew (2001) noted that the none of the springs is highly mineralised, but rather show elevated concentrations of particular parameters such as iron (4.5 and 3.0 mg L$^{-1}$ in the chalybeate and magnesia wells, respectively), sulphate (150 mg L$^{-1}$ in the chalybeate well) and total hardness (344 and 300 mg L$^{-1}$ [as $CaCO_3$?] in the chalybeate and magnesia wells, respectively). He also noted that the Sulphur well has low TDS (but does not quote a figure), consistent with the EC measurement made by the current author (527 µS cm$^{-1}$), which is typical of Irish groundwaters and does not indicate a high degree of mineralisation. The hydrochemistry of these wells is discussed in more detail in Section 6.4.1 and Section 7.8.

[27] http://www.burrengeopark.ie/discover-and-experience/geosites-discovery-points/lisdoonvarna-spa-wells/; accessed 5/2/2020)

A curious feature about the Sulphur well water is that the tap and water are hot at the beginning of pumping each day. The water was certainly hot for the first few seconds after the electric pump was switched on during this researcher's visit in August 2018, and then cooled rapidly to a normal groundwater temperature. It is not clear whether this is due to some exothermic biogeochemical reaction leading to a build-up of heat overnight, or perhaps it is related to the type of pump and pumping arrangement (the details of which were not available). An issue with the pump is considered the more likely explanation.

### 5.11.2 Drumod spa well Swanlinbar, Co Cavan

Drumod is one of several spa wells that once existed in the Swanlinbar area. The Drumod spa well (signposted as 'Drumod Sulphur Spa') is accessed from a minor road 1 km southeast of Swanlinbar. There is a smell of sulphur (hydrogen sulphide) as one approaches the well. The well is inside a whitewashed stone well house close to a small stream (0.3 m wide), which runs from the road to the Swanlinbar River valley to the northwest. The landscape is characterised by drumlins (the physiographic unit is drumlin and ribbed moraine topography).

The near cubic-shaped well house is 1.2 m wide, 1.25 m high and 1.4 m from front to rear. The well is circular, with a diameter of 0.78 m (Figure 5.68). It has an uneven concrete base and contained between 0.5 and 0.6 m of water at time of visit in January 2018. There is a sign near the well advising people not to use the water as it is 'not fit for consumption'. The well water was used to treat rheumatism (according to the signboard at the well); Foley (2010) also reports that the well had a reputation for curing other ailments such as dysentery, leprosy and gout.





a) b)

Figure 5.68 Drumod Spa well Swanlinbar, Co Cavan: a) the well and adjacent stream; b) the circular concrete-lined well. Photos by Bruce Misstear

The well is in the Dartry Limestone Formation (Dinantian pure bedded limestone GRUG). The well is close to the contact between underlying mudbank limestones to the west (Dinantian pure unbedded limestones) - which in turn are underlain by the Drumgesh Shale Formation - with the overlying Meenymore Formation to the east. These rocks, which dip to the east, are in faulted contact with sandstones of the Glenade Sandstone Formation further east, and with the Benbulben Shale Formation to the north (Dinantian shales and limestones; see Figure 5.69).

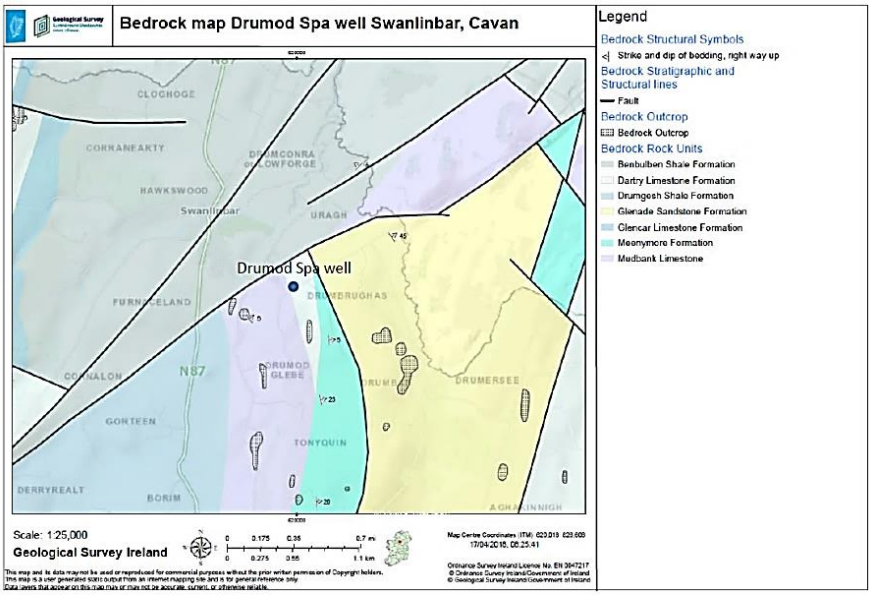



Figure 5.69 Bedrock map for Drumod Spa well Swanlinbar, Co Cavan. (Map prepared using GSI Groundwater Data Viewer)

A signboard at the site refers to the local hydrogeology and includes a sketch geological section. Drumod Spa well is also described in a GSI heritage report that describes the site as 'a small natural spring….that has been enclosed by a walled structure' (Parkes *et al*., 2013b). The report goes on to describe the hydrogeological setting, which is a Lower Carboniferous Limestone aquifer where the water is brought to the surface by contact with 'impermeable' shales i.e. a contact spring. From the geology map, the aquifer appears to be the pure limestone of the Dartry Formation; the 'impermeable shales' may belong to the underlying Drumgesh Shale Formation (see Figure 5.69). The Dartry limestones (and the mudbank limestone) are classed as a regionally important karstic aquifer with conduit flow (Rkc).

Buckley visited and sampled this well during his Masters project in 2012. He referred to the well as being stagnant, without 'a natural flushing system'. He also noted that the well was about 1.5

m deep, much deeper that the measurement by the current researcher, suggesting that the base of the well has been concreted over in the past few years.

During the visit on 31/1/2018, a white precipitate was visible where water flowed over the lip at the well entrance (Figure 5.68a): it is not clear whether this is a chemical precipitate from the well water, or just some of the whitewash from the sides of the well house.

Unsurprisingly, the water quality of the well water is very different to that of the adjacent stream (e.g. EC of 1288 and 145 µS $cm^{-1}$ for the well water and stream, respectively).

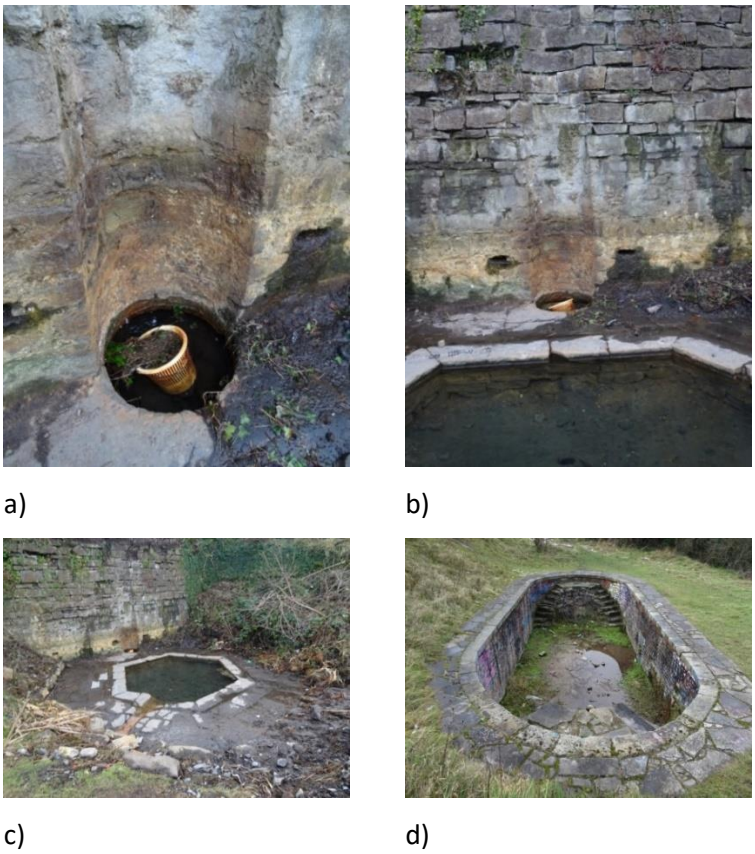
### 5.11.3 Louisa Bridge spa well, Co Kildare

The well is on the west side of the Royal Canal, opposite Louisa Bridge railway station in Leixlip, and accessed by the canal towpath that runs north of the R148. This thermal well is built into the side of the canal embankment wall. Apparently, the warm spring was discovered on the opposite (east) side of the canal during the original canal works in the 1790s, but the spring was moved to its present location at that time and used for the development of Leixlip Spa.

The well is now a small circular basin (0.6 m diameter) at the side of the embankment wall (Figure 5.70). Gas bubbles can be seen rising into this well every few seconds. The well (or cistern as it is referred to on one of the local signboards) feeds into an adjacent hexangular basin (each side is 1.75 m long; and the hexagon width = c. 3 m), which contained between 0.5 and 0.6 m of water when visited in January 2018. Iron staining was visible in both the well and basin. The basin then overflows through a shallow channel cut into the surrounding stonework; the flow rate in January 2018 was probably of the order of 1 l $s^{-1}$.

The outflow from the basin formerly fed into the Romanesque style bath that was built downslope to the north, about 130 m away (Figure 5.70d). When visited in January 2018 there was only a trickle of water entering the bath, so the majority of the flow was bypassing it along an open stream channel, between the canal and the bath. This former spa is now a heritage feature (albeit it contained some rubbish and lacked any protective railings). The brick-lined bath is about 8 to 9 m in length (with semi-circular ends) and 3 to 4 m in width; it has a depth of 1.9 m from the paved surround (granite and limestone paving stones), and contained only

puddles of muddy water. There is an outlet (covered by a grill) in the side wall at its base, which allows water to overflow (through a penstock) to the Rye Water valley to the north-northeast.



a) b)

c) d)

Figure 5.70 Louisa Bridge Spa well Leixlip, Co Kildare: a) the well (referred to as a cistern on one of the signboards nearby): note how the wall of the embankment has been moulded to accommodate this circular well; b) the well discharges into the hexagonal basin in the foreground; c) the outlet from the hexagonal basin can be seen as the small iron-stained channel cut into the stone surround; d) the Romanesque bath that was formerly supplied from the basin outflow. Photos by Bruce Misstear

The thermal spring at Louisa Bridge was one of six warm springs in Leinster monitored by Blake (2016) as part of her PhD research on Irish thermal springs (another of the thermal wells studied was St Gorman's well at Enfield, see Section 5.9.3). She describes the geological setting at Louisa Bridge as comprising gravel deposits overlying limestones of the Lucan Formation. She notes that the thermal springs in Leinster are frequently associated with deep-seated, high angle faults.

During Blake's monitoring period (five sampling rounds in 2013 and 2014), water temperature varied between 17.5 and 13.9 °C (this author's measurement of 15.6 °C in 2018 falls within this range); the maximum EC was 1644 µS $cm^{-1}$ (less than the 2018 measurement of 1880 µS $cm^{-1}$); and the pH range was 6.95–7.77 (the pH measured in January 2018 was slightly below Blake's minimum value). A Wikipedia entry for Leixlip Spa mentions that waters 'bubble from the ground at a constant 23.9 degrees Celsius..'[28], warmer than the contemporary temperature measurements which probably reflect some influence from leakage of cool canal water from above (see Sections 6.4.2 and 7.8).

### 5.11.4 Lady's well Mallow, Co Cork

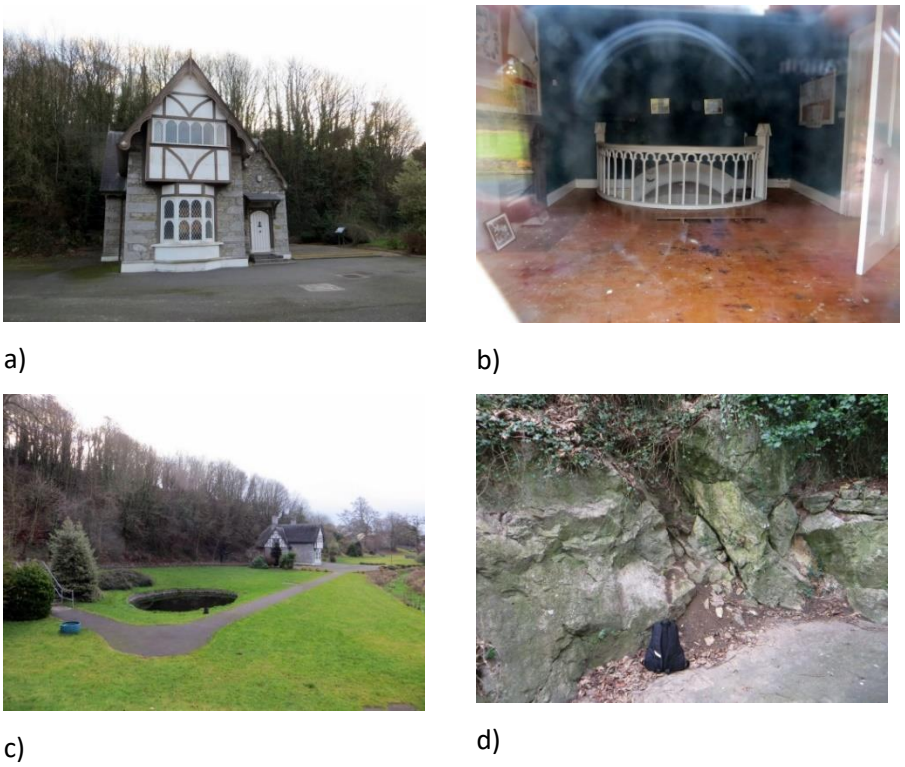
Mallow Spa enjoyed its maximum popularity during the mid-18th century, but its popularity declined later that century and the spa ceased operation by the mid-19th century (Aldwell, 1996). The Spa House was built in 1828, and is located in an area known as Spa Glen on the east side of Mallow, beside the N72. A sign says this old Spa House is now Cork County Council offices (an energy advice centre), but there was no evidence of occupation when visited on 31/12/2016 and 11/1/2017. The old well is located inside the (locked) Spa House. The signboard beside the building discusses the history of the spa, and mentions that a Dr Rogers in the early 18th century reported that a patient found the water from the holy well to possess curative powers. Rutty (1757; see Aldwell, 1996) reported that the warm springs at Mallow were associated with a variety of cures, including respiratory problems, stomach ailments and skin diseases.

There is a pond about 30 m north of the Spa House where warm water can be seen bubbling to the surface (Figure 5.71). The pond is oval shaped (approximately 10 x 5 m), and has a depth of about 0.5 of water. It overflows into the nearby drainage channel between the Spa House and the main road. A local man mentioned to this author that he was involved in the construction of the pond for bathing when he was a boy, and that it always had warm water. Aldwell (1996) reported that one of the springs was made into a children's swimming pool in the 1960s, which ties in with this man's recollection. A photo in Aldwell's paper shows this to be Lady's Well. The old 19th century 6 inch OS map also indicates Lady's well to be at this location.

Lady's well and the Spa House are at the foot of an escarpment on the side of a flat-bottomed valley that runs north-south towards the River Blackwater. The GSI map shows the well site to

[28] https://en.wikipedia.org/wiki/Leixlip_Spa; accessed 5/2/2020)

be located on a slice of Namurian undifferentiated sediments, close to the faulted contact with Dinantian pure unbedded limestones (Hazelwood Limestone Formation) to the north, and the thrust fault contact with DPUL (Waulsortian limestones) to the south (Figure 5.72). Outcrop of massive blocky grey limestone is visible in the cliff face behind the Spa House (Figure 5.71d). The beds dip to the south at 40-60$^{o}$ (variable dip).



a) b)

c) d)

Figure 5.71 Spa well Mallow, Co Cork: a) the Spa House, which dates from 1828; b) the old spa well inside the Spa House; c) the pond at the site of Lady's well, with the Spa House in the background; d) outcrop of reef limestone in the cliff face behind Spa House. Photos by Bruce Misstear

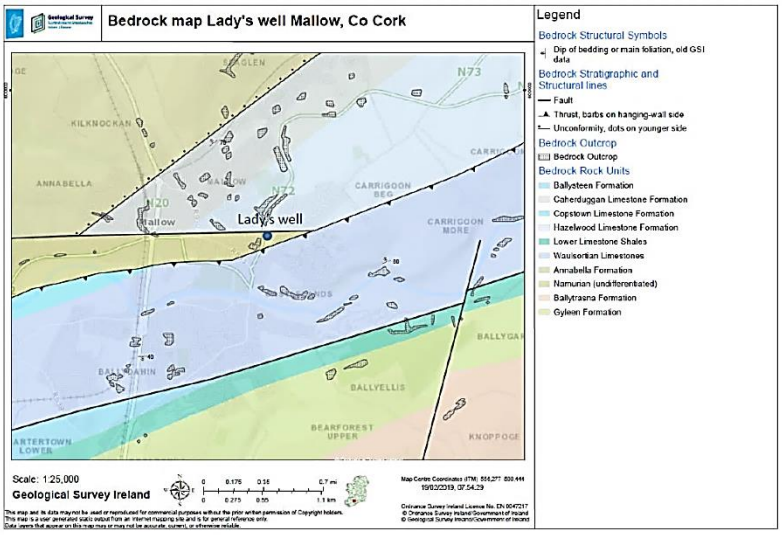



Figure 5.72 Bedrock geology map at Lady's well Mallow, Co Cork. (Map prepared using GSI Groundwater Data Viewer)

The source of the water is believed to be Dinantian Reef Limestone, from a probable depth of over 1000 m - see cross section from Brück *et al*. (1986) reproduced in Figure 5.73. Goodman *et al*. (2004) reported that the warm springs in Mallow 'lie along an east northeast trending Killarney-Mallow thrust fault'. It is believed this deep fault allows rapid upflow of warm water.

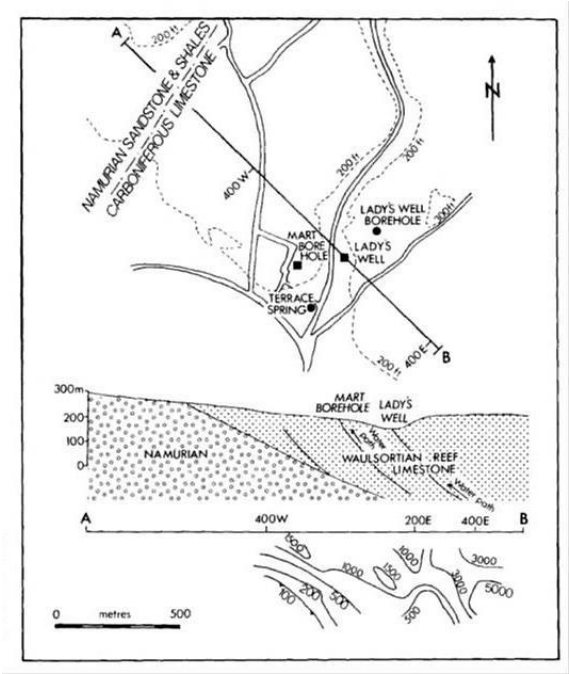



Figure 5.73 Sketch geological cross section at Lady's well Mallow (from Brück *et al*., 1986); the resistivity contours (in ohm m) from an electrical resistivity (dipole-dipole) survey are shown at the bottom of the figure

Brück *et al*. (1986) monitored the chemistry of the spring waters in the early 1980s: for Lady's well, the mean EC was 466 µS $cm^{-1}$, temperature 19.5 $^{o}$C (with seasonal variations from 17 to 22 $^{o}$C) and pH 7.34 (the values measured by the current research on 11/1/2017 were 478 µS $cm^{-1}$, 18.1 $^{o}$C and 7.16, respectively, in line with the earlier figures). The mean flow from Lady's well in the early 1980s was 616 L $min^{-1}$ (about 10.3 l $s^{-1}$). The GSI Groundwater Viewer reports this spring as having a yield of 140 $m^3$ $d^{-1}$ (see also Sections 6.4.2 and 7.8).

### 5.11.5 Classification of spa wells

As discussed in Section 3.1, Mather (2013) classified the heritage spas in Britain into three groups: 1) those spa locations strongly influenced by distinctive hydrogeological conditions at that site; 2) spa locations that have less distinctive hydrogeology, but rather owe their origins to factors such as local entrepreneurial initiatives or chance; and 3) spa locations that owe their origins to human interference with groundwater flow systems through mining or mineral exploration. Mather noted that the second grouping is the largest in Britain, encompassing many different water types, including chalybeate springs. In Ireland, the wells in Lisdoonvarna and Swanlinbar fall within this second group. Lady's well in Mallow, with its deep thermal groundwater source, could possibly be assigned to the first group, although it does not show the highly mineralised waters Mather associates with this category. The spa well at Louisa Bridge in Co Kildare owes its origins to canal construction works in the 1790s and so best falls into Mather's third grouping.

## 5.12 Concluding remarks

Whilst it was obviously not possible to describe all 215 of the holy wells that were investigated during this research, this chapter has attempted to provide a flavour of the range and diversity of their hydrogeological settings by including descriptions of 33 holy wells according to their main lithological groupings: impure limestones (six wells); pure limestones (nine wells); non-calcareous sediments (five wells described in detail, but a further four wells also discussed briefly); igneous (three wells); metamorphic (four wells); sands and gravels (five wells); and mixed bedrock and sand and gravels (one well). In addition, a further seven holy wells were described according to the aquifer condition (confined aquifer, three wells) or coastal setting (four wells), as these aspects can be important in influencing groundwater chemistry, as we will

be discussed in Chapter 7. The final section (5.11) included accounts of the five spa wells surveyed and sampled.

The well descriptions confirm that most of the holy wells surveyed are small shallow, spring wells. Outflows, where observed, were generally small (less than 0.5 l $s^{-1}$ and probably less than 0.1 l $s^{-1}$ in many cases). Exceptions include the large karst springs at Ogulla well in Roscommon and Tobernalt in Sligo, where flows of 10s of l $s^{-1}$ have been recorded. As described previously in Section 4.2.8, water depths were usually less than 0.7 m, and averaged 0.34 m.

A feature common to many of the holy well sites is the likely important role of the transition zone as a groundwater source. The transition zone between the base of the subsoil and upper fractured bedrock (see Section 3.2) can be present in a variety of lithologies, including carbonate and non-carbonate sedimentary rocks, and in igneous and metamorphic bedrock. Examples referred to in this chapter include: St Colmcille's well at Disert in Co Donegal (where the bedrock is non-calcareous sedimentary; see Section 5.4.3.1); St Moling's well at St Mullins in Carlow (igneous bedrock; Section 5.5.1); and St Colman's well at Salterstown in Louth (metasedimentary bedrock; Section 5.10.2).

Being shallow springs, the aquifer condition at the majority of sites is assumed to be unconfined. Obvious exceptions include Bride's well in Calgath and St Gorman's well (both Co Meath), St Brigid's well at Shangarry (Limerick), and the spa wells in Swanlinbar (Cavan), Mallow (Cork) and Louisa Bridge (Kildare) where the groundwater source is a deep confined aquifer (Sections 5.9 and 5.11). However, there are probably also a number of cases where low permeability superficial deposits provide a local confining layer to the underlying bedrock aquifer: one such example is Shrone well in Co Kerry, described in Section 5.4.1.2.

The well site descriptions in this chapter are all based on visual inspections only, backed up by a review of maps, satellite images and existing literature. Whilst further insights into the hydrogeology of the well sites are available from the chemical analysis results in Chapter 7, a more detailed evaluation of the hydrogeology at many of the sites would require invasive investigations such as boreholes or trial pits. Such activities were outside the scope of this research. Moreover, obtaining permissions for drilling boreholes or digging trial pits would likely prove very challenging.

# 6 Groundwater chemistry

The main chemical constituents of groundwater and their relationship to human health are introduced in this chapter. The natural background levels established for various parameters in Irish groundwaters are then discussed, followed by a summary of previous studies concerned with particular parameters of health significance (e.g. arsenic and lithium), plus studies that include data on the hydrochemistry of Irish holy well or spa waters.

## 6.1 Chemical elements and human health

Before considering groundwater chemistry and its relationship to health, it is relevant to include a few introductory remarks about the composition of the human body and, in particular, those chemical elements that are regarded as being bioessential. Four elements – oxygen, carbon, hydrogen and nitrogen – make up 96 percent of the mass of the human body, whilst a further 3.8% of body mass is comprised of the following seven elements: sodium, potassium, calcium, magnesium, phosphorus, sulphur and chlorine (Lindh, 2005). In addition to these abundant elements, there are many elements present in trace amounts in the body that are known – or in some cases only suspected - to be essential for human health. The trace elements that are generally accepted as beneficial from a health perspective include: iron, manganese, copper, zinc, iodine, selenium, molybdenum, chromium, fluorine, cobalt, nickel and silicon. The literature varies concerning which other elements have beneficial properties, but lithium, boron, vanadium, barium, strontium, beryllium and even arsenic feature in various lists (Edmunds and Smedley, 1996; Lindh, 2005; Combs, 2005; Koller and Saleh, 2018). The means by which elements, either singly or as part of molecular combinations, contribute to human physiology are complex and varied, but examples include (Combs, 2005):

- calcium, phosphorus, magnesium and fluoride (fluorine in its ionic form) all contribute to bone and membrane structure;
- sodium, potassium and chloride ions contribute to water and electrolyte balance;
- zinc, copper, selenium, magnesium and molybdenum contribute to metabolic catalysis;
- iron is necessary for oxygen transport;
- iodine and chromium are involved in hormone production.

The largest daily intake of most of these elements is from food (Reimann and Birke, 2010; World Health Organization, 2011). For some elements, however, water consumption is important, including consumption of groundwater from wells and springs. This is especially the case where people have a nutrient-poor diet (Hoque and Butler, 2016).

As will be shown in the next section, whilst there are many elements that are essential for human development, some elements – including several that are bioessential – may also be harmful, especially at high dosages.

## 6.2 Groundwater chemistry and health

### 6.2.1 Introduction

Ninety-nine percent of the chemical composition of (uncontaminated) groundwater is usually made up of the major ions - calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride and nitrate – plus silica, and the remaining one percent comprises minor ions such as iron and manganese, together with a large variety of trace elements, many of which are important in terms of human health e.g. arsenic, chromium, selenium and uranium. Rainfall recharge provides the initial chemical inputs to groundwater systems. Rainfall is acidic, and contains elevated concentrations of chloride, sodium, magnesium, potassium and sulphate near the coast (Tierney, 1967; Jordan, 1997). Rainfall can also be a source of nitrate in some situations where the atmosphere contains nitrogen oxide pollutants. The evolution of groundwater chemistry is a function of a variety of water-rock interactions including dissolution, precipitation, redox reactions and ion exchange, together with any inputs from anthropogenic pollutants. Microbiological activity can be an important influence on the geochemical processes.

Young groundwaters close to recharge areas tend to be of calcium bicarbonate type whilst, further down the flow path, groundwater composition gradually evolves to a sodium bicarbonate type when the groundwater is more mature and ion exchange processes have occurred. Continued dissolution of minerals over long periods (often thousands of years) leads to saline groundwaters dominated by sodium chloride chemistry (Lloyd and Heathcote, 1985; Reimann and Birke, 2010; Hiscock and Bense, 2014). With increasing groundwater age, oxygen in the groundwater tends to be used up in biogeochemical reactions, so that more mature groundwaters tend to be anoxic, with low redox potential. In non-carbonate aquifers such as

granites and non-calcareous sandstones, the groundwater is often acidic, with pH values less than 7 and sometimes less than 6. In carbonate aquifers, on the other hand, the groundwater is buffered by the presence of carbonate minerals and pH values are often closer to 7 (as borne out by the results of this research, in which the mean pH values in the pure and impure limestone well waters are higher than those in the igneous, metamorphic and non-calcareous sandstone lithological groups – see Section 7.5.1). The pH and redox conditions are major controls on the solubility and mobility of ions and elements in water e.g. a decrease in pH of one unit may lead to a ten-fold increase in solubility of certain metals (Edmunds and Smedley, 1996). MacDonald *et al*. (2017) give a useful summary of the main factors influencing groundwater chemistry.

Table 6.1 summarises the elements and ionic species found in groundwater, including their typical concentration ranges. Following the example of Edmunds and Smedley (1996), an attempt has been made in the table to categorize the elements and ions based on their health significance. Three categories are distinguished here, and these form the basis for the discussion of the health significance of groundwater constituents in Sections 6.2.2 to 6.2.4 below. The categories are:

1) Elements or ions in groundwater that are essential or probably essential for human health.
2) Elements or ions in groundwater that are essential or probably essential for health, but which may be toxic or undesirable if present in high concentrations.
3) Elements or ions in groundwater harmful to health.

This categorisation is not always clear-cut. For example, arsenic is sometimes reported as being probably essential for human health (Edmunds and Smedley, 1996; Combs, 2005; Koller and Saleh, 2018), whereas the WHO (2011) states that arsenic 'has not been demonstrated to be essential to humans'. Given its high toxicity at low concentrations in drinking water, arsenic is placed here in category (3) rather than category (2). In contrast, chromium is widely recognised as being bioessential and so is included in category (2), yet (in its hexavalent form) Cr can be toxic (Calabrese *et al*., 1985; WHO, 2011; Lu *et al*., 2015).

Table 6.1 Elements and ionic species in groundwater. Based on Edmunds and Smedley (1996), also taking account of data in Lindh (2005), Combs (2005), World Health Organization (2005; 2011), Koller and Saleh (2018)

| Typical concentration ranges | Elements or ionic species |
|---|---|
| **Major elements/ionic species** | |
| >100 mg $l^{-1}$ | Bicarbonate ($HCO_3$) (note: 1 meq $l^{-1}$ alkalinity = 61 mg $l^{-1}$ bicarbonate) |
| 10-100 mg $l^{-1}$ | Sodium (Na), calcium (Ca), sulphate ($SO_4$), chloride (Cl), nitrate ($NO_3$) |
| 1-10 mg $l^{-1}$ | Magnesium (Mg), potassium (K), silicon (Si) |
| **Trace elements/ionic species** | |
| 0.1-1.0 mg $l^{-1}$ | Strontium (Sr), fluoride (F) |
| 0.01-0.1 mg $l^{-1}$ | Phosphorus (P), boron (B), bromide (Br), iron (Fe), zinc (Zn) |
| 0.001-0.01 mg $l^{-1}$ | Lithium (Li), barium (Ba), copper (Cu), manganese (Mn), uranium (U), iodine (I) |
| 0.0001-0.001 mg $l^{-1}$ | Rubidium (Rb), lanthanum (La), vanadium (V), selenium (Se), arsenic (As), cadmium (Cd), cobalt (Co), nickel (Ni), chromium (Cr), lead (Pb), aluminium (Al), yttrium (Y) |
| 0.00001-0.0001 mg $l^{-1}$ | Caesium (Cs), zircon (Zr), molybdenum (Mo), silver (Ag), beryllium (Be), thorium (Th), cerium (Ce) and the rare earth elements (REE), mercury (Hg), scandium (Sc), antimony (Sb), tin (Sn), tellurium (Te), thallium (Tl), bismuth (Bi), tungsten (W), gallium (Ga), germanium (Ge) |
| < 0.00001 mg $l^{-1}$ | Niobium (Nb), ruthenium (Ru), rhodium (Rh), palladium (Pd), indium (In), hafnium (Hf), tantalum (Ta), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), polonium (Po), gold (Au) |

Note: a) The concentration ranges given in the table are typical values for natural groundwaters, but much higher or lower concentrations can occur in certain situations.

b) Elements/ions marked in blue are considered essential or probably essential for human health; elements/ions marked in green are considered essential or probably essential for human health but may also be harmful or undesirable if present at high concentrations; elements/ions shown in red are harmful to health.

c) Elements/ions not highlighted in colour are considered non-bioessential elements.

The World Health Organization (WHO, 2011) drinking water guidelines are presented in Table 6.2, whilst the European Union drinking water and mineral water standards are summarised in Table 6.3.

Table 6.2 World Health Organization drinking water guidelines (WHO, 2011)

| Chemical | Guideline value (mg $l^{-1}$) | Remarks |
|---|---|---|
| Antimony | 0.02 | |
| Arsenic | 0.01 (A, T) | |
| Barium | 0.7 | |
| Boron | 2.4 (T) | |
| Cadmium | 0.003 | |
| Chromium | 0.05 (P) | For total chromium |
| Copper | 2 | |
| Fluoride | 1.5 | Volume of water consumed and intake from other sources should be considered when setting national standards |
| Lead | 0.01 (A, T) | |
| Mercury | 0.006 | For inorganic mercury |
| Nickel | 0.07 | |
| Nitrate | 50 | Short-term exposure |
| Nitrite | 3 | Short-term exposure |
| Selenium | 0.04 (P) | |
| Uranium | 0.03 (P) | Only chemical aspects of uranium addressed |

Notes: A, provisional guideline value because calculated guideline value is below the achievable quantification level; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

Only inorganic chemical parameters are included in Tables 6.2 and 6.3, as standards for organic chemicals or microbiological parameters are not relevant to this research (see Section 7.1.2 for a discussion of the choice of parameters analysed). It has also been pointed out by several authors (e.g. Hopps and Feder, 1986; Hoque and Butler, 2016) that these drinking water guidelines focus on the potential harmful effects of certain water quality parameters, whereas there are no international standards that cover the *positive* effects of substances essential for health (see Section 8.1.2).

The EU drinking water maximum admissible concentrations (MACs) are generally consistent with the WHO values, although the EU also sets guideline values for some parameters (e.g. chloride, iron) mainly on taste/appearance grounds rather than health.

Table 6.3 Selected European Union drinking water and mineral water standards (European Commission, 1998 and 2003)

| Chemical | EU Directive 98/83/EC Drinking Water | | Directive 2003/40/EC Mineral Water MAC (mg $l^{-1}$) |
|---|---|---|---|
| | MAC (mg $l^{-1}$) | Guideline value (mg $l^{-1}$) | |
| Aluminium | | 0.2 | |
| Ammonium | | 0.5 | |
| Antimony | 0.005 | | 0.005 |
| Arsenic | 0.01 | | 0.01 |
| Barium | | | 1 |
| Boron | 1 | | |
| Cadmium | 0.005 | | 0.003 |
| Chloride | | 250 | |
| Chromium | 0.05 | | 0.05 |
| Copper | 2 | | 1 |
| Cyanide | 0.05 | | 0.07 |
| Fluoride | 1.5 | | 5* |
| Iron | | 0.2 | |
| Lead | 0.01 | | 0.01 |
| Manganese | | 0.05 | 0.5 |
| Mercury | 0.001 | | 0.001 |
| Nickel | 0.02 | | 0.02 |
| Nitrate | 50 | | 50 |
| Nitrite | 0.5 | | 0.1 |
| Selenium | 0.01 | | 0.01 |
| Sodium | | 200 | |
| Sulphate | | 250 | |

Notes: *Natural mineral waters with F >1.5 mg $l^{-1}$ must state on the label 'contains more than 1.5 mg $l^{-1}$ fluoride: not suitable for regular consumption by infants and children under 5 years of age.'

With regard to Table 6.3, it is perhaps worth adding that a 'natural mineral water' is defined in EU Directive 2009/54/EC as a 'microbiologically wholesome water…… originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits' (European Commission, 2009). This definition suggests that any microbiologically wholesome water exploited by a borehole near a spring could be regarded as a mineral water.

Directive 2009/54/EC, which covers exploitation and marketing of natural mineral waters (European Commission, 2009), includes various stipulations regarding the use of terminology to describe the water content: the word 'contains' means that the concentration exceeds a stipulated value for a particular substance e.g. bicarbonate (>600 mg $l^{-1}$), sulphate (>200 mg $l^{-1}$), chloride (>200 mg $l^{-1}$), calcium (>150 mg $l^{-1}$), magnesium (>50 mg $l^{-1}$), fluoride (1 mg $l^{-1}$) and sodium (> 200 mg $l^{-1}$, although 'sodium suitable for a low sodium diet' should have Na <20 mg $l^{-1}$).

### 6.2.2 Elements and ions in groundwater essential or probably essential for health

The occurrence and characteristics of six of these parameters in groundwater (alkalinity, hardness, iodine, lithium, silicon and strontium) will be discussed briefly below.

*Alkalinity (bicarbonate $HCO_3$)*

Alkalinity is a measure of a water's ability to neutralise acid. In most groundwaters alkalinity is mainly due to the presence of bicarbonate ion, although at high pH values carbonate or even hydroxide ions may contribute. Alkalinity is usually reported as mg $l^{-1}$ $CaCO_3$ or in meq $l^{-1}$. The dissolution of calcite and (albeit more slowly) feldspar minerals releases $HCO_3$ into groundwater, and thus alkalinity can indicate the relative maturity of the groundwater. The presence of bicarbonate in drinking water is considered beneficial for the human cardiovascular system (Rylander, 2008). Reimann and Birke (2010) note that bicarbonate may also improve the taste of water and that bottled waters in Europe tend to have higher alkalinities than tap waters. Varner (2009) argues that bicarbonate in water aids digestion and is 'useful in effective treatment of gastric disorders, diabetes (through the increased utilization of blood sugars by the body), pancreatic….. and bile duct disorders'. Drinking water values for alkalinity have not been set by either the WHO or EU.

*Hardness*

Total water hardness is mainly due to the presence of calcium and magnesium ions, but other polyvalent metallic ions such as iron, manganese, aluminium and barium may contribute. WHO (2011) does not establish a guideline value because hardness 'is not of health concern at levels found in drinking water'. Edmunds and Smedley (1996) quoted a number of papers that give a weak inverse relationship between hardness and cardiovascular disease. The reasons are not well understood, and may relate to the fact that low hardness may be associated with increased

concentrations of certain toxic elements or, conversely, that some elements which occur in hard waters may be beneficial. It should be noted that there are numerous causes of cardiovascular disease, such as poor diet, smoking etc., and there are also associations with air quality – an increase in exposure to particulate air pollution can result in a decrease in heart rate variability, with a consequent effect on heart disease (Nyhan *et al*., 2014).

In a detailed review of the supposed health effects associated with water hardness, Rubenowitz-Lundin and Hiscock (2005) noted that much of the evidence is equivocal and commented that 'the reported associations may reflect disease patterns that can be explained by social, climatological, and environmental factors rather than by the hardness of the water'. They concluded that there is much stronger epidemiological evidence for the health benefits of magnesium in drinking water, which helps to reduce mortality from acute myocardial infarction (AMI). Elevated groundwater Mg levels can be found in lithologies such as dolomites (see Section 7.5.8). Hopps and Feder (1986), based on a study of water hardness and the prevalence of cardiovascular mortality (CVM) in two regions of the US, also concluded that the association was strongest for Mg, i.e. that CVM was lower when Mg was present in drinking water at concentrations above 20 mg $l^{-1}$. As well as links between low Mg and CVM, other reported health effects include the possible relationship between magnesium deficiency and low birth weight, with problems extending beyond infancy to increased risk of insulin resistance and type 2 diabetes in later life (Takaya *et al*., 2006). Kozisek (2014) reports that Mg and more especially Ca have benefits as antitoxic agents, as they reduce the harmful effects of some toxic elements such as lead. Kozisek (2014) further suggests that the minimum desirable levels of Ca and Mg in drinking water are 20-30 mg $l^{-1}$ and 10 $mg^{-1}$, respectively, whilst the optimum levels are in the ranges 40-80 mg $l^{-1}$ and 20-30 mg $l^{-1}$, respectively. He also notes that because Ca and Mg are 'metabolic antagonists' (i.e. one can interfere with the other in their biological uptake), then their relative levels are important as well as their absolute concentrations. Razowska-Jaworek (2014) indicates that the optimum Ca:Mg molar ratio for human health in mineral waters is 2:1. (The issue of recommended daily intakes for Ca, Mg and other constituents in drinking water is discussed further in Section 8.1.2).

*Iodine (I)*

Robins and Smedley (2013) discuss the importance of element deficiencies in water being harmful to health, as well as excesses of certain elements. They mention iodine (goitre) and fluoride (dental). An iodine deficiency is linked to goitre, as it is an essential element for the

production of thyroid hormones. Iodine occurs in water as iodide, and its main source is seawater, so groundwater concentrations are often lower in inland aquifers, away from rainfall recharge influenced by the sea (Fuge, 1989). In his 1989 paper Fuge found that iodine values in the UK tended to be higher in groundwater (mean 4.11 µg $l^{-1}$, n = 30) than surface water samples (mean 2.42 µg $l^{-1}$, n = 97), with higher values often associated with limestone aquifers or streams draining from limestone areas. He also observed that most peats are enriched in iodine, hence that waters draining peats may have high iodine concentrations (Whitehead [1979] noted that the organic matter content influences the retention of iodine in soils). In attempting to link goitre to low iodine in drinking water, Fuge noted that only about 20% of daily iodine intake is from drinking water, with the remainder from food, and thus he urged caution in making correlations between goitre and iodine content in water and soils (Fuge, 1989). The WHO considers iodine in the context of chemicals used in water treatment but does not set a GV for iodine because 'Available data [are] inadequate to permit derivation of health-based guideline value, and lifetime exposure to iodine through water disinfection is unlikely'. Unfortunately, it was only possible to test for a small number of samples for iodine in this research (Section 7.1).

*Lithium (Li)*

The alkali metal lithium has been used for many decades to treat mood disorders, including manic-depression and bipolar disorder, and lithium may reduce the risk of dementia in humans (Terao *et al*., 2014). There is also increasing evidence that lithium in drinking water may reduce the risk of suicide. Several studies have found a negative correlation between lithium concentrations in drinking water and suicide rates. Ohgami *et al*. (2009) investigated lithium levels in tap water in 18 municipalities in Oita prefecture in Japan over a period of 5 years (2002-2006), and found that suicide mortality rates were significantly and negatively associated with Li values, which ranged from 0.7 to 59 µg $l^{-1}$. Blüml *et al*. (2013) compared suicide rates and Li levels in public groundwater supplies in Texas. The water sample data were collected in 254 Texas counties between 1999 and 2007 (n = 3123 samples), with mean Li concentrations in the counties ranging from 2.8 to 219 µg $l^{-1}$. Blüml *et al*. found these Li levels were negatively associated with suicide mortality rates 'in most statistical analyses'. An advantage of the Blüml *et al*. study compared to the earlier Ohgami *et al*. (2009) study is that Blüml *et al*. were able to adjust their statistical analyses to account for socio-economic factors that also have an influence on suicide rates. A limitation of both studies, however, is that they were unable to account for dietary sources of lithium (lithium occurs in cereals and vegetables).

Not all studies comparing lithium in tap water and suicide rates have produced similar results. A study in eastern England found no association between suicide rates and lithium in drinking water, albeit here the Li concentrations were only in the range <1 to 21 µg $l^{-1}$, which may be too low for establishing a correlation (Kabacs *et al*., 2011). The European bottled water survey found that Li values ranged enormously, from less than 0.2 up to 9,860 µg $l^{-1}$, with a median of 10 µg $l^{-1}$ and 95%ile of 744 µg $l^{-1}$ (n = 884; Reimann and Birke, 2010).

*Silicon (Si)*

Silicon is probably essential for human nutrition (WHO, 2005) and its most abundant mineral is crystalline silica, or quartz ($SiO_2$). In water, Si concentrations are often reported as silica (multiply by 2.14 to convert Si to $SiO_2$ values). In most natural waters silica concentrations range between 1 and 30 mg $l^{-1}$ (Hem, 1985), although higher values have been reported in some groundwaters: e.g. 46 and 85 mg $l^{-1}$ in waters from granitic terrains in Senegal and Chad, respectively (Tardy, 1971). Silica solubility increases with temperature and so much higher concentrations are often found in geothermal waters (Reimann and Birke, 2010). There are no WHO or EU limit values for Si.

*Strontium (Sr)*

Strontium is indicated by Edmunds and Smedley (1996) to be probably beneficial to health (Table 6.1). Strontium is an abundant alkali earth element that is intermediate in size between Ca and K, and often substitutes for those elements in rock-forming minerals (Hem, 1985). The main carbonate and sulphate strontium minerals are strontianite ($SrCO_3$) and celestine ($SrSO_4$), respectively. There are no WHO or EU drinking water limits established for Sr, although a MAC of 7 mg $l^{-1}$ has been set in Russia (Reimann and Birke, 2010). In the study of bottled waters in the EU, the median Sr value was 326 µg $l^{-1}$ (n = 884), whilst about 5% of samples exceeded the Russian MAC (Reimann and Birke, 2010).

### 6.2.3 Essential or probably essential elements or ions that may be harmful or undesirable if present at high concentrations

There are many parameters in water that are beneficial (or probably beneficial) to health in small or moderate amounts, but are harmful or at least undesirable if they occur in excess. Several examples are described below, starting first with the essential parameters that may be

toxic at high concentrations, and then considering those that are not normally considered as harmful, but for which high levels may be undesirable on grounds of e.g. taste.

*Chromium (Cr)*

Chromium in its Cr(III) form has low toxicity and is regarded as a nutritionally essential element (for hormone functions), whereas Cr(VI) is more toxic and has been linked to increased risk of lung cancer via the inhalation pathway in humans (Calabrese *et al*., 1985; WHO, 2011; Koller and Saleh, 2018). Therefore, 'data on speciation would be required to determine any health risk' (Reimann and Birke, 2010). A 1995 US EPA factsheet refers to effects of long-term exposure to chromium as including liver and kidney damage, and the current MCL is 100 μg $l^{-1}$ (US EPA, 2018).

*Copper (Cu)*

Copper is a transition metal that is essential for health, as it is required for metabolic catalysis, infant growth, bone development and other functions (WHO, 2005), but Cu is also harmful – especially to the digestive system – in excessive concentrations. Its main source in drinking water is from corrosion of water pipes.

*Fluoride (F)*

It is a common element in the earth, and is contained in minerals such as fluorspar and fluorapatite. Its solubility is controlled by saturation of the mineral fluorite ($CaF_2$) – high F usually occurs only when there is low calcium. In hydrogeology, groundwaters with low Ca and high F are often found in volcanic terrains, such as in the volcanic aquifers along the East African rift valley (Gaciri and Davies, 1993; Ashley and Burley, 1994). Other factors associated with high F concentrations in groundwater include hydrochemical 'maturity', with slow flow rates, high pH and alkalinity, and a sodium bicarbonate major ion chemistry (Misstear *et al*., 2017). In Ireland, many groundwaters are hard, with relatively high Ca levels, so fluoride is not usually a problem. An exception is the Carboniferous limestone aquifer at Knockatallon in County Monaghan, where high F (up to 3.8 mg $l^{-1}$) has been found in some boreholes dominated by Mg/Na-$HCO_3$ major ion chemistry (Misstear *et al*., 2008). Reimann and Birke (2010) report that about 5% of European bottled water samples (n = 884) exceeded the MAC of 1.5 mg $l^{-1}$ and the maximum value was 10.7 mg $l^{-1}$.

Globally, Edmunds and Smedley (2005) estimated that more than 200 million people drink water with F levels above the WHO guideline value. As well as exposure from drinking water, F is found

in foods – tea, for example, can contain high F – therefore the WHO advises setting a lower standard than 1.5 mg $l^{-1}$ in drinking water where intake from other sources is high (above 6 mg $d^{-1}$) (WHO, 2011). The WHO notes that F 'may be an essential element for humans; however, essentiality has not been demonstrated unequivocally'. The WHO does acknowledge, however, that F is a beneficial element for preventing dental caries, and an Irish study has shown that the levels of dental caries are lower in children with fluoridated domestic water supplies (Whelton *et al*., 2004). The adverse health impacts of high F in drinking water are increased risk of dental fluorosis at concentrations in excess of 1.5 mg $l^{-1}$, especially in children, and long-term exposure to higher F concentrations in drinking water can lead to skeletal fluorosis.

*Manganese (Mn) and iron (Fe)*

Manganese is 'essential for normal physiological function of animals and humans' (US EPA, 2003a) and most of the Mn daily intake is in people's food – nuts, grains and leafy vegetables can be especially rich in Mn. Where there is high exposure to Mn toxicity, this is generally via inhalation, and high exposure can cause damage to the nervous system; however, Mn has 'very low toxicity by oral ingestion and reports of adverse effects by this route are rare' (US EPA, 2003a). Notwithstanding its low oral toxicity, the EU has set a drinking water guideline value for Mn of 50 µg $l^{-1}$, but this is probably based mainly on aesthetic rather than health grounds, especially as the EU mineral water limit is ten times higher at 500 µg $l^{-1}$ (Table 6.3). The WHO does not set a GV because Mn is 'not of health concern at levels causing acceptability problems in drinking water'. The WHO does, however, derive a health-based value for Mn of 0.4 mg $l^{-1}$, noting that this is well above the acceptability threshold of 0.1 mg $l^{-1}$. High Mn concentrations in drinking water have been linked to adverse effects on the neurological system. For example, a study in Bangladesh has linked reduced intellectual function in children to Mn exposure in drinking water (the average Mn concentration in well water in the study area was 793 µg $l^{-1}$; Wasserman *et al*., 2006).

Iron is an essential element for the human diet (e.g. for oxygen transport and DNA synthesis), and low bioavailability of dietary iron results in anaemia in about 40% of the world's women (WHO, 2005). Iron-rich waters at holy wells and spas have been popular for treatment of anaemia and other ailments (Varner, 2009; see Section 8.1.1). As with Mn, no WHO GV has been established for iron, as it is 'not of health concern at levels found in drinking water'.

*Molybdenum (Mo)*

Mo is essential for human health as it is involved in enzyme catalysis (required daily intake for adults = 0.1 - 0.3 mg; WHO, 2011). Mo is a transition metal that occurs in several oxidation states, the most stable of which are Mo(IV) and Mo(VI) (Smedley *et al*., 2014a). The WHO did introduce a guideline value of 70 µg $l^{-1}$ in 1993 (WHO, 1993), owing to the concern that high Mo intake could be harmful to the human metabolism. However, the 2011 WHO guidelines, whilst continuing to advise this value for health-based reasons, decided to remove Mo from the list of formal guideline values since this concentration is rarely found in drinking water. This decision is supported by a study of Mo in drinking water in England and Wales, where concentrations in all instances were below 2 µg $l^{-1}$ (Smedley *et al*., 2014b).

A parallel study by the same authors (Smedley *et al*., 2014a) found that the median concentration in groundwater samples was only 0.2 µg $l^{-1}$ (n = 1735 samples), with 82% of samples having concentrations below 1 µg $l^{-1}$, and only two samples with concentrations above the 1993 WHO GV of 70 µg $l^{-1}$. Smedley *et al*. (2014a) found that the higher concentrations tended to occur in anoxic and mildly reducing conditions in a range of aquifer types (including Cretaceous greensand, Permo-Triassic sandstone and Carboniferous limestone aquifers) and attributed these higher values to reductive dissolution of iron and manganese oxide minerals. The solubility controls are complex, however, and in some hydrogeological situations internationally, values above the WHO health-based value have been found in oxic and alkaline groundwaters, for example in some volcanic aquifers.

*Nickel (Ni)*

Food is the main source of exposure of humans to nickel. Concentrations of Ni in drinking water are generally low except where the water has been impacted by pollution or from leaching of Ni from metal pipes, including water well casing. Contact with nickel can cause skin irritation, which is the most common symptom of Ni exposure in people (WHO, 2011).

*Nitrate ($NO_3$) and nitrite ($NO_2$)*

Natural background levels of nitrogen compounds in groundwater are normally low, except in some arid regions where high nitrate concentrations can result from N fixation by leguminous vegetation and subsequent concentration in recharge water by evapotranspiration. High nitrate levels in groundwater are usually associated with human activities like farming and sewage disposal. The principal exposure pathway to nitrate (and nitrite) is eating vegetables and meat

(WHO, 2011), and so exposure through food – as well as drinking water - is also relevant to assessing the health risk.

The main health concern is methaemoglobinaemia in babies, a condition caused by reduction of nitrate to nitrite in the stomach and the binding of this nitrite to haemoglobin, which impedes the uptake of oxygen and hence causes 'blue-baby syndrome'. It is the risk of methaemoglobinaemia in infants that is the basis for the WHO GVs of 50 mg $l^{-1}$ for nitrate and 3 mg $l^{-1}$ for nitrite. There are studies that show that methaemoglobinaemia is often linked to gastrointestinal infections and hence that children drinking water from private wells, where the microbial contamination risks are high (Hynds *et al*., 2013), may be particularly susceptible to methaemoglobinaemia (Knobeloch *et al*., 2000; Fewtrell, 2004). Whilst there have been many epidemiological studies investigating the links between nitrate and cancer, the WHO concludes that 'The weight of evidence indicates that there is unlikely to be a causal association between gastric cancer and nitrate in drinking water'.

*Selenium (Se)*

Selenium is essential for health in trace concentrations (US EPA, 1995; FAO and WHO, 2001), and the main dietary sources of Se are foods such as meat, fish and cereals. A deficiency can lead to problems including anaemia, muscular degeneration and impeded growth (Edmunds and Smedley, 1996). Reimann and Birke (2010) observed that 'In large parts of the world, Se deficiency is probably a greater threat to the health of the general population than Se toxicity'. Excessive amounts of Se can be toxic, leading to tooth decay and gastric problems, and damage to kidney and liver tissue (US EPA, 1995). Fordyce (2005) noted that Se has one of the narrowest ranges of all elements between a dietary deficiency level (<40 µg $d^{-1}$) and a toxic level (>400 µg $d^{-1}$). The WHO has set a provisional GV of 40 µg $l^{-1}$ ('provisional' owing to scientific uncertainty); whereas the MAC set by the EU for drinking water and mineral waters is 10 µg $l^{-1}$ (Table 6.3), and the US EPA MAC is 50 µg $l^{-1}$ (US EPA, 2018). Se tends to be more abundant in sedimentary rather than igneous rocks, and high levels are associated with shales and phosphate-rich rocks (Fordyce, 2005).

Se occurs in four oxidation states ($Se^{2-}$, $Se^{0}$, $Se^{4+}$ and $Se^{6+}$), of which the $Se^{6+}$ (selenite) form is highly soluble under oxidising and alkaline conditions. Se is normally only found at low concentrations in groundwater (< 1 µg $l^{-1}$), although groundwaters containing up to 1 mg $l^{-1}$ Se have been reported in Se-rich aquifer deposits in the US (Fordyce, 2005). In the study of bottled

waters in the EU, only 0.2% of samples (n = 884) exceeded the EU MAC – although the maximum recorded concentration was 371 µg $l^{-1}$ (in a water marketed as a medicinal water; Reimann and Birke, 2010).

*Vanadium (V)*

Vanadium is found in relatively high levels in ultramafic rocks (Reimann and Birke, 2010). It occurs in several oxidation states, with its highest solubility occurring in oxic aquifers. The physiological role of vanadium is not well established, although it has been noted that V can be used in the treatment of diabetes (Lindh, 2005). There is no WHO guideline value or EU MAC for vanadium, but some European countries have set limits in drinking water e.g. 5 µg $l^{-1}$ in Bosnia and Herzegovina (Reimann and Birke, 2010).

*Zinc (Zn)*

Zinc is present in a large number of enzymes, and it plays a key role in the immune system (FAO and WHO, 2001). The main dietary source of Zn is food. It is usually found at low concentrations in groundwater, except where there are sources of industrial pollution (notably mining) or where Zn has leached into the water supply from borehole casings or water pipes. The WHO does not set a GV as Zn is 'not of health concern at levels found in drinking water'.

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Some essential elements or ions are undesirable if present in excessive concentrations, and may affect the taste or acceptability of the water, but are not considered harmful to health (at least at the concentrations consumers may be exposed to) e.g.:

*Sodium (Na) and potassium (K)*

Even though the EU has only set a guide level (200 mg $l^{-1}$) for sodium, and although Na levels in some bottled waters can be very high (8160 mg $l^{-1}$ was the maximum recorded in the EU bottled water survey, and the 95%ile was 620 mg $l^{-1}$ [n = 884]; Reimann and Birke, 2010), high Na can lead to high blood pressure and be harmful to kidneys. The WHO notes that the average taste threshold for Na at room temperature is 200 mg $l^{-1}$, and that no health-based GV has been derived as the Na contribution from drinking water is small compared to that from food (the main food intake is in sodium chloride i.e. salt). The WHO does not set a GV as Na is 'not of health concern at levels found in drinking water'. For consumers on a low-sodium diet, the US

EPA has recommended that sodium concentrations in drinking water should be less than 20 mg $l^{-1}$ Na (US EPA, 2003b).

Similarly, the WHO has not set a GV for potassium since K also occurs in drinking water at 'concentrations well below those of health concern'. Potassium is essential for human health – the required daily intake is more than 3000 mg (WHO, 2011). Adverse health effects would only be expected in susceptible individuals (e.g. people with kidney problems or heart disease) who are exposed to drinking waters where potassium salts are used in water treatment.

*Sulphate ($SO_4$)*

The WHO does not set a GV for sulphate because there is no evidence of adverse health effects at levels found in drinking water. However, high concentrations of sulphate in drinking water can have a laxative effect (loose stools) or cause diarrhoea (frequent bowel movements), so the WHO (2011) recommends that health authorities should be notified where drinking water supplies contain sulphate above 500 mg $l^{-1}$. Whilst the US EPA concurs that a mild laxative effect can result from sulphate concentrations in drinking water greater than 500 mg $l^{-1}$, it notes that laxative effects are unlikely to be observed at concentrations up to about 1000 mg $l^{-1}$ unless there are other osmotically-active substances present like magnesium and sodium: these increase the 'osmolality' of the contents of the intestines, causing water to be drawn into the intestines by osmosis from the surrounding body fluids, thereby increasing the liquidity and volume of faecal material (US EPA, 2003c).

The laxative effects of sulphate salts may be considered beneficial for tackling digestive problems in some cases, and sulphate-rich waters are common in many spa treatments (see Section 8.1). Also, the reduction of sulphate to hydrogen sulphide gas means that some spa waters are noticeable by the characteristic rotten egg smell of $H_2S$. Varner (2009) argues that bathing in sulphur-rich waters can aid respiration problems as $H_2S$ vapours help to clear mucus (but it should be noted that high levels of $H_2S$ are toxic).

### 6.2.4 Elements or ions in groundwater harmful to health

This section describes elements or compounds that are harmful to health and for which there is little or no evidence that they are bioessential. When considering their toxicity, however, we should bear in mind that the groundwater supply might form only a small part of the total intake.

*Aluminium (Al)*

The solubility of Al is strongly pH dependent, with very low concentrations in water at pH above 5.5 (Edmunds and Smedley, 1996). Al has relatively low toxicity but is potentially of health concern because of its links to Alzheimer's disease. For example, a study in southwest France found that aluminium in drinking water at levels greater than 0.1 mg $l^{-1}$ increased the risk of Alzheimer's disease (AD) in an elderly population (Rondeau *et al*., 2000). (The same study concluded that high silica in drinking water decreased the risk of AD, possibly because silicon interacts with Al to reduce its bioavailability). However, the WHO cautions that 'strong reservations about inferring a causal relationship [between aluminium in drinking water and Alzheimer disease] are warranted' because of the failure of epidemiological studies to take account of various confounding factors and total Al intake from all sources. The WHO has not set a guideline value because Al 'occurs in drinking water at concentrations well below those of health concern.'

*Antimony (Sb)*

There is a WHO guideline value (GV) (Table 6.2) and an EU MAC (Table 6.3) for Sb, and the US EPA MCL is 6 µg $l^{-1}$ (US EPA, 2018). The WHO notes that its toxicity depends on the form of Sb in drinking water. It is mostly found as Sb(V), which is less toxic than Sb(III). However, total concentrations in groundwater are usually very low: e.g. < 0.1 µg $l^{-1}$ according to Edmunds and Smedley (Table 6.1). Adverse health effects from Sb exposure include increase in cholesterol and increased risk of cancer. According to WHO (2003) Sb compounds have various therapeutic uses, including in the treatment of the parasitic disease leishmaniosis.

*Arsenic (As)*

The metalloid arsenic occurs in water in several oxidation states, the most common of which in drinking water are As(III) and As(V). The controls on arsenic solubility and mobility are complex, and it can occur in groundwaters under both oxidising and reducing conditions and where the pH is high or low. Arsenic is both toxic and carcinogenic. Skin lesions, bladder problems and skin and lung cancer are amongst the health impacts in populations exposed to high As concentrations in drinking water.

Traditionally, it was believed that the main risks of arsenic in drinking water came from industrial pollution (mining, smelting, use in paints and wood preservatives) or from areas with

geothermal waters. However, in recent decades, it has become apparent that tens of millions of people worldwide are exposed to high levels of As in their drinking water. Murcott (2012) estimates that 226 million people globally are exposed to arsenic values above the WHO drinking water guideline value of 10 µg $l^{-1}$. The largest exposed populations occur in Bangladesh and West Bengal: one estimate puts the annual number of arsenic-related deaths at 43,000 in Bangladesh alone (Flanagan *et al*., 2012). Other regions where high As levels have been found in groundwater include China (Inner Mongolia, Xinjiang and Shanxi), Vietnam (Red River delta), Myanmar, the Bolivian Altiplano, the Chaco-Pampean plain in Argentina, and in western USA (BGS and DPHE, 2001; Banks *et al*., 2004; Ravenscroft *et al*., 2009). The aquifers in many of these areas occur within alluvial plains and river deltas. There are several possible causes for the presence of high natural As levels in these groundwaters, one of which is reduction of ferric oxyhydroxides that releases As into solution (Ravenscroft *et al*. 2009). In environments such as the deltaic region of Bangladesh, the groundwater gradients are so low that the As is not flushed from the aquifers.

The WHO GV of 10 µg $l^{-1}$ is provisional 'on the basis of treatment performance and analytical achievability'. The US EPA MCL is also 10 µg $l^{-1}$, although the MCL Goal is set at zero (US EPA, 2018), an indication of the toxicity of this element. Given its toxicity, Reimann and Birke (2010) expressed surprise that nearly 1% of all European bottled water samples (n = 884) exceeded the EU MAC of 10 µg $l^{-1}$. Notwithstanding the toxic properties of As, it is referred to in some publications (but not in WHO, 2011) as being a bioessential element - Koller and Saleh refer to As, along with Cr, as being 'vital poisons' – and arsenic trioxide has been used in cancer treatments (Antman, 2001). Moreover, some people believe that soaking an infected foot or hand in arsenic-containing water is helpful in the treatment of skin diseases (Varner, 2009).

*Barium (Ba)*

The alkali earth element barium is a common industrial pollutant associated with e.g. the electronics industry. It is also found in wastes from well drilling (barytes - barium sulphate - is used to increase the density of drilling muds). It occurs naturally in groundwaters associated with acid igneous rocks but is also found in sedimentary rocks. The solubility of Ba is controlled by the solubility of the mineral barite, so high Ba concentrations are most likely where sulphate concentrations are low (e.g. through sulphate reduction). In the survey of European bottled waters, about 1% of samples (n = 884) had Ba levels above the EU mineral water MAC of 1 mg $l^{-1}$, with a highest value of 26.8 mg $l^{-1}$ (Reimann and Birke, 2010). Ba has been linked to high blood

pressure and cardiovascular disease (US EPA, 2006; WHO, 2011). The US EPA MCL is 2 mg $l^{-1}$ (US EPA, 2018).

*Beryllium (Be)*

Beryllium (another alkali earth element) is of potential concern in groundwater in that it may be mobilised with Al at low pH; however, the main health risk may be related to air pollution (Reimann and Birke, 2010). The US EPA has established an MCL of 4 µg $l^{-1}$ in drinking water (US EPA, 2018), and Russia has set a very low drinking water limit of 0.2 µg $l^{-1}$ (Misstear *et al*., 2017), but there is no WHO or EU GV value. The WHO states that a GV has not been established because Be is 'rarely found in drinking water at concentrations of health concern'. A health-based value of 12 µg $l^{-1}$ has been calculated by the WHO (2011) based on epidemiological data from animal tests (in which dogs developed intestinal lesions). A survey of wells in crystalline rock aquifers in Scandinavia found a median Be concentration of 0.012 µg $l^{-1}$ (n = 476), with a maximum value of 6.6 µg $l^{-1}$ (Frengstad *et al*., 2000).

*Boron (B)*

Boron occurs naturally in groundwater at low concentrations through dissolution of minerals in soils and rocks, but is also found in drinking water as a result of pollution from agriculture or industrial activities. It is also present in discharges of wastewater because of the use of borates in detergents and soaps: B is sometimes therefore used as a tracer during investigations of sewage pollution (Misstear *et al*., 1996). Health impacts of high B doses in animal studies include damage to the male reproductive organs. The US EPA (2008) noted that B is an element for which 'essentiality is suspected but has not been directly proven in humans'; as such, it could therefore be included in the previous category of elements described in Section 6.2.3. It occurs widely in groundwaters at low concentrations. The US EPA (2008) reported that 81.9% of groundwater public water supplies detected B concentrations (at minimum reporting levels above 5 µg $l^{-1}$), whilst Reimann and Birke (2010) found that 10% of European bottled water samples (n = 884) exceeded the EU drinking water MAC of 1 mg $l^{-1}$ (the median concentration was 39.2 µg $l^{-1}$, and the maximum concentration was 120 mg $l^{-1}$). It was not possible to analyse for boron in this research (Section 7.1).

*Cadmium (Cd)*

Cadmium is a transition metal that exhibits some chemical similarities to zinc. It is often associated with industrial (including metal plating and coatings), agricultural and mining

pollution (the WHO includes Cd in its GV table of chemicals associated with industrial sources), but Cd also occurs naturally in e.g. shale deposits and is released from volcanic activity. The major dietary source of Cd is food – leafy vegetables contain 0.05 to 0.12 mg $kg^{-1}$ of Cd (Water Quality Association, 2013a). Cd is a toxin, and can lead to kidney, liver and bone damage (WHO 2011, Water Quality Association, 2013a). The US EPA MCL is 5 µg $l^{-1}$ (US EPA, 2018).

*Lead (Pb)*

Lead in water is mainly a risk from old piping in water supply systems. Levels in groundwater are usually low (except e.g. in acidic waters associated with old mine workings). The survey of European bottled waters did not show any exceedances of the EU drinking water limit of 10 µg $l^{-1}$. Health impacts of exposure to high levels of lead include cardiovascular disease, impaired neurological development and adverse effects on fertility and pregnancy (WHO, 2011).

*Mercury (Hg)*

The main exposure pathway to Hg is in food, and concentrations in groundwater are normally low (below 0.5 µg $l^{-1}$ according to the WHO) except where there are impacts from industrial activities such as mining. Kidney damage has been observed in people exposed to high Hg levels (US EPA, 1995; WHO, 2011). The US EPA (2018) MCL is 2 µg $l^{-1}$. Hg was not analysed for during this research (Section 7.1).

*Thallium (Tl)*

The US EPA (2018) has set an MCL of 2 µg $l^{-1}$ for Tl in drinking water, but the MCL Goal is set at 0.5 µg $l^{-1}$, whilst the limit in Russia is set at an even lower value of 0.1 µg $l^{-1}$ (Misstear *et al*., 2017). Long-term exposure may lead to problems with kidneys, intestines, liver, or cause hair loss (Agency for Toxic Substances and Disease Registry, 2013). It is classed as a post-transition metal and is associated with coal burning and smelting (and Tl is also widely used in the electronics industry), but Tl can occur in trace concentrations in unpolluted groundwaters. For example, a survey of crystalline rock wells in Norway by Frengstad *et al*. (2000) found a median Tl concentration of 0.007 µg $l^{-1}$ (n = 476), with a maximum Tl concentration of 0.25 µg $l^{-1}$.

*Uranium (U), radium (Ra) and radon (Rn)*

These are all radioactive isotopes. The most common uranium isotope is $^{238}U$ - the other uranium isotopes $^{234}U$ and $^{235}U$ occur in much smaller amounts. $^{238}U$ decays (via intermediary nuclides) to radium $^{226}Ra$ which in turn decays to radon $^{222}Rn$. There are uncertainties about the

toxicity of U to humans and so the WHO has set a provisional GV of 30 µg $l^{-1}$. This is also the MCL in the US, although the MCL Goal is set at zero (Water Quality Association, 2013b; US EPA, 2018). Potential adverse health effects of exposure to high U in drinking water include damage to the kidneys. However, Robins and Smedley (2013) suggest that the uranium present in some mineral waters may have benefits for treating rheumatism, since U gives off alpha radiation. U is usually associated with crystalline rock terrains and can occur at relatively high concentrations under oxic conditions. There are many reported cases where groundwater supplies exceed the WHO provisional recommended level for drinking water of 30 µg $l^{-1}$. Reimann and Birke (2010), for example, describe examples of exceedances in Scandinavian groundwaters, with maximum values reported in Norway and Finland of 2 and 14 mg $l^{-1}$, respectively. Radium is chemically similar to barium (see above) and is usually only found at elevated concentrations in waters with low sulphate concentrations (since its sulphate salt has low solubility).

Because $^{222}$Rn is produced by radioactive decay of radium ($^{226}$Ra), then, as with radium and its parent uranium, radon is normally found in crystalline rock terrains like granites and gneisses – although it is also associated with organic shales and phosphate-rich rocks (Appleton, 2005). $^{222}$Rn is an inert gas with a very short half-life (3.8 days), and tends to de-gas from water when exposed to air. In primary-porosity aquifers, groundwater moves slowly, at rates of metres per year, so there is plenty of opportunity for radon to decay. Radon transport in groundwater over distances longer than tens of metres is more likely to occur in fractured rock systems. In the USA, high radon concentrations in groundwater are associated with shear-zones in granites where there is uranium enrichment (Appleton, 2005). However, according to research quoted by the WHO (2011), '90% of dose attributable to radon in drinking water comes from inhalation rather than ingestion', so setting a GV for ingestion of radon from drinking water is not usually necessary.

Most holy wells are springs or shallow open wells (Chapter 5), and therefore it is likely that radon would generally dissipate to the atmosphere. Interestingly, Varner (2009) has remarked that radon gas is linked with some holy wells that are reputed to put people to sleep – he cites examples from Cornwall, where Rn concentrations are elevated owing to the granitic terrain. He also mentions that Rn is regarded as a healing agent in a number of spas (Section 8.1). Nevertheless, radon inhalation in indoor air has been linked to lung cancer (20,000 lung cancer deaths per year in the USA have been attributed to radon inhalation – Appleton, 2005), but the effects of radon ingestion in water are not certain: the WHO says that links to stomach cancer

are unproven. An action level of 500 Bq $l^{-1}$ has been set by the Norwegian Radiation Protection Authority, and it has been estimated that 14% of wells in that country exceed this value (Banks *et al*., 1998). The EU recommends in its directive 2013/51/EURATOM (European Commission, 2013) that possible risks should be evaluated if Rn in drinking water exceeds 100 Bq $l^{-1}$, whilst a remedial action would be justified if the radon level were greater than 1,000 Bq $l^{-1}$.

## 6.3 Background levels of chemical parameters in Irish groundwaters

### 6.3.1 Introduction

There have been three studies that have attempted to define natural background levels (NBLs) of chemical parameters in Irish groundwaters. Some discussion of these NBL studies is relevant here, since one of the objectives of the holy wells sampling exercise was to try and identify well waters where health-related parameters may be elevated (or deficient) compared to typical values recorded in other Irish groundwaters (Chapter 7); it should also be noted that even those groundwaters in which the chemical constituents are not particularly elevated may provide essential nutrients (Section 8.1.2). Previous studies into the distribution of certain individual parameters in Irish groundwaters are also summarised in this Section 6.3, specifically arsenic (Section 6.3.3) and lithium (Section 6.3.4).

The first two studies of NBLs were undertaken in relation to the characterisation of Irish groundwaters under the implementation of the European Water Framework Directive (European Commission, 2000). Buss *et al*. (2004) were the first authors to develop a methodology for characterising unpolluted groundwater in Ireland. Their methodology involved a hierarchy of approaches, with priority given to analysis of historical datasets. They trialled their methodology in the Southeastern River Basin District.

This initial characterisation methodology was developed further by O'Callaghan Moran & Associates (OCM, 2007), partly because there was a lack of reliable historical groundwater quality records, but also to take account of recently-developed procedures to assess pollution risk (i.e. impact potential maps) when choosing groundwater quality records for analysis. Applying risk screening and data reliability checks to candidate monitoring boreholes, they selected a total of 30 boreholes nationally (with 747 groundwater quality records) as being suitable (i.e. not affected by anthropogenic activities) for establishing natural background levels

(NBLs). OCM applied statistical and cumulative frequency (probability) plot techniques - described in the earlier report by Buss *et al*. (2004) - to derive the NBLs.

Although the Environmental Protection Agency (EPA) had identified 43 parameters for which NBLs should be established, the OCM study was only able to derive NBLs for 24 of these, 16 of which were classed as 'global parameters' and eight as 'bedrock parameters' influenced by lithology. The global parameters included (*inter alia*): ammonia, barium, chloride, chromium, copper, fluoride, iron, manganese, nickel, nitrate, sulphate and zinc. The remaining eight 'bedrock' parameters were (alphabetically): alkalinity, calcium, EC, magnesium, pH, potassium, sodium and total hardness. The results for these eight bedrock parameters were presented according to four main lithological groupings: Lower Palaeozoics and Precambrian (mainly metasediments and igneous rocks), Devonian (Old Red Sandstone and Kiltorcan-type sandstones), karst (Dinantian pure bedded limestones) and Mixed (mainly Carboniferous impure limestones, sandstones and shales, but also including Precambrian marbles). The classification also took account of whether the aquifer was confined or unconfined, since it was recognised that confinement can have a strong influence on e.g. redox conditions and hence on the solubility of some parameters. Parameters for which there were insufficient data to derive NBLs included: arsenic, antimony, beryllium, boron, cadmium, cobalt, mercury, lead, molybdenum, radon, silica, strontium and uranium.

### 6.3.2 EPA natural background levels (NBLs)

The third and most recent study of NBLs was undertaken as part of a research fellowship at the EPA (for which the current writer was a contributor). Data from 223 EPA groundwater quality monitoring points (147 boreholes, 76 springs) were used in this study (Tedd *et al*., 2017). The 40 parameters measured at these monitoring points were categorised into those that may potentially be affected by agriculture and those where an agricultural impact is unlikely. For the parameters that might be affected by agricultural activities (alkalinity, boron, cadmium, calcium, chloride, EC, copper, dissolved oxygen, fluoride, iron, magnesium, manganese, molybdenum, nickel, nitrate, pH, phosphorus, potassium, sodium, sulphate, total hardness, turbidity and zinc) the zones of contribution (ZOCs) of the individual monitoring sites were assessed in terms of agricultural pressures. Only those sites with nitrate values of less than 10 mg $l^{-1}$ $NO_3$ and with low tillage or low livestock rates were selected. These criteria resulted in only 22 monitoring points being chosen for establishing NBLs. In the case of screening for the agricultural nutrients

$NO_3$ and P, the criteria were modified to include low $NO_3$ and P susceptibility rates within the ZOCs (based on pathway criteria for nitrate and molybdenate reactive phosphorus - see EPA, 2013), reducing the number of monitoring points selected for $NO_3$ and P to 12 and 21, respectively. For the parameters not considered to be potentially affected by agriculture, the records from 217 MPs were used. It should be added that there was an underlying assumption here and in previous NBL studies that the monitoring records were not influenced by point pollution sources, an assumption that may not be valid in all instances.

In the Tedd *et al*. study, six lithological groupings were identified (as described in Table 3.1 and Section 3.2) rather than the four groups used in the earlier OCM study. Information on other hydrogeological factors such as aquifer confinement and flow regime (e.g. fissured, karstic, or intergranular flow) were also considered in the data analysis. The results according to lithological groupings and other hydrogeological criteria are included in Table 6.4. When interpreting how representative these results may be, it should be appreciated that monitoring points are more often located in the more productive aquifers, even though 70% of the country is underlain by poorly productive aquifers (Section 3.3). Moreover, the boreholes are mostly completed with long open-hole sections, so the groundwater samples reflect a mixture of waters from different depths. By contrast, holy wells are mainly shallow, and discharge mainly from unconfined aquifers (Chapter 5).

The NBLs were mainly based on the 95%ile values (in the case of pH, a lower NBL was also selected using the 5%ile value). For most of the parameters there are variations in background levels of several orders of magnitude. In some cases concentrations were found to differ significantly (using one-way analysis of variance tests – see Section 7.4) between different lithological groups and therefore separate background levels were defined for each of the groups. These parameters included pH, EC, Ca, Alkalinity, Ba, Si, Sr, Al and Zn (Table 6.4). For the majority of parameters, the associations with lithology were less clear-cut and therefore national background levels were defined. In some instances, differences between values in confined compared to unconfined aquifers were noted and are in included in Table 6.4. For example, higher Fe and Mn values were observed in confined aquifers, which is to be expected since the solubility of these ions increases under the reducing conditions that are often encountered in confined aquifers. The NBL for total P was defined for three different flow regimes: karst systems, intergranular flow, and poorly productive aquifers (where the majority of groundwater flow occurs in shallow fractures). When reviewing the NBL data in Table 6.4 it

should be remembered that many of the values are derived from a small number of monitoring points, especially for the parameters that may be affected by agriculture and for which the screening of monitoring points was most prescriptive. Furthermore, in the case of several of the trace elements, large numbers of sample results were below the limits of detection.

Table 6.4 Natural background levels for parameters defined by (a) lithological groups; (b) groundwater vulnerability categories; (c) flow regime (adapted from Tedd *et al*., 2017)

(a) Lithological group

| Parameter | Unit | Sand & gravel | Impure lst | Pure lst | Non-calc sed | Igneous | Met |
|---|---|---|---|---|---|---|---|
| pH | | (7.5) | (8.3) | 7.9 | 7.1 | (7.5) | (7.7) |
| EC | µS $cm^{-1}$ | (583) | (554) | 601 | 392 | (60) | (546) |
| Calcium | mg $l^{-1}$ | (111) | (113) | 117 | 64 | (8.2) | (114) |
| Alkalinity | mg $l^{-1}$ as $CaCO_3$ | (350) | (290) | 322 | 216 | (43) | (310) |
| Silica | mg $l^{-1}$ $SiO_2$ | (13) | (17) | 10 | 14 | (19) | (16) |
| Aluminium | µg $l^{-1}$ | 15 | 19 | 26 | 16 | 131 | 19 |
| Barium | µg $l^{-1}$ | 586 | 195 | 179 | 427 | 179 | 114 |
| Chromium | µg $l^{-1}$ | 11 | 11 | 11 | 9 | 4.3 | 8 |
| Radon | Bq $l^{-1}$ | 33 | 28 | 35 | 141 | 268 | 164 |
| Strontium | µg $l^{-1}$ | 651 | 2900 | 575 | 320 | 498 | 772 |
| Total hardness | mg $l^{-1}$ as $CaCO_3$ | (310) | (294) | 328 | 212 | (42) | (303) |
| Uranium | µg $l^{-1}$ | 5 | 3.1 | 2.8 | 3.8 | 1 | 2.6 |
| Zinc | µg $l^{-1}$ | (16) | (30) | 31 | 67 | (17) | (37) |

(b) Groundwater vulnerability

| Parameter | Unit | | X | E | High | Mod | Low |
|---|---|---|---|---|---|---|---|
| Dissolved oxygen | mg $l^{-1}$ $O_2$ | Lower limit | 4.4 | 0.8 | 3.9 | 0.7 | (0.5) |
| | | Upper limit | 12 | 11 | 12 | 8.1 | (5.9) |

(c) Flow regime

| Parameter | Unit | | Inter-granular | Karstified | Poorly productive | Productive fissured |
|---|---|---|---|---|---|---|
| Total phosphorus | µg $l^{-1}$ | Upper limit | 13 | 26 | 16 | - |

Note: values in brackets are derived from only one or two monitoring points and are for information only

Table 6.4 (continued) Natural background levels for parameters defined d) nationally for unconfined conditions; and (e) nationally for all data (adapted from Tedd *et al*., 2017)

| (d) Influence of confined and unconfined aquifers | | | |
|---|---|---|---|
| Parameter | Unit | Unconfined | Confined |
| Sodium | mg $l^{-1}$ | 13 | (105) |
| Magnesium | mg $l^{-1}$ | 17 | (42) |
| Potassium | mg $l^{-1}$ | 2.1 | (5.9) |
| Sulphate | mg $l^{-1}$ | 13 | (223) |
| Fluoride | mg $l^{-1}$ | 0.2 | (2.6) |
| Nitrate | mg $l^{-1}$ $NO_3$ | 8.7 | (1.5) |
| Ammonium | mg $l^{-1}$ N | 0.1 | (0.4) |
| Boron | µg $l^{-1}$ | 15 | (573) |
| Iron | µg $l^{-1}$ | 268 | (762) |
| Manganese | µg $l^{-1}$ | 23 | (176) |
| Nickel | µg $l^{-1}$ | 2.1 | (4.7) |
| (e) National parameters | | | |
| | Unit | | All preselected data |
| Chloride | mg $l^{-1}$ | | 21 |
| Molybdate reactive phosphorus | µg $l^{-1}$ | | 17 |
| Antimony | µg $l^{-1}$ | | 0.5 |
| Arsenic | µg $l^{-1}$ | | 2 |
| Copper | µg $l^{-1}$ | | 16 |
| Lead | µg $l^{-1}$ | | 2.9 |
| Nitrite | mg $l^{-1}$ | | <0.05 |
| Beryllium | µg $l^{-1}$ | | <1 |
| Cadmium | µg $l^{-1}$ | | <0.4 |
| Cobalt | µg $l^{-1}$ | | <1 |
| Mercury | µg $l^{-1}$ | | <0.05 |
| Molybdenum | µg $l^{-1}$ | | <1 |

Note: values in brackets are derived from only one or two monitoring points and are for information only

The box plots in Figures 6.1 and 6.2 and the Piper diagram in Figure 6.3 show that the majority of natural groundwaters in Ireland are dominated by calcium and bicarbonate ions. This is especially evident for the groundwaters from the pure limestones. The impure limestone groundwaters exhibit slightly elevated Mg and $SO_4$ compared to the pure limestones – the highest $SO_4$ levels were observed in samples from the confined impure limestone aquifer at Tydavnet in County Monaghan (Misstear *et al*., 2008). The major ion chemistry of the other

bedrock formations is more variable, with greater enrichment in Mg and Na in the metamorphic and igneous aquifers. The sands and gravels are dominated by Ca and $HCO_3$, especially where the gravels are derived from limestone areas (Tedd *et al*., 2017).

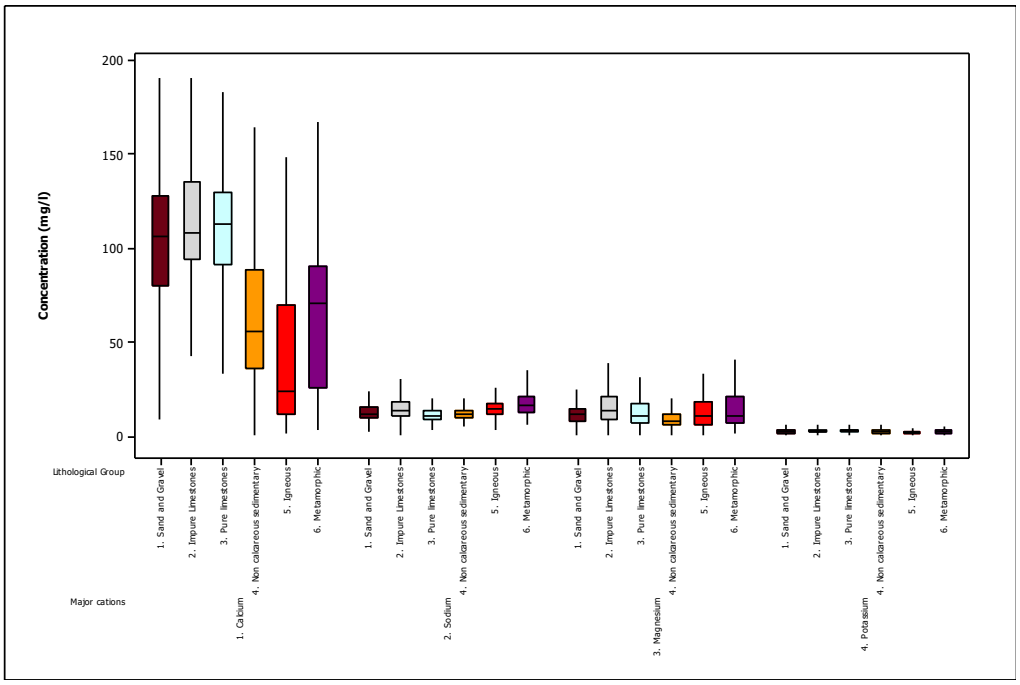



Figure 6.1 Box plots showing cation distributions for the main lithological groups (Tedd *et al.,* 2017)

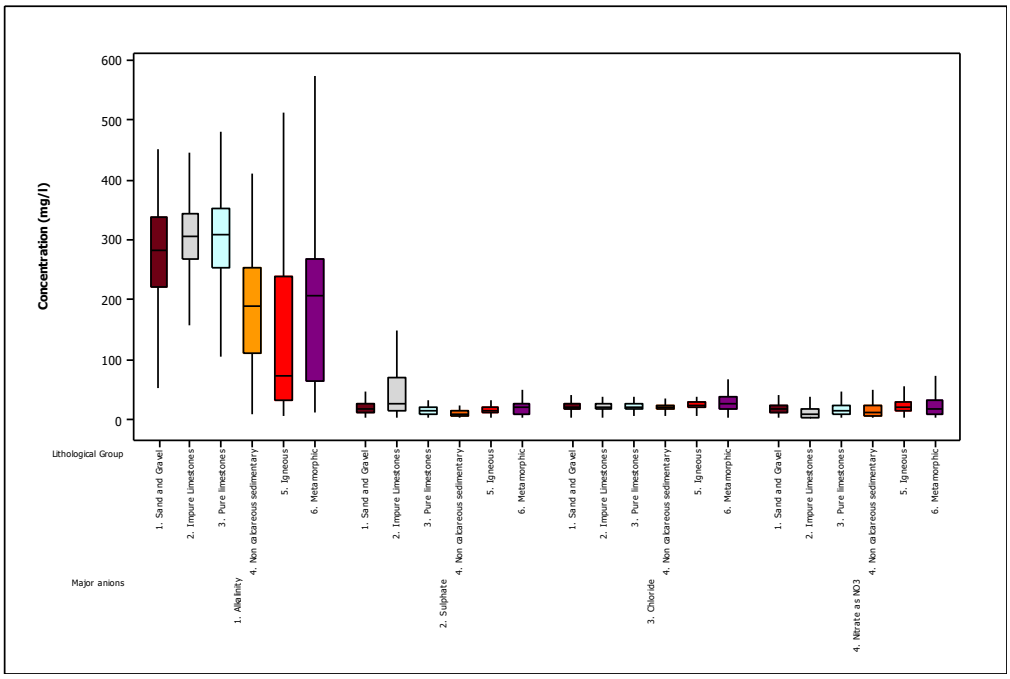



Figure 6.2 Box plots showing the anion distributions for the main lithological groups (Tedd *et al*., 2017)

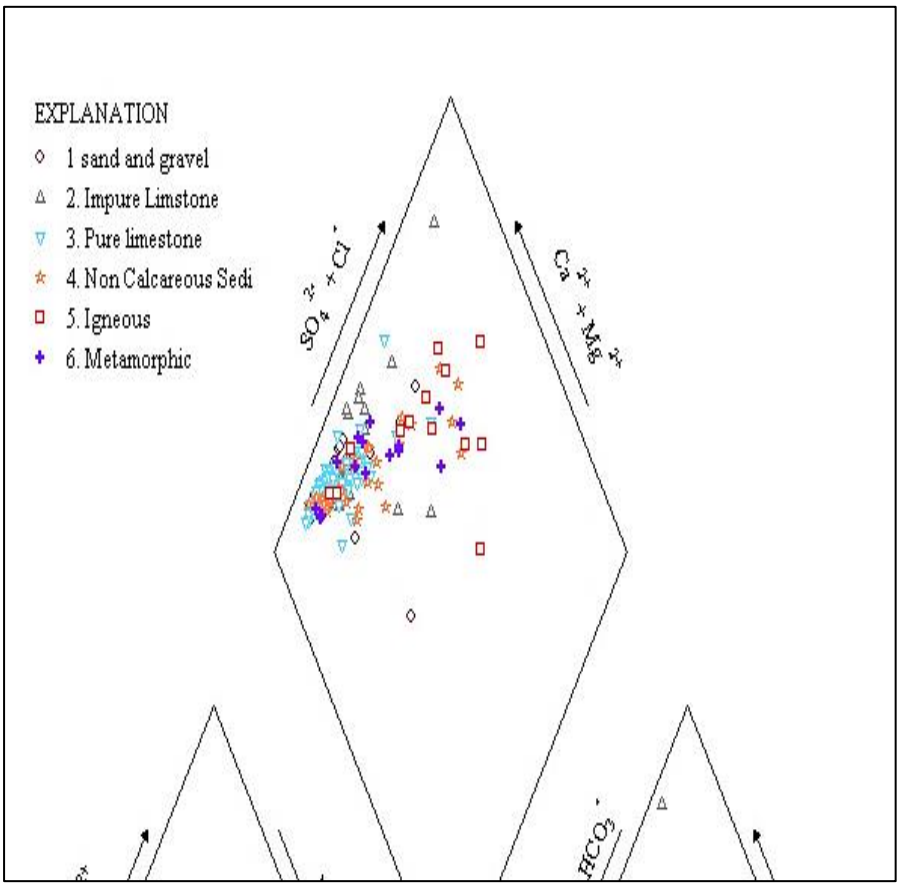



Figure 6.3 Piper diagram illustrating the major ion distributions for the main lithological groups (Tedd *et al.*, 2017)

For the minor ions and trace elements the NBLs are generally well below the WHO or EU drinking water values, although e.g. the Mn concentrations in confined aquifers exceed the EU guideline value of 0.05 mg $l^{-1}$. With Ba, the NBL values for some of the lithological units (non-calcareous sediments and sands and gravels) are relatively high and individual samples occasionally exceed the WHO guideline of 0.7 mg $l^{-1}$. The highest Ba values seem to be associated with mineralisation in an area known as the Rathdowney trend (an anticline that forms the Slieve Bloom and Silvermines mountains). The NBL for fluoride was set at 0.2 mg $l^{-1}$, but significantly higher values (over 2 mg $l^{-1}$) are found in the aforementioned confined impure limestone aquifers at Tydavnet (Misstear *et al.*, 2008). The cause of this high F is not known: it could come from fluorite mineralization, but there are no reports of fluorite minerals in the local rocks; alternatively, the occurrence of elevated phosphate concentrations (0.01-0.31 mg $l^{1}$ as P) may indicate the presence of fluorapatite as a source of phosphate and fluoride (Misstear *et al.*, 2008). The Tydavnet site also has relatively high Sr and B concentrations.

Some other observations on background levels of trace elements in the Tedd *et al*. (2017) report, and which are relevant to the current research, are:

a) The highest aluminium values occur in igneous aquifers, where groundwaters are generally acidic (i.e. pH < 7).
b) Arsenic concentrations are generally low (with 67% of samples below the limits of detection). The borehole with the highest As concentrations (median = 54 µg $l^{-1}$) taps an Ordovician volcanic aquifer in County Waterford (the Campile formation).
c) Values for Cu and Pb varied over three orders of magnitude (up to circa 100 µg $l^{-1}$). The highest Cu values were in the non-calcareous sedimentary aquifers, whereas there was very little variation in Pb observed between the different lithological groups.
d) The highest levels of zinc were found in the non-calcareous sedimentary aquifers, with a 95%ile value of 67 µg $l^{-1}$.
e) Uranium concentrations varied across three orders of magnitude; however, 41% of samples were below the limits of detection (the most frequent LOD being 1 µg $l^{-1}$) and the NBL was set at 3 µg $l^{-1}$. The statistical analysis did not reveal significant variations between U values in different lithological groups, although higher U concentrations would be expected in igneous terrain. Radon values were generally higher in the igneous, metamorphic and non-calcareous aquifers, but none of the samples exceeded the Radiological Protection Institute of Ireland public water supply guideline of 500 Bq $l^{-1}$ (RPII, 2013).

### 6.3.3 Arsenic studies

McGrory *et al*. (2017) carried out an analysis of existing data on arsenic concentrations in Irish groundwaters. The sources of data used in the analysis were EPA groundwater monitoring data from their established network for the period 1993 to 2012 (222 sites, mainly in productive aquifers – i.e. regionally and locally important aquifers), data for the EPA's Poorly Productive Aquifer (PPA) monitoring boreholes from 2007 to 2012 (65 sites), and data from regional studies carried out by the Health Service Executive (2001-2007) and by local authorities (2001-2011). No new As data were collected.

The arsenic data were subjected to sophisticated statistical treatment, especially in dealing with the problems of non-detects and the different detection limits for different datasets. The majority of As results were below the drinking water limit of 10 µg $l^{-1}$ and also below the groundwater threshold value of 7.5 µg $l^{-1}$ set by the EPA (Craig and Daly, 2010). For example, of the total EPA dataset (287 boreholes, 8270 samples), there were only 27 analyses above the 7.5 µg $l^{-1}$ threshold and 22 above the 10 µg $l^{-1}$ drinking water limit.

The As data were analysed for their spatial distribution according to the main rock types, aquifer categories and vulnerability categories, as well as by region. The analysis was performed using ArcGIS 10.2. It was concluded that elevated As concentrations were more likely in groundwaters from the following lithological groups: sandstones and shales (including Ordovician and Silurian metasediments which were included in this lithological group in the analysis), rhyolites and impure limestones. The following aquifer categories were identified as being at higher risk: PPAs, locally important fractured bedrock and regionally important fissured bedrock aquifers. Interestingly, the authors did not discover any significant differences in arsenic risk between the different vulnerability categories, suggesting a mainly geogenic (i.e. non-anthropogenic) origin for the arsenic. Several regional 'hot spots' were identified, including in the south, southwest and northeast of (the Republic of) Ireland. The maximum groundwater As value in the EPA database was 234 µg $l^{-1}$, whereas a borehole (in the southwest) monitored by local government reported a maximum value of 21,020 µg $l^{-1}$; McGrory *et al*. (2017) attributed this to the possible presence of arsenic-rich pyrites within the Namurian black shales in this area.

A current (2020) study, which is being carried out under the auspices of iCRAG (Irish Centre for Research into Applied Geology) is investigating elevated values of arsenic in three areas in eastern Ireland: a) an area of Silurian metasediments in Co Louth, north of Faughart (see Section 5.6.3); b) an area near Saggart, west of Dublin, also underlain by Silurian metasedimentary bedrock; and c) an area of Ordovician metasediments near Inistioge in Co Kilkenny (Russell *et al*., 2019). The study areas were chosen following regional geochemical mapping of stream waters, soils and sediments available from the ongoing Geological Survey of Ireland Tellus project[29]. Private wells were sampled, and As values of up to 60 µg $l^{-1}$ were detected. The primary process for the mobilisation of As in all three areas was oxidation of sulphide minerals. In two of the areas, there were associations between groundwater As and Co values (Russell *et al*., 2019).

[29] https://www.gsi.ie/en-ie/programmes-and-projects/tellus/Pages/default.aspx (accessed 25/3/2020)

### 6.3.4 Lithium study

Owing to interest in possible future mining of lithium in County Carlow, and hence concerns about the potential contamination risks, a study of Li concentrations in groundwaters and surface waters in that county was carried out to establish background levels (Kavanagh *et al*., 2017). Two-thirds of the county is underlain by Lower Palaeozoic granites, which contain pegmatite rocks with lithium-rich spodumene minerals. The study included the collection of 320 groundwater samples from private wells at 80 sites along five transects across the county. The authors report a mean background lithium concentration in Carlow groundwater of 23 µg $l^{-1}$, with a standard deviation of 20 µg $l^{-1}$ (and similar values in surface water). The authors comment that these values are consistent with published figures elsewhere, citing examples including those studies from Japan and England referred to in Section 6.2.2.

Interestingly, although the Carlow study did not identify any significant spatial variations in groundwater lithium values across the county (even though the source granitic rocks are mainly located in the east), the authors did find temporal variations, with higher lithium values obtained (in both groundwater and surface waters) in the May and September 2015 sampling rounds compared to those collected in March and July 2015. They did not discover an explanation for these differences, although they speculate that agricultural practices (fertiliser spreading) may have had some bearing.

The NBL study described in Section 6.3.2 did not include Li, as there were insufficient data, so it is not possible to discuss the Carlow results in that context. However, as well as Li, the Carlow study also included results for seven other trace metals: Cd, Cu, Fe, Mn, Ni, Pb and Zn (albeit that Cd was not detected). When the results are compared with the relevant NBL values in Table 6.4, it is noticeable that the mean values for Cu (120 µg $l^{-1}$), Ni (10 µg $l^{-1}$), Pb (40 µg $l^{-1}$) and Zn (140 µg $l^{-1}$) all exceed the NBLs, with the mean value for Pb also exceeding the European drinking water limit of 10 µg $l^{-1}$.

## 6.4 Hydrochemical data from previous studies of Irish holy wells and spas

### 6.4.1 Study by Buckley in 2012

As reported in Section 3.1.2, Buckley sampled 12 holy wells and three spa wells in 2012 as part of an unpublished Master's dissertation. The physico-chemical parameters EC, pH and temperature and the major ion analyses for five of these holy wells plus the three spas are presented in Table 6.5. The holy well samples are those from the three wells included as monitoring wells in the present research – St Brigid's well Tully (Co Kildare), St Kieran's well Castlekeeran (Co Meath) and Bride's well Calgath (referred to by Buckley as St Brigid's well Mulhussay, Co Meath; see Section 4.1.4 and Section 7.7) – plus two wells of particular interest, St Gorman's well near Enfield in Co Meath (a warm water well, see Section 5.9.3) and Tobar na nGealt in Co Kerry, a well with reported high lithium and a reputation for curing mental illness (Section 5.4.1.3 and Section 8.2.3).

Table 6.5 Physico-chemical parameters and major ion analyses from holy wells and spas sampled by Buckley (2012). All concentrations are in mg $l^{-1}$ except EC, pH and temperature

| Well name | EC (µS $cm^{-1}$) | pH | Temp (°C) | Ca | Mg | Na | K | $HCO_3$ | $SO_4$ | Cl | $NO_3$ (as N) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| St Brigid's well, Co Kildare | 365 | 7.43 | 10 | 150 | 19.3 | 10.9 | 5.2 | 554 | <25 | 19.3 | 4.5 |
| St Kieran's well Castlekeeran, Meath | 356 | 7.35 | | 141 | 13.1 | 8.5 | 1.9 | 362 | 15.3 | 10.9 | 7.1 |
| St Brigid's well Mulhussay, Co Meath | 284 | 7.45 | 14 | 150 | 25.7 | 10.9 | 1 | 525 | 15.8 | 17.2 | 0.7 |
| St Gorman's well, Co Meath | 450 | 7.52 | 15 | 132 | 12.7 | 9.1 | 2.8 | 466 | 9 | 15.2 | 1.4 |
| Tobar na nGealt, Co Kerry | 195 | 6.8 | | 16.3 | 3.6 | 12.4 | 0.5 | 70 | 5.7 | 20.7 | 10.9 |
| Spa well Swanlinbar, Co Cavan | 558 | 7.21 | 8 | 188 | 77.2 | 40.9 | 3.6 | 902 | 349 | 15.2 | 0.5 |
| Spa well Lisdoonvarna, Co Clare | 554 | 7.31 | 9 | 74 | 23.9 | 45.6 | 1.7 | 226 | 9.2 | 32.9 | 0.05 |
| Spa well Mallow, Co Cork | 290 | 6.79 | 14 | 85.8 | 10.3 | 13.4 | 1.4 | 276 | 20.4 | 21.7 | 12.1 |

Three of the wells – all with reputations as warm springs - have elevated water temperatures: the spa well at Mallow, St Brigid's well at Mulhussay in Co Meath and St Gorman's well, Co Meath, where the recorded water temperatures are all above normal groundwater temperatures, which are typically in the range 9-12 °C for Ireland, similar to average air temperatures (Section 7.5.1). The EC values in Table 6.5 seem to be rather low in some instances (e.g. St Brigid's well Mulhussay and St Kieran's well Castlekeeran, Co Meath) when compared to the ionic concentrations (and are lower than those recorded during the present research; Section 7.9).

The present author checked the ion balance errors for these samples (see Section 7.3 for method), and found errors of more than 10% for the water sample from St Kieran's well at Castlekeeran in Co Meath and the Swanlinbar and Lisdoonvarna spa samples. (It should be added here that there are some inconsistencies in Buckley's dissertation between data in the appendices and the data in the main text).

The major ion data in Table 6.5 indicate that the holy wells have a Ca-$HCO_3$ water chemistry. The samples from two of the spa wells were more mineralised, and the Swanlinbar sample had elevated Mg and $SO_4$ concentrations. Four of the wells had elevated nitrate concentrations when compared to the NBL of 2 mg $l^{-1}$ as N (Tedd *et al*., 2017). These are St Brigid's well in Co Kildare, St Kieran's well in Co Meath, Tobar na nGealt in Co Kerry and the Spa well at Mallow in Cork.

Buckley's trace element and minor ion results for the same wells are included in Table 6.6. Of note in the table, *inter alia*, are an elevated Al value for St Brigid's well in Co Kildare (a sand and gravel well – see Section 5.7.1.1); low As values for all the wells; elevated F and Fe in the spa well at Lisdoonvarna; and elevated Li concentrations at Swanlinbar and the Lisdoonvarna spa well (the elevated Li at Tobar na nGealt in Co Kerry is an analysis from another source – see Section 8.2.3).

Table 6.6 Trace element and minor ion concentrations in the water samples analysed by Buckley (2012). All values are in µg $l^{-1}$

| Well name | Al | As | Be | Cu | F | Fe | Li | Mn | Zn |
|---|---|---|---|---|---|---|---|---|---|
| St Brigid's well, Co Kildare | 47 | <0.37 | <0.3 | 16 | 100 | 143 | 1.4 | 28 | <1.9 |
| St Kieran's well Castlekeeran, Co Meath | 15 | <0.37 | <0.3 | 9 | 100 | 41 | 1.5 | 10 | <1.9 |
| St Brigid's well Mulhussay, Co Meath | <5 | 1.4 | <0.3 | 5 | 100 | 245 | 5.2 | 142 | 23 |
| St Gorman's well, Co Meath | <5 | 0.4 | <0.3 | 10 | 100 | 218 | 5.1 | 19 | <1.9 |
| Tobar na nGealt, Co Kerry | 6 | 0.43 | <0.3 | 8 | <100 | 9 | 55.6* | 2 | <1.9 |
| Spa well Swanlinbar, Co Cavan | <5 | <0.37 | 0.3 | 4 | 1000 | 10 | 34 | 32 | <1.9 |
| Spa well Lisdoonvarna, Co Clare | 6 | 0.37 | 0.3 | 31 | 2100 | 1221 | 51 | 15 | 8 |
| Spa well Mallow, Co Cork | 5 | 0.86 | <0.3 | 9 | <100 | <7.2 | 5.1 | 4 | <1.9 |

*Li result from Southern Scientific

Comparisons between Buckley's results and the findings of the current research are included in Section 7.9.

### 6.4.2 Previous studies of warm water spa wells

The first major report on the hydrochemistry of warm springs in Ireland was produced by Aldwell and Burdon in 1980. Major ion and some trace element analysis results were presented for 17 warm springs and boreholes in Leinster and Munster. These included five wells studied in the current research (and three of the wells sampled by Buckley in 2012): St Gorman's well near Enfield in Co Meath, Bride's River near Kilcock in Co Meath (referred to as Bride's well Calgath here, and as St Brigid's well Mulhussay by Buckley), St Bridget's well at Shangarry near Newcastle West (Co Limerick), the spa well at Louisa Bridge in Leixlip (Co Kildare) and the spa well (Lady's well) at Mallow (Co Cork). The major ion results are summarised in Table 6.7. In the original reference, the Ca and Mg concentrations are apparently given as mg $l^{-1}$ $CaCO_3$ (this is not stated, but can be inferred from the meq $l^{-1}$ values), and so have been adjusted in Table 6.7. In addition, one bicarbonate value has been corrected based on the meq $l^{-1}$ level.

Whilst Aldwell and Burdon made some preliminary observations about the origins of the warm waters at the individual sites, an interesting overall finding was that no direct relationships were observed between the major ion chemistry and the water temperature, leading to the conclusion that the 'chemical composition of Irish warm water springs is not related to the temperature of these springs'. The trace elements and minor ions analysed for included: Si, I, F, B, Se and Ba. However, the authors stated that the accuracy of some of the results is doubtful.

Table 6.7 Major ion analyses from previous studies of warm water spa wells

| Well name | Date | Ca | Mg | Na | K | $HCO_3$ | $SO_4$ | Cl | $NO_3$ (as N) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| St Gorman's well, Co Meath | 7/12/79 | 96 | 14.6 | 9 | 1 | 354 | 7 | 18 | 0.8 | Aldwell & Burdon (1980) |
| Bride's well Calgath, Co Meath[1] | 7/12/79 | 92 | 24.9 | 10 | 1 | 393 | - | 17 | 3.4 | Aldwell & Burdon (1980) |
| St Brigid's well Newcastle West, Co Limerick | 4/12/79 | 68 | 16.1 | 14 | 1 | 282 | - | 21 | 3.4 | Aldwell & Burdon (1980) |
| St Brigid's well Newcastle West, Co Limerick[2] | 11/79 – 12/83 | 68 | 13 | 16 | 1 | 257 | 13 | 24 | 0.3 | Brück *et al*. (1986) |
| Louisa Bridge spa well, Co Kildare | 7/12/79 | 118 | 33.2 | 209 | 9 | 329 | - | 446 | 1.4 | Aldwell & Burdon (1980) |
| Spa well Mallow[3] | 15/11/79 | 72 | 15.6 | 12 | 1 | 254 | 22 | 22 | 2.4 | Aldwell & Burdon (1980) |
| Spa well Mallow[4] | 11/79 – 12/83 | 73 | 11 | 15 | 2 | 234 | 17 | 27 | 0.7 | Brück *et al*. (1986) |

Notes: 1 Referred to as "Bride's River", or Breda's well, Kilcock.
2 Mean values from 10 analyses.
3 Two analyses are given for this spa well site on this date, one having normal groundwater temperature (11.3°C) and the other with warm water (20.7°C). The warm water analysis is included here.
4 Mean values from 14 analyses.

Between 1979 and 1983 Brück *et al*. (1986) monitored the water chemistry of several warm springs in Munster, including St Brigid's well at Shangarry near Newcastle West and Lady's well in Mallow. The mean values of the major ions are included in Table 6.7. St Brigid's well at Shangarry is described in Section 5.9.2 (as an example of a holy well in a confined aquifer). The likely groundwater source is Waulsortian pure unbedded limestone. The groundwater chemistry in St Brigid's well was reported by Brück *et al*. to be similar to that in local wells except for lower bicarbonate (bicarbonate has reduced solubility in warm water) and higher magnesium (possibly indicating the presence of some dolomite in the source aquifer).

The site hydrogeology for Lady's well (spa well) at Mallow has been described in Section 5.11.4. The major ion results indicate a calcium bicarbonate water chemistry, again similar to that in cold springs nearby, albeit – as in St Brigid's well at Shangarry - with higher magnesium and lower bicarbonate. These results are in line with Aldwell and Burdon's (1980) earlier observation that the water chemistry is not directly related to the temperature characteristics. Isotopic and silicon geothermometry results suggested that the warm waters at Mallow probably have their origins in Dinantian limestones at a depth of around 1100 m.

Some of the Leinster warm springs have been studied in detail in recent years, including St Gorman's well near Enfield and the former spa well at Louisa Bridge in Leixlip (Blake, 2016; Blake *et al*., 2016). The work at St Gorman's well included detailed statistical analyses (principal component analyses and multivariate statistics) of historical and contemporary water chemistry data, including water samples collected from an artesian borehole close to the spring (the latter dries up frequently – see Section 5.9.3). The raw chemical data were not included in Blake's thesis, so are not reproduced in Table 6.7. Blake *et al*. (2016) noted that the groundwater is of a calcium-bicarbonate type, and that the major ion hydrochemistry did not vary appreciably throughout the year (but the concentrations of some trace metals such as Mo and Co did vary, with increases detected in summer). The groundwater is relatively enriched in silica and bicarbonate compared to other Ca-$HCO_3$ type groundwaters. From the principal component analysis of groundwater chemistry it was found that the groundwater in winter is less evolved hydrochemically than in summer, consistent with a conceptual model whereby cool recharge water infiltrates rapidly in winter and mixes and heats up at depth (at least to 500 m and possibly up to 1000 m), before rising rapidly through the karst conduit flow system to release warm water at the surface. As noted in Section 5.9.3, St Gorman's well lies on massive unbedded lime-

mudstones of the Waulsortian, close to the faulted contact with limestones and shales of the younger Lucan Formation.

The water at Louisa Bridge Spa well was classed by Blake (2016) as being of sodium-chloride type and saline. She refers to Burdon's earlier study on Irish geothermal sources (Burdon, 1983), which observed that the elevated temperature and relatively high salinity seen at this site suggested a long residence time, and which provided isotopic evidence that the water at Louisa Bridge has a component with a residence time of more than 30,000 years. Based on her detailed analysis of major ion and trace element hydrochemistry, including evidence for dissolution of evaporitic minerals, Blake (2016) concluded that the groundwater source for the Louisa Bridge Spa well is from below the Dublin carbonate basin, possibly from Devonian strata.

The water chemistry results from these warm water spa wells are discussed further in relation to the present research findings in Section 7.9.

# 7 Chemical sampling and results

The chemical sampling methods and results are described in this chapter. Summary statistics of the main results are presented, together with a discussion of these findings in relation to previous hydrochemical studies in Ireland. The implications of the results in terms of health and reputed cures for holy wells are considered in Chapter 8.

## 7.1 The sampling programme

### 7.1.1 Number of wells sampled

The sampling programme involved 167 out of the 215 surveyed holy wells, together with the five spa wells. In addition, the four wells selected for monitoring (Section 4.1.4) were resampled over a 2-year period to assess whether their hydrochemistry varied across the seasons. The total numbers of water samples, wells sampled, monitoring well samples, duplicates etc. are indicated in Table 7.1. Not all the surveyed wells were sampled, since many were either dry or contained too little water to sample, or were inaccessible (covered over, or overgrown), or because several other wells in the area had already been sampled.

Table 7.1 Number of water samples

| Item | Number | Comment |
|---|---|---|
| Wells surveyed | 221 | Includes 215 holy wells, five spa wells and one other well |
| Wells sampled | 172 | Includes 167 holy wells and five spa wells, but excludes one well sampled which was later found not to be a holy well |
| Water samples | 238 | Includes duplicates, monitoring well samples, repeat samples and spa wells |
| Monitoring well samples | 33 | Collected from four monitoring wells |
| Re-sampled wells | 21 | Excludes duplicates and monitoring wells. Note: one well (St Kevin's well Glendalough) was resampled twice |
| Duplicate samples | 15 | Includes one spa well (Lady's well Mallow) |
| Split samples/partial duplicates | 10 | These are samples for which some of the major ions were also analysed at a second lab |

The method proposed by Cochran (1977) for examining the size of a survey, which was applied to the well surveys in Section 4.1.1, was also applied to the number of wells (*N*) sampled for chemical analysis. Here, the total population of potentially sampleable wells is likely to be much less than the nominal total well population of 3000, since many wells are dry, covered over or otherwise inaccessible for sampling. Assuming that 50% of the 3000 wells could potentially be sampled then, for a confidence level of 95% and *p* value of 0.5 (*p* here is the proportion of population with a particular attribute), the margin of error (in survey terms) associated with sampling 167 of these wells would be 7.15% (which would increase to e.g. 7.26% for a population of 2000 sampleable wells).

The distribution of the sampled holy wells according to the main lithological groupings is summarised in Table 7.2. Margins of error (*e*) calculated using the Cochran method are included (see Eq 4.1). Comparing *e* values in the table, it is likely that the samples from the igneous and the sand and gravel lithologies are less representative of the full well populations for those lithologies. As stated in Section 4.1.1, these margin of error calculations do not include the mixed bedrock and gravel lithological group (because this group was not part of the GIS analysis of the total well population in Chapter 3). Several of these wells would fall within the sand and gravel group, which would reduce the margin of error for that group. The *e* values should be regarded merely as giving some indication of how representative the chemical analysis results are for the total number of wells in the particular lithology: they do not in any way indicate the *accuracy* of the analysis results, which is considered in Section 7.3.

Table 7.2 Number of wells sampled in each lithological group

| Lithological group | Number wells in GIS analysis (Section 3.3) | Wells surveyed (Section 4.1.1) | Wells sampled | Percent | Calculated margin of error |
|---|---|---|---|---|---|
| Impure limestone | 492 | 35 | 26 | 74.3 | 18.7 |
| Pure limestone | 686 | 49 | 38 | 77.6 | 15.5 |
| Non-calcareous sedimentary | 657 | 47 | 39 | 83.0 | 15.2 |
| Igneous | 215 | 16 | 14 | 87.5 | 25.4 |
| Metamorphic | 470 | 46 | 35 | 76.1 | 16.0 |
| Sands & gravel | 49 | 8 | 6 | 75.0 | 37.9 |
| Mixed bedrock & gravel | - | 13 | 9 | 69.2 | N/A |
| TOTAL | 2569 | 214[a] | 167 | 78.0 | N/A |

Note: [a]The total surveyed wells in this table is given as 214 rather than 215, as it excludes a bullaun stone (the Wart well, Timoleague) which is not a well

### 7.1.2 Choice of parameters

The choice of parameters for analysis took into account the findings of the literature review of hydrochemistry in Chapter 6, especially of the links between groundwater quality and health (Section 6.2), and the baseline chemical characteristics of Irish groundwaters established in previous studies (Section 6.3). It also took account of which parameters could practicably be analysed for, either on site, in the Trinity College Dublin labs, or in the external labs also used (see Section 7.2 below). The parameters analysed included the major ionic species plus a large number of minor ions and trace elements.

The main purpose of analysing water samples for major ions was to provide information on water types, although certain major ions have health implications (e.g. magnesium and sulphate – Sections 6.2 and 8.1). The major ions (as defined here) are calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), bicarbonate ($HCO_3$), sulphate ($SO_4$), chloride (Cl) and nitrate ($NO_3$). Nitrate was considered especially important as an indicator of potential anthropogenic contamination (Section 7.5.2). The results for silicon (Si) are presented with the major ions: although Si does not behave in solution like a charged ion (Hem, 1985), its abundance in groundwater is similar to that of the major ions (see Table 6.1).

The minor ions and trace elements analysed included those elements that were identified (based on the literature review in Section 6.2) as being beneficial for health, and/or are harmful when present in excess. The full list of minor ions and trace elements analysed is shown in Table 7.3. The elements are arranged by chemical group, and by increasing atomic mass within each group.

In total, 51 minor ions and trace elements were analysed. An additional parameter, iodide, was measured in a small number of samples (Section 7.2.3). Not all parameters could be determined in every sample, owing to e.g. some values being below the blank limit for the analysis, or a particular calibration standard not being available. Moreover, the TCD Geochemistry lab where these analyses were performed was out of action for a few months in 2017 (owing to a building refurbishment programme), and thus samples from 11 out of the 167 wells were subjected to major ion analyses only (in an external laboratory).

Table 7.3 Minor ions and trace elements analysed in this research

| Chemical group | Element |
|---|---|
| Alkali metals | lithium (Li), rubidium (Rb), caesium (Cs) |
| Alkali earth elements | beryllium (Be), strontium (Sr), barium (Ba) |
| Metalloids | arsenic (As), antimony (Sb) |
| Non-metals | fluoride (F), phosphorus (P), selenium (Se) |
| Transition elements | scandium (Sc)[1], titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y)[1], zircon (Zr), niobium (Nb), molybdenum (Mo), cadmium (Cd), hafnium (Hf), tantalum (Ta), tungsten (W) |
| Post-transition elements | aluminium (Al), gallium (Ga), indium (In), tin (Sn), thallium (Tl), lead (Pb) |
| Lanthanide rare earth elements[2] | lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), terbium (Tb), gadolinium (Gd), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutelium (Lu) |
| Actinides (radionuclides) | thorium (Th), uranium (U) |

Note [1] Sc and Y are also classified as rare earth elements

[2] There are 14 lanthanides listed here (a 15th REE, promethium [Pm] does not occur naturally on earth)

From the outset, it was not proposed to test the wells for their microbiological water quality, since the current microbiological quality is unlikely to bear much relationship to that at the time when the well first gained a reputation as a holy well. Furthermore, there would have been practical difficulties in carrying out the microbiological analyses on the same day as the collection of samples (same-day analysis being generally required for parameters such as *E coli*), since the wells are located all over Ireland and it would not have been possible to travel back to the Trinity College laboratory each day. Nor was it proposed to test for synthetic organic chemicals, since it was not the objective of this research to determine the nature and full extent of anthropogenic impacts on water quality in holy wells. However, nitrate was tested for, to give a general indication as to whether there were anthropogenic impacts (Section 7.5.2).

### 7.1.3 Sampling procedures

The sampling procedures followed the general protocols outlined in Barcelona *et al*. (1985), US Geological Survey (2015) and Misstear *et al*. (2017). However, it should be noted that it was not

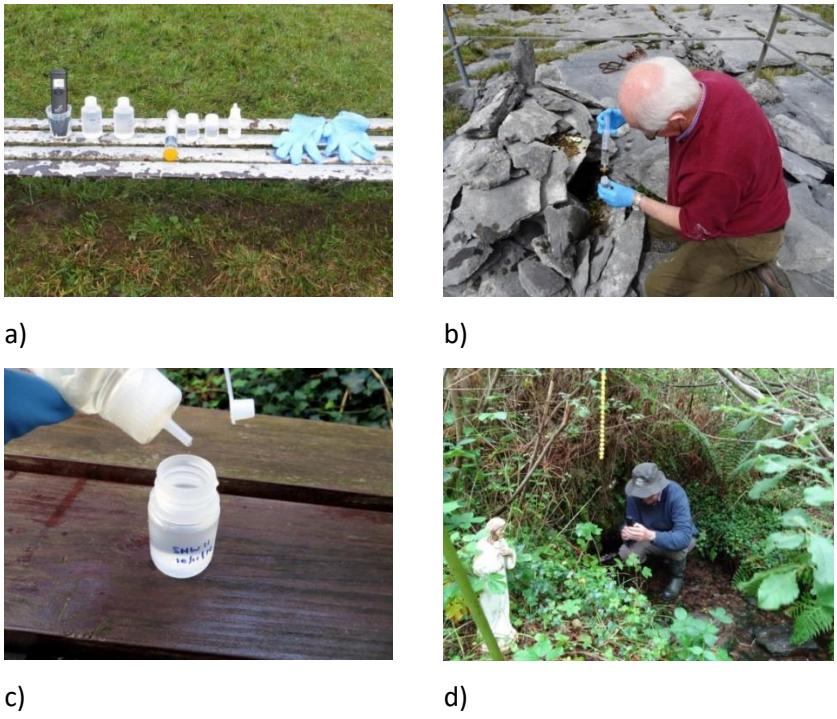
possible to collect pumped samples, or to 'purge' the wells (which are mainly shallow spring wells – Chapter 5) as would normally be done when collecting groundwater samples from boreholes. Parameters that are particularly sensitive to redox conditions include iron, manganese and many of the trace elements (Section 7.6). Nevertheless, collecting 'grab' samples from the open wells and springs in the manner of this research is likely to give results more reflective of the water quality experienced by pilgrims drinking from these sources.

The basic physico-chemical parameters of temperature, pH and electrical conductivity were determined on site using a Hanna Instruments Cambio portable meter. The pH probe was calibrated each day using pH 4 and 7 buffer solutions. The EC was calibrated periodically using a standard KCl solution but was found to be very stable. The EC readings were automatically corrected by the meter to give values at 25 $^{o}$C.

Water samples intended for trace element and cation analysis were collected in 30 ml polypropylene (Nalgene brand) bottles: these were preferred to glass bottles since the latter can contaminate water with many elements, including the REEs (Cicchella *et al*., 2010), albeit plastic bottles can 'seriously contaminate the water with Sb' according to Reimann and Birke (2010). The bottles were acid washed in Milli-Q ultrapure deionised water and then soaked in 5% (about 0.75 molar) ultra-pure nitric acid for one to two weeks prior to sampling. The bottle caps were rinsed and refilled with Milli-Q and then wrapped with Parafilm M seals and placed in plastic bags prior to transportation to the field. In the field, each sample was collected in a 50 ml BK Plastipak Luer-Lok syringe, which was rinsed with the target sample prior to being fitted with an Acrodisc filter (MilliPore) with a 0.45 µm polyethersulfone membrane and PP housing. A new syringe and filter tip was used for each sample. After removing the seal and decanting the ultrapure water, the 30 ml bottle was filled to about three-quarters full from the filter-syringe and then 25 drops of concentrated nitric acid were added (to give an approximate 2% [0.3 molar], solution), before filling the remainder of the bottle from the filter-syringe; care was taken to ensure that as little air as possible remained in the head space. The full bottles were then sealed with Parafilm M seals and placed in a cool box on site, prior to transportation to a fridge (for keeping at about 4 $^{o}$C) and then to the laboratory for analysis. The main purpose of acidizing samples intended for trace element and cation analysis was to ensure that these parameters stayed in solution, and to reduce the likelihood that trace metals would adsorb to the sample container.

Samples for anion analysis were collected in 125 ml or 250 ml Nalgene bottles. The bottles were cleaned with deionised water prior to transport to the field and were rinsed three times with water from the target source prior to collecting the sample. These samples were neither filtered nor acidified. For samples to be sent to an external laboratory for determination of all major ions, the samples were normally collected in 500 ml Nalgene bottles (again the samples were neither filtered nor acidified).

Examples of field sampling procedures are illustrated in Figure 7.1.



a) b)

c) d)

Figure 7.1 Field sampling: a) sampling equipment, including two sets of 30 ml and 125 ml sample bottles (for duplicate samples), syringe and filter, plastic gloves and EC/pH meter; b) adding sample from a filter-syringe to a 30 ml sample bottle (Poll Insheen, Co Clare); c) adding drops of nitric acid preservative to a 30 ml sample bottle (which was then filled with sample to the top, trying to avoid any air being trapped in the headspace); d) measuring the EC at Tobar na nGealt in Co Kerry. Photos by Bruce and Gillian Misstear

## 7.2 Chemical analysis methods

The parameters analysed and the methods used are summarised in Table 7.4. The table also indicates where the analyses were carried out.

Table 7.4 Summary of water analysis parameters, main analysis locations and methods

| Category | Parameters | Where analysis carried out | Method |
|---|---|---|---|
| Main physico-chemical characteristics | EC, pH, temperature | At the well site | Portable meter |
| Major cations | Ca, Mg, Na, K | TCD Geochemistry lab | ICP-MS |
| Major anions | Alkalinity ($HCO_3$) | TCD Envir Engineering lab | Titration |
| | $SO_4$, Cl, $NO_3$ | TCD Envir Engineering lab & external labs | Photometric |
| Minor ions / elements | Fe, Mn, P<br>F<br>Si | TCD Geochemistry lab<br>External labs<br>TCD Geochemistry lab & external labs | ICP-MS<br>Ion electrode<br>ICP-MS (TCD)<br>ICP-OES (external lab) |
| Trace elements, including REE | Li, Be, Al, Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Th, U | TCD Geochemistry lab | ICP-MS |

Note: several duplicate samples were tested at the external labs for all major ions

### 7.2.1 Cation and trace element analyses in TCD Geochemistry laboratory

The cations and trace elements were analysed in the TCD Geochemistry laboratory by Cora McKenna. The method used was inductively coupled plasma – mass spectrometry (ICP-MS). Analyses were carried out using a Thermo Scientific iCAP-Qc quadrupole ICP-MS coupled with an ESI SC-2 DX microFAST autosampler fitted with a 1.5 ml loop. The instrumentation is shown in Figure 7.2. ICP techniques involve the creation of a high temperature plasma of ionized gas, which is generated by applying a strong magnetic field to an inert gas (such as argon). A small amount of liquid sample is introduced through a nebulizer, which converts the liquid to a fine

aerosol mist using a separate stream of argon gas. The sample aerosol is fed into the central region of the plasma where it is ionised. In quadruple ICP-MS, the charged particles are filtered using a dynamic electrostatic field created between four conductive rods, such that only analyte ions of a single mass-to-charge ratio (m/z) are transmitted to the detector at one time. By changing the voltages applied to the rods, the quadrupole can switch between target m/z in order to measure different elemental ion abundances in the sample. The detector, a scanning electron multiplier, receives and amplifies an ion signal that is proportional to concentration, as determined through calibration with one or more reference materials of known composition. This technique allows a large number of elements to be analysed, and to very low detection limits. However, there can be polyatomic interferences between elements that have similar mass to charge ratios; notably for this study, the results for elements such as Ti, V, Cr, Co, Zn and As can be prone to interferences from molecules of the potentially major constituents chlorine, calcium and sulphur.



Figure 7.2 The ICP-MS set-up in the TCD Geochemistry laboratory. Photos by Cora McKenna

The following description of the analysis methodology was provided by Cora McKenna. The ICP-MS trace element analysis method is adapted from the experimental design of Lawrence *et al*. (2006a) and Babechuk *et al.* (2010), and is described in detail in Babechuk *et al*. (2020). Centrifuge tubes were prepared containing 1.8 g of sample mixed with 0.2 g of internal standard (IS). Addition of the internal standard mix enabled correction of matrix-related signal drift during the measurement session. A mixture of $^{6}$Li, $^{103}$Rh, $^{187}$Re, $^{209}$Bi and $^{235}$U was chosen for the internal standard to cover the full mass and ionization potential range of the analysed elements. Groups of five unknowns were bracketed using the USGS W-2a rock standard in order to monitor instrumental drift over the course of each analytical session. Internal standard and external

monitor drift corrections were carried out offline in accordance with procedures described in Eggins *et al.* (1997), while spectral interference corrections followed Ulrich *et al*. (2010) using production rates measured on pure elemental solutions in routine pre-experiments.

Multiple dilutions from six separate digestions of USGS rock standard W-2a were used for calibration, while the USGS rock standards BIR-1, BHVO-2 and AGV-2 and NRC natural river water standard SLRS-6 were analysed as unknowns to test external precision of the trace element data.

Dwell times varied between 5 ms and 30 ms, depending on the expected concentration of each analyte. Three runs were completed on each 1.5 ml sample aliquot comprising 26 sweeps each across three channels. Relative standard deviations (RSD) of the analysed rock and natural river water standards ranged from 0.2% to 5%, averaging <2% for the 55 major cations and trace elements measured and the concentrations were comparable to GeoReM preferred values.

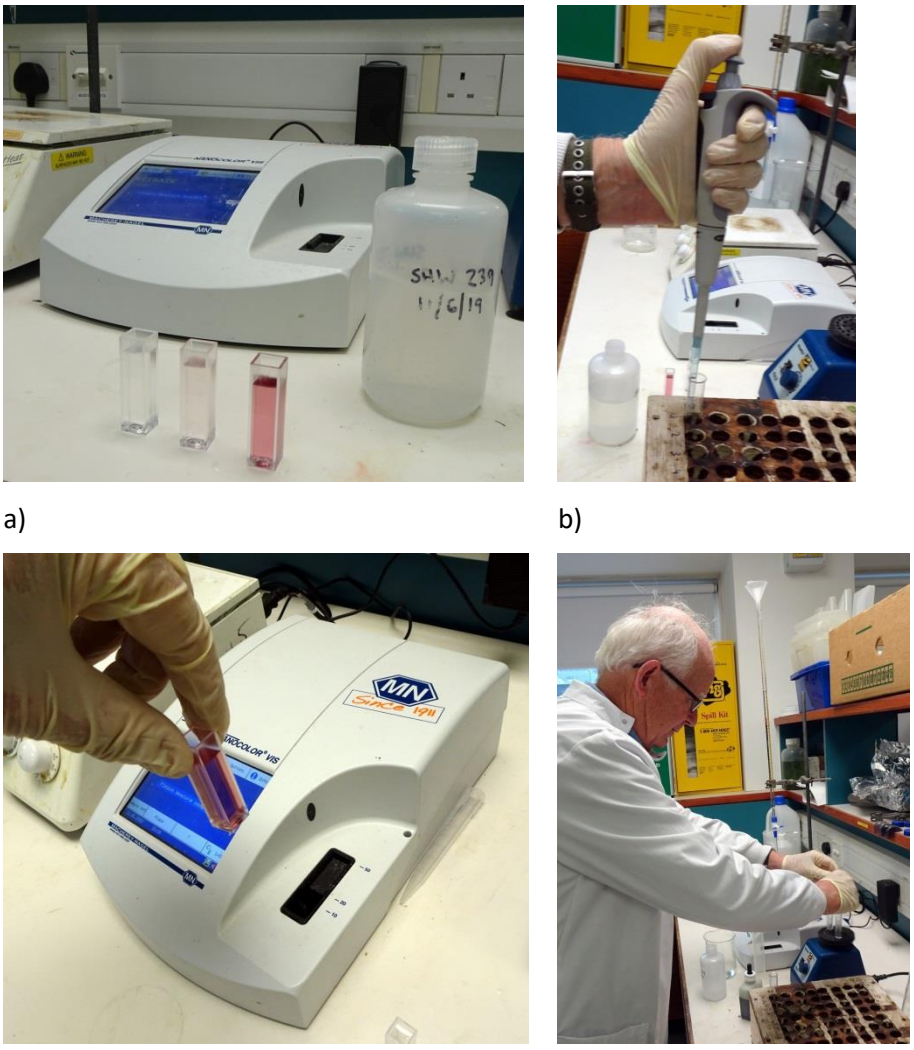
### 7.2.2 Anion analyses in TCD Environmental Engineering laboratory

Alkalinity was determined by this researcher in the TCD Environmental Engineering lab using a standard titration technique (Figure 7.3). A 50 ml water sample was titrated with a 0.02 N solution of $H_2SO_4$ with pH 4.5 as the end point, using a bromocresol green-methyl red indicator solution. As alkalinity can change over time due to degassing or absorption of $CO_2$ from the atmosphere, the samples were normally analysed within 24 to 48 hours of collection.



Figure 7.3 Alkalinity titration in TCD Environmental Engineering lab

Nitrate was analysed in the Environmental Engineering lab using a spectrophometric method (Figure 7.4). The ionic concentrations were determined using a Merck Spectroquant Nova 60 spectrophotometer and associated reagent test kit. The nitrate test is based on the reaction of nitrate ions with 2,6-dimethylphenol in a sulphuric and phosphoric solution to form 4-nitro-2,6-dimethylphenol that is determined photometrically. Using a 10 mm measurement cell, the measurement range was 1.0 – 25 mg $l^{-1}$ as N.



a) b)

c) d)

Figure 7.4 Nitrate analyses: a) three sample cells: from left, blank (clear), standard (slight pink colour) and high nitrate sample with strong pink reagent colour (sample from St Colman's well, Salterstown, Co Louth – see Section 7.5.2); the spectrophotometer is in the background; b) pipetting a sample for nitrate analysis; c) inserting sample cell into the spectrophotometer; d) ensuring samples are well mixed, using an auto stirrer. Photos by Bruce Misstear

In some samples, sulphate and chloride were also determined using the Merck spectrophotometer. The sulphate Spectroquant test is based on the reaction between sulphate ions and barium ions to produce barium sulphate, with the resulting turbidity measured in the photometer. Using a 10 mm measurement cell, the measurement range for sulphate was 2.5 – 50 mg $l^{-1}$. Several samples were also analysed for $SO_4$ in the TCD Environmental Engineering lab photometrically using a Konelab 20XT (Thermo Fisher Scientific Inc), with a method detection limit of 0.26 mg $l^{-1}$. Other samples were analysed in a commercial laboratory (see below).

The chloride Spectroquant test in the Merck spectrophotometer is based on the following reactions (to quote the test leaflet): 'chloride ions react with mercury (II) thiocyanate to form slightly dissociated mercury (II) chloride. The thiocyanate released in the process reacts in turn with iron (III) ions to form red iron (III) thiocyanate that is determined photometrically'. With a 10 mm measurement cell and using 1 ml of sample, the measurement range for chloride was 10 – 250 mg $l^{-1}$. Chloride analyses proved to be unreliable (when compared against standard solutions), even after exhaustive checks using different equipment, reagents, glassware, standard solutions, etc. Hence, samples were also analysed for Cl photometrically in the TCD Environmental Engineering lab using the Konelab 20XT (with a detection limit of 0.035 mg $l^{-1}$), and at a commercial laboratory (see below).

### 7.2.3 Analyses carried out in external laboratories

Two accredited external laboratories were used, mainly for analysis of anions and duplicate samples: City Analysts Ltd, based in Ringsend in Dublin, and CAL Ltd, in Dun Laoghaire, Co Dublin.

*City Analysts Ltd methods*

In this project, the main analyses performed by this lab were for fluoride, nitrate, chloride and sulphate. Unfiltered and unacidified samples were provided to the lab for these anion analyses.

Fluoride was determined using a Thermo Orion specific ion electrode with a range of 0.1 to 5.0 mg $l^{-1}$, although values less than 0.1 mg $l^{-1}$ were reported in the data sheets.

The laboratory method for chloride is based on the reaction between chloride, mercuric nitrate, 2,4,6-tripyridyl-s-triazine (TPTZ) and ferrous ions to produce a blue colour, which was measured at a wavelength of 660 nm. An AQ2 Automated Discrete Analyser was used (Seal analytical Products). The range was 10-500 mg $l^{-1}$, although values less than 10 mg $l^{-1}$ were reported in the raw data sheets.

The determination of sulphate was by the turbidimetric measurement of the precipitated barium salts. The barium sulphate precipitate is held in suspension by the addition of a small amount of gelatine to the barium chloride reagent. The turbidity is measured at 520 nm. The range was 20-500 mg $l^{-1}$, although values less than 20 mg $l^{-1}$ were also reported in the raw data sheets.

Nitrate was determined by calculation from the total oxidized nitrogen (TON) and nitrite analysis results: the method for TON is based on the reduction of nitrate to nitrite by hydrazine under alkaline conditions, using cupric ions as a catalyst. The total nitrite was then treated with sulphanilamide and N-1-naphthylethylenediamine dihydrochloride under acidic conditions to form a pink azo-dye, which is measured at 520nm. The range was 2-100 mg $l^{-1}$ as N, although values less than 2 mg $l^{-1}$ were reported in the raw data sheets.

Where samples were submitted to City Analysts for full major ion analyses, the cations were determined by ICP-OES (inductively coupled plasma – optical emission spectrometry) – using an iCAP 6000 series Spectrometer (Thermo Fisher Scientific) - and the anions by the methods already described. Silica was also determined by ICP-OES (reporting limit 0.1 mg $l^{-1}$).

*CAL Ltd methods*

The CAL lab was used for some samples, involving anions (chloride, sulphate, nitrate and fluoride), plus a number of full major ion analyses. Samples were sent by CAL to ALS Environmental in Kildonan, Dublin. The analysis methods adopted were broadly similar to those reported for City Analysts, and are only described briefly here.

Chloride and nitrate were both determined by a photometric technique using an Aquakem 600 Discrete Analyser. The reporting limit for chloride was 0.6 mg $l^{-1}$. In the case of nitrate, this was again calculated by difference between TON and nitrite (with a reporting limit of 0.3 mg $l^{-1}$ as

$NO_3$). Alkalinity was also determined using the Aquakem 600 Discrete Analyser (reporting limit of 3.9 mg $l^{-1}$ as $CaCO_3$). Sulphate (reporting limit 0.34 mg $l^{-1}$) plus cations were analysed using an ICP-OES, whilst fluoride was measured with an ion electrode (reporting level 0.1 mg $l^{-1}$).

Ten water samples were also tested for iodide, using the Dionex ion chromatography method, giving values below the reporting limit of 0.1 mg $l^{-1}$ in all cases. One sample was checked for lithium (Li was one of the suite of analyses performed in the TCD Geochemistry lab), and the method used was a Perkin-Elmer Nexion ICP-MS, with a reporting limit of 0.4 µg $l^{-1}$. This sample was provided in a 30 mL HDPE sample bottle that had been filtered and acidified in the field.

## 7.3 Quality assurance checks and ion balance errors

Quality control procedures included analysis of field blanks (acidified and filtered), analysis of samples of the nitric acid used in the acidification, and analysis of duplicate samples. For the trace element analyses, results were checked against a number of standard solutions and compared to results from different geochemical databases, as described in Section 7.2.1. The major ion determinations, on the other hand, were checked by calculating the ion balance error. IBE determinations were considered especially important in this project, in view of the fact that samples were part-analysed in different laboratories (cations in the TCD Geochemistry lab, anions in the TCD Environmental Engineering lab and/or in an external lab; see Section 7.2).

The ion balance errors (IBEs) were calculated using the relationship:

$$IBE = \frac{[\text{sum cations - sum anions }]}{[\text{sum cations + sum anions }]} \times 100\% \qquad (7.1)$$

where the ionic concentrations are given in meq $l^{-1}$. Ideally, the ion balance errors should be < ±5% (Fritz, 1994). The IBE results for the holy well and spa well samples are shown in Table 7.5.

All but two of the wells with IBEs >10% were resampled (the exceptions were St Menaghan's well in Co Westmeath and Tobar Mhuire Titeskin Co Cork), as were several of the wells with IBEs in the range 6-10%. Excluding the four monitoring wells (which were sampled several times during the project; Table 7.1), 21 wells were resampled in total, including 16 wells with water sample IBEs >10%. In 17 of the 21 wells, the repeat analyses gave IBEs <5%. In the case of St Kevin's well Glendalough (Co Wicklow), the well was resampled twice because the IBE remained

high in the second analysis result (-38% compared to -40% for the first sample), but the IBE for the third sample was still high, albeit improved (-17.5%). St Aidan's well Preban (Wicklow) and St John's well Mushera (Cork) also gave high IBEs second time round (-13% and -11%, respectively). All three of these wells have low EC values (around 40, 50 and 110 µS $cm^{-1}$ for the Glendalough, Preban and Mushera wells, respectively), indicating low TDS, so a small error in one parameter can have a large impact on the IBE. The other well that gave a high IBE in the first analysis produced an IBE of 6% when sampled a second time. This was St Brigid's well at Mountbridget in Cork, and it also had a fairly low EC (160 µS $cm^{-1}$). At the other end of the TDS spectrum, the well with the highest EC value also gave a high IBE: St Brendan's well Roskeen in Co Mayo, which contained seawater (EC = 61,150 µS $cm^{-1}$; IBE = -29%). Here, the sodium result, in particular, was suspect (Section 7.5.5). This well was not resampled, as analysing such saline water was problematic for the TCD Geochemistry laboratory.

Table 7.5 Ion balance errors

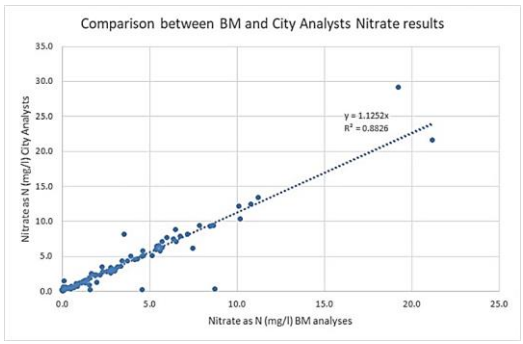
| Ion balance error range (%) | Number of analyses[a] | Percent |
|---|---|---|
| 0-5 | 174 | 74 |
| 6-10 | 35 | 15 |
| 11-15 | 13 | 5 |
| >15 | 14 | 6 |
| Total | 236 | 100 |

Note: [a]The total of 236 analyses excludes a well believed not to be a holy well and one sample (SHW221) where only cations were analysed

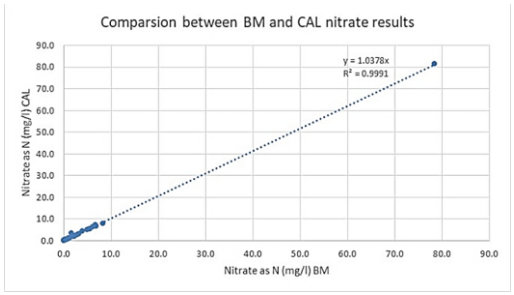
Importantly, taking the best (i.e. lowest IBE) single results for the 172 wells sampled (167 holy wells plus five spa wells), only nine samples (5%) had IBEs greater than 10%. Moreover, of the 167 holy wells sampled, 136 (81.4%) had IBEs in the range 0-5%. For these 167 wells, the IBE was negative in 83 cases, positive in 56 cases and neutral (i.e. IBE = 0%, when expressed to the nearest whole number) in 28 cases.

A major ion of particular importance for this study was nitrate, as nitrate is normally a good indicator of anthropogenic pollution (since it occurs naturally in groundwater only in low concentrations, and elevated values are indicative of contamination from sources such as agriculture and wastewater – see Section 6.2.3 and Section 7.5.2). In addition to the analyses carried out by this researcher in the TCD Environmental laboratory, 109 samples were analysed

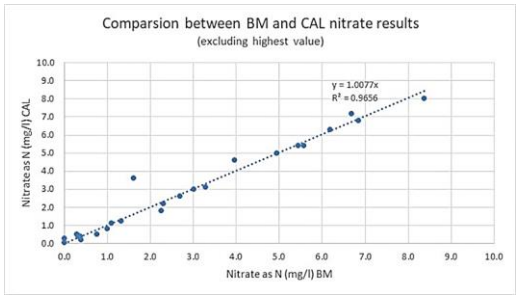
for nitrate in external labs. The comparisons between the datasets are illustrated in Figure 7.5. It can be seen that there was a good correlation between the data from the TCD lab and those from the two external labs (and especially with the nitrate values from the CAL lab). The nitrate results from the latter included a sample with very high nitrate (81.5 mg $l^{-1}$ as N), which is represented on Figure 7.5b, whilst the scatter plot for the remaining results excluding this value is illustrated in Figure 7.5c.




a)




b)




c)

Figure 7.5 Comparison between nitrate results from different laboratories: a) results from the TCD Env Eng lab plotted against those from City Analysts (n = 83 samples); b) results from the TCD Env Eng lab plotted against those from CAL (n = 26 samples); c) results from the TCD Env Eng lab plotted against those from City Analysts, but excluding the single high nitrate value shown in Figure 7.5b (n = 25 samples)

Finally, cation and trace element analyses for six samples (SHW230 to SHW235) were repeated by the TCD Geochemistry lab owing to anomalies in the cation values in the first set of results, especially when compared to the major ion results from duplicate samples analysed in an external lab. The repeat cation values were in line with the external lab results.

## 7.4 Statistical treatment of the water chemistry data

Before presenting the results of the chemical analyses, it is worth saying a few words about the statistical treatment of the chemical data. Statistical analyses were carried out using Excel and the statistical package Minitab (both the 17 and 19 versions were used). Standard descriptive statistics such as medians, means and percentiles were calculated for all the main parameters. The results were also plotted using histograms, cumulative probability diagrams and box plots.

Differences between selected groups of results were examined for their significance using one-way analysis of variance (ANOVA) and Mann-Whitney U tests. ANOVA has been used previously in studies of water chemical data in Ireland (e.g. Fennell, 2017; Tedd *et al*., 2017; Kavanagh *et al*., 2017). In this method, the null hypothesis $H_0$ (that the *means* of the groups are equal) is tested and a significant result occurs when the means are found not to be equal. The significance of the result of the ANOVA analysis is assessed using two factors: the F value and the p value. The F value is the variance of the group means (mean square between) to the mean of the within-group variances (mean square error). This is compared with the F critical value: if the F value is greater than F critical then it indicates that the result is significant i.e. the null hypothesis can be rejected. The p value is the probability that the differences could have occurred by chance; a p value of <0.05 is normally used for tests of significance (or sometimes $p < 0.01$ to indicate a higher level of significance). When comparing data from three or more groups, the ANOVA test is followed by a post hoc analysis to see which of the groups differ. This post hoc analysis involves a pair-wise comparison between all the groups. The method used here for the post hoc analysis in Minitab was the Fisher least significant difference test. However, it should be noted that, as with the basic statistical method itself, the results of the posthoc test can vary according to the posthoc method used (Fisher, Tukey, Dunnett, etc).

The ANOVA test assumes continuous data with a normal distribution. However, the test is said to be robust against the normality assumption i.e. it can tolerate data that are skewed and/or

that have high kurtosis. According to Sawyer (2009), the ANOVA test is robust against non-normality provided the samples size is ≥30. Kolmogorov-Smirnov tests for normality were carried out on all the chemical analysis results (and other tests such as chi-square goodness of fit, the Anderson-Darling and the Ryan-Joiner tests were also tried), but the tests showed that the null hypothesis (that the distribution was normal) was rejected in the majority of cases.

Where the data were not normally distributed, comparisons between two groups were carried out using the non-parametric Mann-Whitney U test. This tests the null hypothesis that the *medians* of the groups are the same. However, the Mann-Whitney U test cannot be used to compare more than two groups. For more than two groups where the data are non-parametric, the Kruskal-Wallace test could be used. However, whilst this test can show up that one pair of groups are significantly different, it does not indicate which pair. Moreover, there is no direct equivalent to the Fisher post hoc test that is used with ANOVA (Dytham, 2011).

Therefore, when comparing multiple groups (such as differences in a mean chemical value between several lithological groups), the chemical data were first log-transformed ($\log_{10}$ was found to be the most suitable transformation) to try to induce normality. (Kavanagh et al. [2017] also found log-transformation to be the most useful with their data on lithium in groundwater). Examples of the Kolmogorov-Smirnov test for goodness of fit are shown in Figure 7.6, for a major ion (K, all data) and a trace element (Al, igneous lithological group).

It can be seen in Figure 7.6 that whereas the raw data fail the normality test (i.e. the null hypothesis of normal distribution is rejected, with $p < 0.05$), the data after log transformation satisfy the null hypothesis that the data are not significantly different from normal ($p > 0.15$). When log transformations were applied to the pH, EC and major ion data for the seven lithological groups, the percentage of test results that achieved normality increased from 44% to 75%, thus making the parametric assumption of the ANOVA method more applicable. For the 51 minor ions and trace elements, log-transformations resulted in 88% of the data for the seven lithological groups achieving normal distributions.

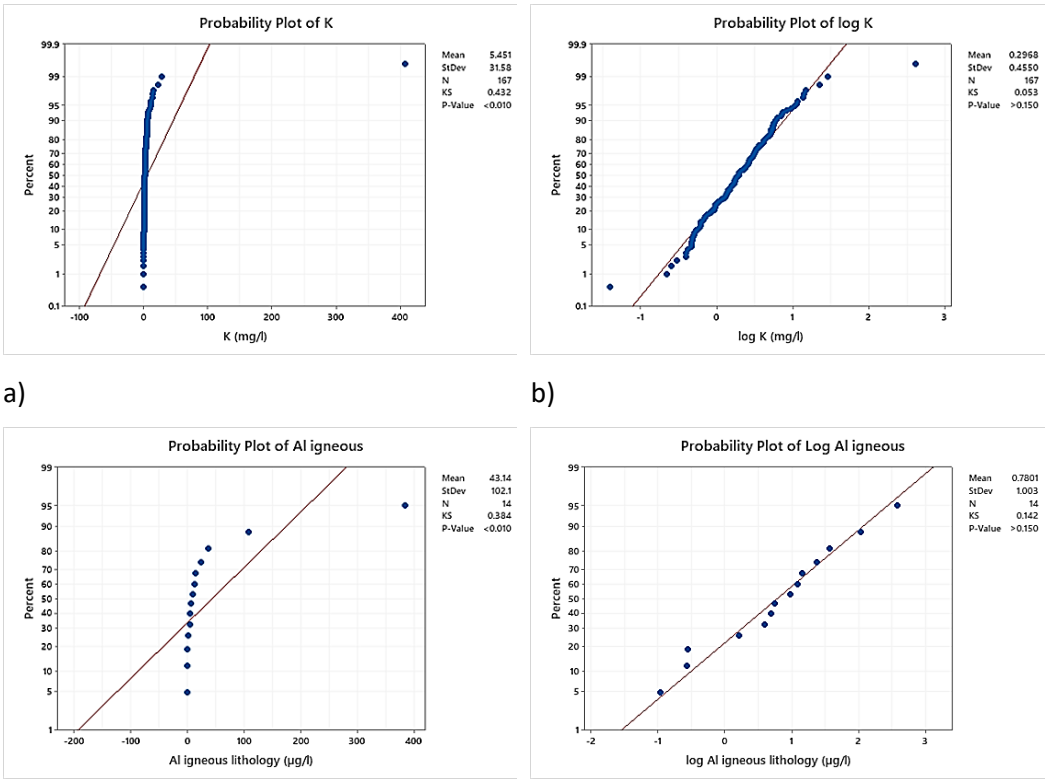



Figure 7.6 Examples of normality checks using the Kolmogorov-Smirnov test: a) K data (full dataset, n = 167; b) K data after log transformation; c) Al data (igneous lithological group, n = 13); d) Al data after log transformation

Examples of the Minitab print output for ANOVA and Mann-Whitney U tests are included in Figures 7.7 and 7.8, respectively. In both cases, these are comparisons of EC values between coastal and non-coastal well samples (coastal wells being regarded here as those wells within approximately 500 m of the shoreline; see Section 5.10). Both tests showed that the null hypothesis was rejected and that the mean (ANOVA) and median (Mann-Whitney) EC values were significantly different between the coastal and non-coastal well samples (see Section 7.5.5 for further discussion). It should be noted that the EC values for the ANOVA test in this example were not log-transformed (but that the test still gave a similar result to the non-parametric Mann-Whitney U test).

**One-way ANOVA: EC coastal, EC non-coastal**

**Method**

| | |
|---|---|
| Null hypothesis | All means are equal |
| Alternative hypothesis | Not all means are equal |
| Significance level | α = 0.05 |

*Equal variances were assumed for the analysis.*

**Factor Information**

| Factor | Levels | Values |
|---|---|---|
| Factor | 2 | EC coastal, EC non-coastal |

**Analysis of Variance**

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Factor | 1 | 121445690 | 121445690 | 5.64 | 0.019 |
| Error | 165 | 3551899059 | 21526661 | | |
| Total | 166 | 3673344749 | | | |

**Model Summary**

| S | R-sq | R-sq(adj) | R-sq(pred) |
|---|---|---|---|
| 4639.68 | 3.31% | 2.72% | 0.00% |

**Means**

| Factor | N | Mean | StDev | 95% CI |
|---|---|---|---|---|
| EC coastal | 31 | 2662 | 10868 | (1017, 4307) |
| EC non-coastal | 136 | 468.6 | 248.2 | (-317.0, 1254.1) |

*Pooled StDev = 4639.68*

Figure 7.7 Example of an ANOVA test output for a comparison of EC data between coastal wells and other wells (note: DF = degrees of freedom; SS = sum of squares; MS = mean square; other terms are described in the text)

**Mann-Whitney: EC coastal, EC non-coastal**

**Method**

$\eta_1$: median of EC coastal
$\eta_2$: median of EC non-coastal
Difference: $\eta_1 - \eta_2$

**Descriptive Statistics**

| Sample | N | Median |
|---|---|---|
| EC coastal | 31 | 589.0 |
| EC non-coastal | 136 | 486.5 |

**Estimation for Difference**

| Difference | CI for Difference | Achieved Confidence |
|---|---|---|
| 139 | (39, 280) | 95.02% |

**Test**

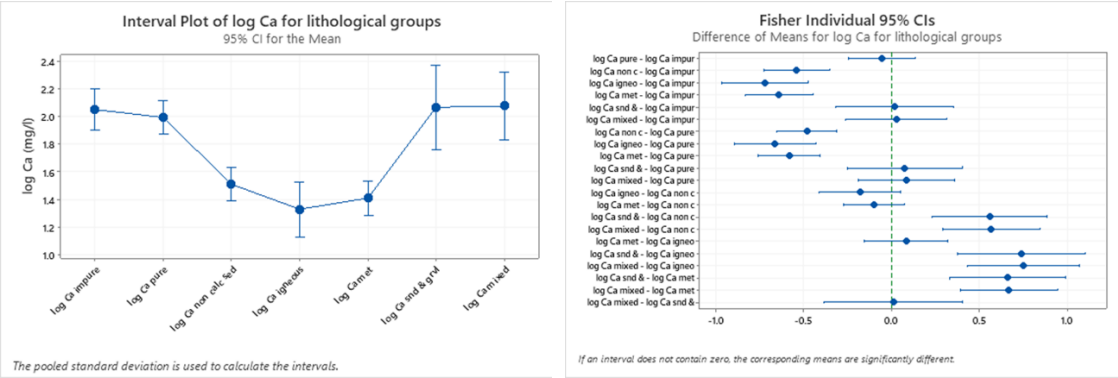
| | |
|---|---|
| Null hypothesis | $H_0$: $\eta_1 - \eta_2 = 0$ |
| Alternative hypothesis | $H_1$: $\eta_1 - \eta_2 \neq 0$ |

| Method | W-Value | P-Value |
|---|---|---|
| Not adjusted for ties | 3254.50 | 0.007 |
| Adjusted for ties | 3254.50 | 0.007 |

Figure 7.8 Example of a Mann-Whitney U test output for a comparison of EC data between coastal wells and other wells (note: η1 and η2 = median values [point estimates]; W = test statistic)

An example of the ANOVA test visual output when applied to the log transformed data for the seven lithological groups is given in Figure 7.9. Figure 7.9a shows the interval plot, and it can be clearly seen that the mean values for the non-calcareous sedimentary, igneous and

metamorphic groups are lower than those for the other four groups. Figure 7.9b confirms that these differences are significant, as indicated by the cases where the 95% confidence intervals of the differences in means do not contain a zero.




a) b)

Figure 7.9 Example of ANOVA test applied to the seven lithological groups: a) interval plot of log Ca; b) Fisher individual 95% confidence intervals for log Ca

## 7.5 Main physico-chemical parameters and major ion results

### 7.5.1 pH, EC and temperature

As noted in Section 7.1.3, the physico-chemical parameters pH, EC and temperature were measured in the field using a portable meter.

pH is a measure of the hydrogen ion concentration in water. Young groundwaters close to the recharge area would generally be expected to be acidic, with pH values less than 7, whereas older, more experienced groundwaters, especially where buffered by the dissolution of carbonate minerals, are generally more alkaline, with pH values above 7 (see e.g. Lloyd and Heathcote, 1985). A histogram showing the distribution of pH values is shown in Figure 7.10 (n = 167). The numbers on the x-axis refer to the maximum value of each 'bin'. Thus, the first bar shows the number of well samples with pH values in the range 4.51-5.00, the second bar 5.01-5.50, etc. It can be seen from the graph that the most frequently occurring pH values fall in the ranges 6.01-6.5 (n = 53) and 6.51-7.00 (n= 55). Of the 167 sampled wells, the pH is less than 7 in 141 (84%) wells, indicating that the majority of the groundwaters in the holy wells are mildly acidic. This is consistent with generally short flow paths, given that 62% of the sampled wells are in poorly productive aquifers (see Section 4.2.6).

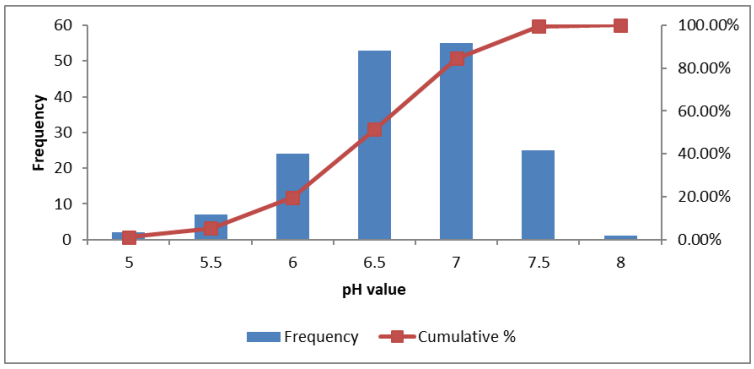



Figure 7.10 Histogram of pH values for all wells (n = 167)

EC is an indirect measure of the total dissolved solids content in a water sample. Again, groundwaters close to a recharge area will tend to have a low mineralisation, whereas groundwaters that are older - and thus have had more time to undergo dissolution and other geochemical processes with the aquifer material - will be more mineralised. The most highly mineralised groundwaters occur where flow paths are restricted and water becomes relatively 'stagnant', or where there is interaction with saline coastal waters, or because of gross pollution. A histogram illustrating the distribution of EC values in the sampled holy wells is shown in Figure 7.11. As with the pH histogram, the numbers on the x-axis refer to the maximum value of each 'bin'. Thus, the first bar shows number of well samples with EC values in the range 0-100 µS $cm^{-1}$, the second bar 101-200 µS $cm^{-1}$, etc. There are only seven samples with EC values above 1000 µS $cm^{-1}$, one of which is the saline water sample from St Brendan's well Roskeen (Co Mayo), with an EC of 61,150 µS $cm^{-1}$ (albeit there are likely inaccuracies in the measurement – see Section 7.5.5). Figure 7.11 suggests a bimodal EC distribution, which may relate to the EC differences between the carbonate and non-carbonate lithological groups (Section 7.5.4.1).

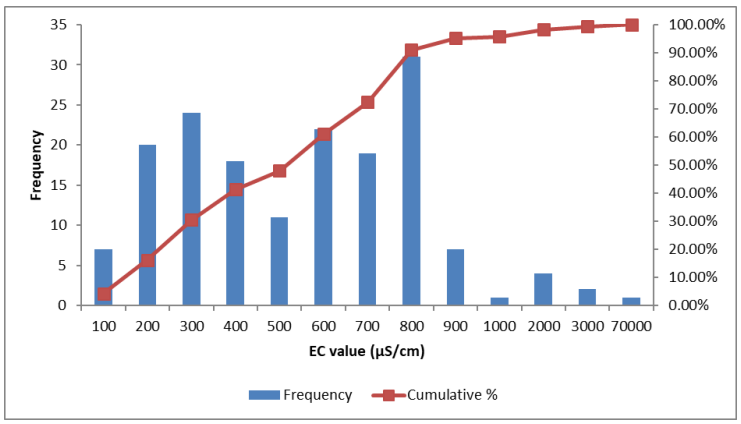



Figure 7.11 Histogram of EC values for all wells (n = 167)

Water temperature data for the 167 sampled wells are illustrated by the histogram in Figure 7.12. It should be emphasised that these measurements were made at different times of the year, and hence seasonal influences will have had a strong influence on the results. Nevertheless, certain aspects of the histogram are worth noting. Firstly, the data follow an approximately normal distribution, with 70% of the measurements falling between 9 and 13 °C. (The mean and median values are similar, at 10.8 and 10. 6 °C, respectively – see Table 7.7).

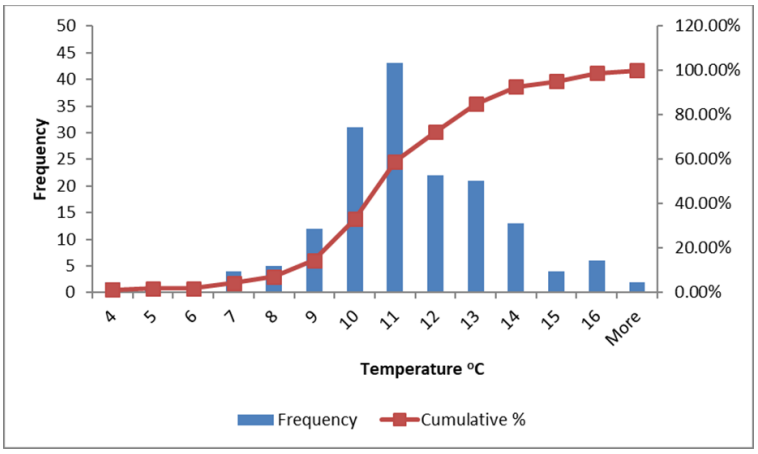



Figure 7.12 Histogram of temperature values for all wells (n = 167)

It is also apparent in Figure 7.12 that there is a large spread of water temperatures, well outside those normally seen for deeper groundwaters (which are more typically in the range of 9 to 11 °C). As was demonstrated by the well survey results in Chapter 5, most of the holy wells are shallow spring wells, and many are little more than small seepages, which are sometimes not shaded by a well building and hence are particularly susceptible to warming and cooling during the day and between the seasons. The highest water temperature recorded in a holy well was at St Patrick's well Ballyelan in Co Limerick: here the water temperature was 16.3 °C, compared to an air temperature of about 17 °C (measured on 12/6/2016). Such a high water temperature is a little surprising in this Ballysteen Formation (impure limestone) well, as it is relatively deep for a holy well (with 0.5 m of water) and is partly shaded by a well house. The minimum temperature observed during the well surveys was in St Kilian's well at Mullagh in Co Cavan: 3.8 °C water temperature was measured on a cold, snowy January day where the air temperature was about 2 °C. This is a shallow (0.14 m water depth), uncovered well that taps Silurian metasediments (a metamorphic aquifer). A cold winter air temperature does not always result in a low water temperature, even in a shallow well. For example, at St Brigid's well at Cullion in Co Westmeath, the water temperature was 11.3 °C on a very frosty day in November 2016 when

the air temperature was at about 0 °C. This suggests a relatively long and possibly deep flow path for this well (in Lucan Formation impure limestones), as discussed in Section 5.2.1.4.

### 7.5.2 Nitrate

Of the major ions, nitrate is the most diagnostic as an indicator of anthropogenic influences on water quality. The nitrate results are therefore discussed here first, and the results for the other major ions are then presented (in Section 7.5.3) both for the full well datasets and separately for the wells with low nitrate levels, where anthropogenic influences will be less.

A total of 232 samples from 167 holy wells were analysed for nitrate, and the results in relation to background (2 mg $l^{-1}$ as N, or 8.7 mg$l^{-1}$ as $NO_3$; see Section 6.3.2), a threshold of concern value (5.65 mg $l^{-1}$ as N, or 25 mg$l^{-1}$ as $NO_3$; Eurostat, 2012) and EU maximum admissible and WHO recommended drinking water levels (11.3 mg $l^{-1}$ as N, or 50 mg$l^{-1}$ as $NO_3$; see Section 6.2.1) are summarised in Table 7.6. The data from the five spa well samples are not included in this table (see Section 7.8). Where holy wells were sampled more than once (i.e. monitored wells, repeat sampling and duplicates), the nitrate value used in Table 7.6 to calculate the number of wells with nitrate above a particular threshold (notably above 2 mg $l^{-1}$ as N) is the value included in the major ion analysis with the lowest ion balance error (IBE). For the monitored wells and the duplicate samples, the nitrate results were consistently either above or below 2 mg $l^{-1}$ as N. For the repeat analyses, the second sample result (i.e. with the lower IBE) was used in the table and the summary statistics which follow. There were two wells where the repeat analyses gave a $NO_3$ value above the 2 mg $l^{-1}$ threshold when the first analysis was < 2 mg $l^{-1}$, and two wells where the opposite was the case. It should be noted that the majority of results were from one-off sampling, and so the nitrate values represent a snapshot at the particular time of sampling.

Table 7.6 Nitrate values in relation to NBL and drinking water values.

| | Nr | % | Total Nr |
|---|---|---|---|
| Nr of samples with nitrate > 2.0 mg/L as N | 124 | 53.4 | 232 |
| Nr of wells with nitrate > 2.0 mg/L as N | 87 | 52.1 | 167 |
| Nr of samples with nitrate > 5.65 mg/L as N | 43 | 18.5 | 232 |
| Nr of samples with nitrate > 11.3 mg/L as N | 6 | 2.6 | 232 |
| Nr of wells with nitrate > 5.65 mg/L as N | 24 | 14.4 | 167 |
| Nr of wells with nitrate > 11.3 mg/L as N | 3 | 1.8 | 167 |

The most striking feature about the nitrate data is that slightly over half the wells (87 out of 167, or 52%) had nitrate concentrations above the NBL (Figure 7.13), suggesting that many holy wells are impacted by anthropogenic activities, with likely sources of elevated nitrate being from agricultural activities or waste disposal (septic tank systems). This finding is unsurprising because the majority of holy wells are shallow spring wells, often in areas with an Extreme or High groundwater vulnerability rating (Section 4.2.7).

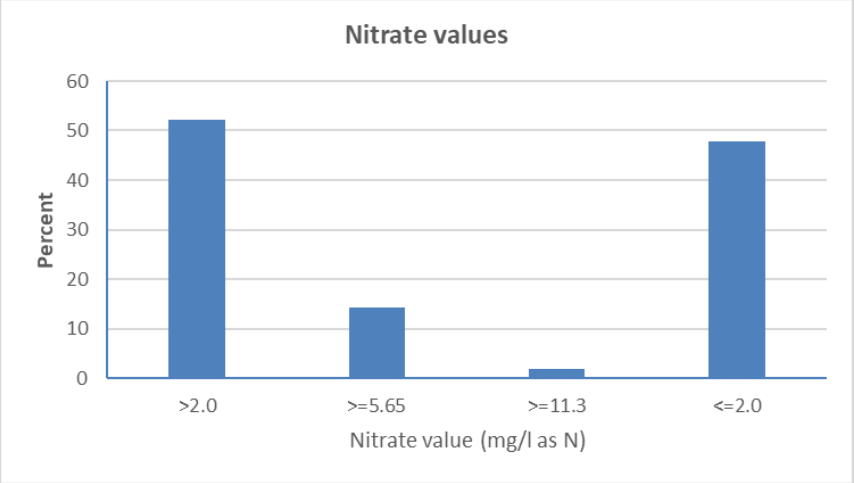



Figure 7.13 Percent wells with nitrate values exceeding the NBL (2 mg $l^{-1}$ as N) and the EU Drinking water Directive MAC and WHO recommended guideline value of 11.3 mg $l^{-1}$ as N or 50 mg $l^{-1}$ as $NO_3$ (see Table 6.3); the percent wells exceeding the threshold of concern level of 5.65 mg $l^{-1}$ as N or 25 mg $l^{-1}$ as $NO_3$ is also shown (n = 167 samples)

Only three of the wells had nitrate values above the EU MAC / WHO recommended guideline value of 11.3 mg $l^{-1}$. These were St John's well Toberboe in Co Laois (21.2 mg $l^{-1}$ nitrate as N), Lady's Island well in Co Wexford (12.6 mg $l^{-1}$ nitrate as N) and St Colman's well at Salterstown in Co Louth (81.5 mg $l^{-1}$ nitrate as N). St John's well at Toberboe is a karst spring in Dinantian pure bedded limestones, located in a relatively flat area with High groundwater vulnerability, and where cattle were observed grazing close to the spring well.

Lady's Island well is on the pilgrim path around the island (actually a promontory), close to the shore of a tidal lake (the better known and older Our Lady's well is on the mainland to the east, facing the 'island'). The water in this tidal lake is salty (EC = 23,000 µS $cm^{-1}$), so it is interesting that there is a thin lens of relatively fresh groundwater at the well site (EC = 418 µS $cm^{-1}$), especially as the 'island' is so small (32 acres, or 13 ha). The geology comprises sandstone and

shale till overlying Precambrian gneiss. It has been suggested that this well 'is most likely formed from the run-off from the farmers fields on the flat top above'[30]. Whilst the relatively high water EC, and the fact that the well contained water even after the long dry October that preceded two visits in November 2016, suggest a groundwater source for the well, the high nitrate does tie in with that observation about field runoff. There is a sign at the well indicating that the water is not suitable for drinking.

St Colman's well at Salterstown is the most interesting of the high nitrate wells, both because the nitrate level is indeed so high, and also because it is located in an isolated coastal site with no obvious high nitrate source nearby (or at least, no adjacent point source of pollution). The well and its hydrogeological setting have been described in Section 5.10.2. It is a small shallow depression in beach gravel at the base of an embankment. The well has a reputation for treating sore eyes. The groundwater source is the transition zone at the top of the Silurian metasedimentary bedrock that outcrops along the beach. The well is close to the high water mark and obviously gets inundated by the sea occasionally, especially during spring tides or storms. The EC of the well water was measured on five occasions: 715 µS $cm^{-1}$ and 895 µS $cm^{-1}$ on 9th and 16th March 2017, respectively; 1500 µS $cm^{-1}$ and 1380 µS $cm^{-1}$ on 9th April and 11th June 2019, respectively; and 1258 µS $cm^{-1}$ on 10th March 2020. The somewhat higher water EC during the second of the two visits a week apart in March 2017 was consistent with a lower water level observed on that date, with likely less dilution from recent rainfall, whilst the more brackish water observed in April 2019 probably followed an inundation of the well during a recent spring tide (there was sea weed in the well); no weed was observed in the well on 11/6/2019 or 10/3/2020, but the EC was still elevated.

Two water samples were collected from St Colman's well for analysis. The sample collected in March 2017 gave a nitrate value of 19.3 mg $l^{-1}$ as N (this is the TCD Environmental Engineering lab result; the sample sent to City Analysts showed a higher nitrate value of 29.1 mg $l^{-1}$ as N), whereas the sample collected in April 2019, when the water was more brackish, gave a much higher nitrate value of 81.5 mg $l^{-1}$ as N (or 361 mg $l^{-1}$ as $NO_3$); this value was from the analysis carried out by CAL lab (the value determined in the TCD Environmental Engineering lab was similar – 78.4 mg $l^{-1}$ as N; see the photo of the sample with the strong pink reagent colour used in the spectrophometric analysis in Figure 7.4a). The land inland of the well – and inland of the

[30] http://irelandsholywells.blogspot.ie/2012/03/our-ladys-island-county-wexford.html; accessed 25/3/2020)

coast road – is used for arable agriculture, but it is not evident why this landuse might lead to such high groundwater nitrate at this location, or whether there is some other source for the nitrate (an inspection of the surrounding area did not point towards a potential alternative source, for example, a nearby sewer).

Apart from these three wells, three other wells showed nitrate slightly above the EU MAC in the City Analysts results, but not in the TCD Environmental Engineering lab results. These wells are Tobar Mhuire Titeskin in Co Cork (11.2 and 13.4 mg $l^{-1}$ nitrate as N for the TCD and City Analysts results, respectively), Trinity well Farrannagark in Co Cork (10.1 and 12.1 mg $^{l-1}$ as N, respectively) and St Mochua's well Clashmore in Co Waterford (10.8 and 12.4 mg $^{l-1}$ as N, respectively). The two Cork wells tap Dinantian mudstones and sandstones, whereas the Waterford well has a Dinantian pure unbedded limestone source (Waulsortian). All three sites are surrounded by pastureland.

The significance of the differences between EC and major ions for the wells with elevated nitrate and those with low nitrate was tested using the non-parametric Mann-Whitney U test (see Section 7.4). For a significance level p of less than 0.05, the parameters that showed significant differences in the median values between the two groups (apart from nitrate itself, of course) were EC, calcium, magnesium, bicarbonate, sulphate and silica. In all cases, the median values were higher in those wells with elevated nitrate. Interestingly, potassium, which is often associated with pollution from waste or agricultural activities, did not exhibit a significant difference between the wells with elevated nitrate and those with low nitrate (see Section 7.5.8.3 for a discussion of K:Na ratios as potential indicators of pollution sources).

### 7.5.3 Summary descriptive statistics for major ions and comparisons with NBLs

Figure 7.14 and Figure 7.15 contain, respectively, a box and whisker plot and a cumulative probability diagram summarising the major ion results for the 167 holy wells sampled. Silica is included with the major ions owing to its relative abundance (even though, as noted earlier, it does not normally behave like a charged ion in water). Additional summary statistics are presented in Table 7.7, which include the physico-chemical parameters pH, EC and temperature. The box plot, cumulative probability diagram and table do not include the data from the five spa wells, which are described separately in Section 7.8. Where more than one sample analysis was available for a holy well (such as for the four monitoring wells, plus the wells where sampling

was repeated owing to high IBEs, or where duplicate analyses were performed), the sample with the lowest IBE was selected for inclusion in the summary well statistics.

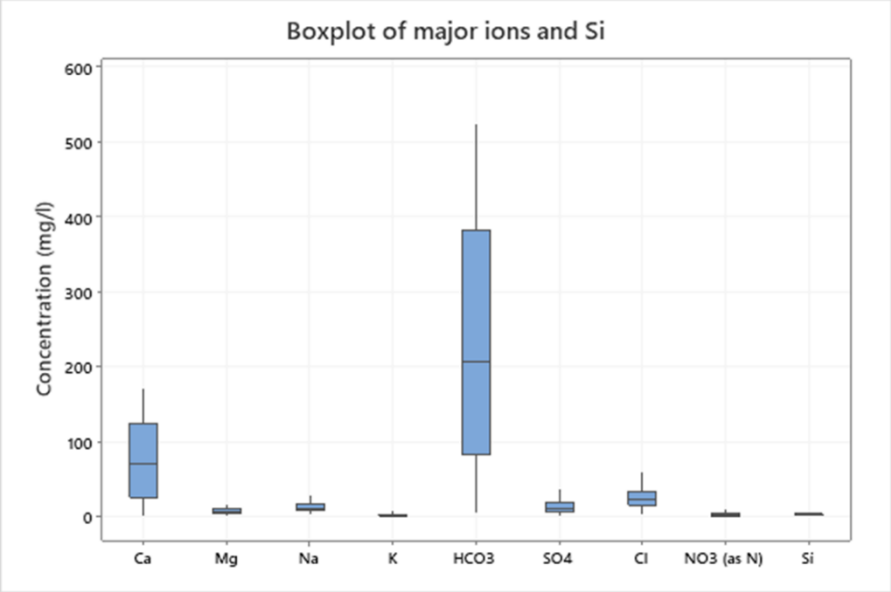



Figure 7.14 Box and whisker plot for major ions and Si (n = 167 samples for major ions).

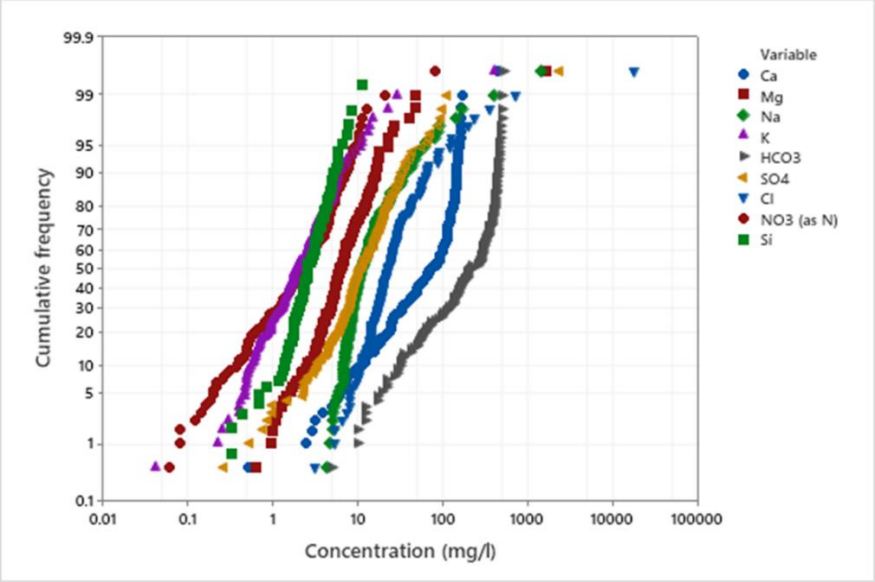



Figure 7.15 Cumulative probability diagram for major ions and Si (n = 167 samples for major ions).

The box plot shown in Figure 7.14 and the other box plots and the cumulative probability diagrams included in this chapter were all prepared using the statistical package Minitab. In Minitab, the upper whisker in a box plot by default extends to the highest data value within the upper limit, where the upper limit is given by = Q3 + 1.5 (Q3 - Q1), where Q3 is the upper quartile

(75% of values are less than or equal to this value) and Q1 is the lower quartile (25% of values are less than or equal to this value). Similarly, the lower whisker extends to the lowest value within the lower limit given by Q1- 1.5 (Q3 - Q1). Outliers are not included in the box plots presented here.

Cumulative probability diagrams like the example in Figure 7.15 are a useful way of characterising the distributions of hydrochemical data, and have been used in a number of baseline groundwater geochemical studies (Shand *et al*., 2007; Reimann and Birke, 2010; MacDonald *et al*., 2017; Tedd *et al*., 2017). They are most useful when comparing the distributions of parameters in different lithological groups (Section 7.5.4 below), but certain characteristics are apparent from the full major ion dataset in Figure 7.15. For example, the steepening of the curves for Ca and $HCO_3$ suggest mineral solubility controls. In contrast, the positive skew of the plot for Na and Cl suggest the influence of brackish waters.

Table 7.7 Summary statistics of pH, EC and major ion values for all holy wells sampled (n = 167)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 167 | 4.65 | 5.44 | 6.50 | 6.44 | 7.18 | 7.70 | |
| EC (µS $cm^{-1}$) | 167 | 38 | 112 | 516 | 876 | 876 | 61150 | |
| Temperature (°C) | 167 | 3.8 | 7.4 | 10.6 | 10.8 | 14.7 | 16.3 | |
| Ca (mg $l^{-1}$) | 167 | 0.5 | 6.4 | 71.0 | 78.7 | 154.5 | 440.7 | |
| Mg (mg $l^{-1}$) | 167 | 0.6 | 1.7 | 6.2 | 18.3 | 21.4 | 1688 | 17[a] |
| Na (mg $l^{-1}$) | 167 | 4.3 | 6.1 | 10.9 | 28.8 | 58.2 | 1476.1 | 13[a] |
| K (mg $l^{-1}$) | 167 | 0.04 | 0.47 | 1.94 | 5.45 | 10.3 | 408.4 | 2.1[a] |
| $HCO_3$ (mg $l^{-1}$) | 167 | 4.9 | 20.2 | 207.4 | 233.3 | 471.0 | 524.6 | |
| $SO_4$ (mg $l^{-1}$) | 167 | 0.0 | 2.3 | 10.5 | 30.7 | 52.0 | 2394.8 | 13[a] |
| Cl (mg $l^{-1}$) | 167 | 3.1 | 8.4 | 22.7 | 147.3 | 114.3 | 18271.1 | 21[b] |
| $NO_3$ (mg $l^{-1}$ as N) | 167 | 0.0 | 0.1 | 2.3 | 3.5 | 8.7 | 81.5 | 2.0[a] |
| Si (mg $l^{-1}$) | 98 | 0.3 | 0.8 | 2.6 | 3.1 | 6.0 | 11.4 | |

Note: [a] National NBL values for unconfined aquifers

[b] National NBL value

Concerning the descriptive statistics in Table 7.7, mean values of EC, Na and Cl are strongly influenced by the very high value for the single seawater sample taken from St Brendan's well at Roskeen in Co Mayo. Indeed, the mean Cl concentration exceeds the 95$^{th}$ percentile value.

The right-hand column of Table 7.7 includes natural background levels (NBLs) established for Irish groundwaters, where applicable. The NBLs were defined based on the 95$^{th}$ percentile values for data from monitoring points that were believed to be unaffected by anthropogenic pollution (Tedd *et al.*, 2017; see Section 6.3.2). Where sufficient data were available, NBLs were determined for each of the main lithological groupings (including for EC, Ca and $HCO_3$). For certain parameters, including chloride, a national value was established, and for some parameters (including Mg, Na, K, $SO_4$ and $NO_3$) a distinction could be made between a NBL for a confined versus unconfined aquifer. In the latter situations, the NBL value for the unconfined aquifer is included in the above table since, as has been described in Chapter 5, the majority of holy wells are springs that issue from shallow unconfined aquifers. In all examples where NBLs are included in Table 7.7, the 95$^{th}$ percentile of the surveyed holy well sample parameter exceeds the NBL. The median value is less than the NBL, except for chloride and nitrate.

However, it the NBLs of all nine parameters in the Table 7.7 could potentially be impacted by anthropogenic activities (see Table 2.2 and p. 16 in Tedd *et al.*, 2017). Therefore, Table 7.8 presents the descriptive statistics for only those wells with nitrate concentrations less than 2.0 mg l$^{-1}$ as N. Again, the 95$^{th}$ percentile values of all the parameters for which national NBLs have been established exceed those NBL values, except for nitrate itself, of course.

Table 7.8 Summary statistics of pH, EC and major ion values for holy wells with low nitrate concentrations ($NO_3$ < 2 mg l$^{-1}$ as N; n = 80)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 80 | 4.65 | 5.70 | 6.45 | 6.46 | 7.22 | 7.70 | |
| EC (µS cm$^{-1}$) | 80 | 38 | 90 | 383 | 1225 | 885 | 61150 | |
| Temperature (°C) | 80 | 3.9 | 8.2 | 10.7 | 11.2 | 15.2 | 16.1 | |
| Ca (mg l$^{-1}$) | 80 | 0.5 | 3.9 | 51.8 | 69.4 | 145.9 | 440.7 | |
| Mg (mg l$^{-1}$) | 80 | 0.6 | 1.1 | 5.1 | 28.0 | 23.4 | 1688 | 17[a] |
| Na (mg l$^{-1}$) | 80 | 4.3 | 5.4 | 12.2 | 41.8 | 82.1 | 1476.1 | 13[a] |
| K (mg l$^{-1}$) | 80 | 0.04 | 0.39 | 1.76 | 7.85 | 9.77 | 408.4 | 2.1[a] |
| $HCO_3$ (mg l$^{-1}$) | 80 | 4.9 | 12.2 | 167.2 | 202.7 | 457 | 524.6 | |
| $SO_4$ (mg l$^{-1}$) | 80 | 0.0 | 1.0 | 8.9 | 45.0 | 87.8 | 2394.8 | 13[a] |
| Cl (mg l$^{-1}$) | 80 | 5.4 | 8.2 | 23.1 | 271.5 | 130.5 | 18271.1 | 21[b] |
| $NO_3$ (mg l$^{-1}$ as N) | 80 | 0.0 | 0.1 | 0.7 | 0.9 | 1.9 | 2.0 | 2.0[a] |
| Si (mg l$^{-1}$) | 53 | 0.3 | 0.6 | 2.0 | 2.5 | 5.1 | 8.6 | |

Note: [a] National NBL values for unconfined aquifers

[b] National NBL value

The number and percent exceedances of the major ion data with respect to the NBLs are summarised in Table 7.9 below. Two sets of comparisons are given: firstly (in blue), for the whole dataset (with samples from 167 wells) and secondly (in red), for the well samples that had nitrate values below the NBL of 2 mg $l^{-1}$ as N (n = 80 samples) and which, therefore, were less likely to have been impacted by anthropogenic activities. In addition to the national NBLs, the data here include the NBLs (where established) for the different lithological groupings and indicative values for confined aquifers in brackets. (Because there were too few data to establish NBLs for confined aquifers, Tedd *et al*. [2017] provided values for information only). In every case, the number of exceedances is the total compared to the relevant NBL (national, unconfined, lithological group, whichever is relevant).

Table 7.9 Number of exceedances of NBLs in sampled holy wells (n = 167). The NBLs are from Tedd *et al*. (2017). NBL values in brackets are based on limited data, and can be regarded as only provisional values

| NBLs | pH | EC (µS $cm^{-1}$) | Ca (mg $l^{-1}$) | Mg (mg $l^{-1}$) | Na (mg $l^{-1}$) | K (mg $l^{-1}$) | $HCO_3$[1] (mg $l^{-1}$) | $SO_4$ (mg $l^{-1}$) | Cl (mg $l^{-1}$) | $NO_3$ (mg $l^{-1}$) | Si (mg $l^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| National | | | | | | | | | 21 | | |
| Unconfined | | | | 17 | 13 | 2.1 | | 13 | | 2.0 | |
| Confined | | | | (42) | (105) | (5.9) | | (223) | | (0.3) | |
| Impure lsts | (8.3) | (554) | (113) | | | | (354) | | | | (7.9) |
| Pure lsts | 7.9 | 601 | 117 | | | | 393 | | | | 4.7 |
| Non-calc seds | 7.1 | 392 | 64 | | | | 264 | | | | 6.6 |
| Igneous | (7.5) | (60) | (8.2) | | | | (52) | | | | (8.9) |
| Metamorphic | (7.7) | (546) | (114) | | | | (378) | | | | (7.5) |
| Sand & gravel (incl Mixed) | (7.5) | (583) | (111) | | | | (427) | | | | (6.1) |
| Nr samples | 167 | 167 | 167 | 167 | 167 | 167 | 167 | 167 | 167 | 167 | 98 |
| Nr exceedances | 1 | 87 | 67 | 11 | 65 | 76 | 51 | 67 | 91 | 87 | 2 |
| % exceedances | 0.6 | 52.1 | 40.1 | 6.6 | 38.9 | 45.5 | 30.5 | 40.1 | 54.5 | 52.1 | 2.0 |
| Nr low $NO_3$ smpls | 80 | 80 | 80 | 80 | 80 | 80 | 80 | 80 | 80 | 80 | 53 |
| Nr exceedances | 1 | 32 | 24 | 4 | 36 | 31 | 19 | 24 | 41 | 1[2] | 1 |
| % exceedances | 1.3 | 40 | 30 | 5 | 45 | 38.8 | 23.8 | 30 | 51.3 | 1.3[2] | 1.9 |

Note: [1] The $HCO_3$ NBLs in Tedd *et al*. (2017) are given as alkalinity (mg $l^{-1}$ as $CaCO_3$)

[2] This nitrate exceedance is of the provisional confined value (0.3 mg $l^{-1}$)

It is clear from Table 7.9 that not only are there large numbers of exceedances of NBLs for the full dataset, but also for the parameters in samples from the low nitrate wells (albeit the exceedance percentages are generally smaller for the latter, as would be expected). For

example, 52% of the EC values for the full holy well dataset exceeded the relevant lithological group values, compared to 40% for the low nitrate dataset. In the case of Na, the percent exceedance is actually higher for the low nitrate well samples (45% compared to 39% for the full dataset).

The non-parametric Mann-Whitney U test was used to investigate whether there were statistically significant differences in the median values of the major ions and pH and EC values between the holy well dataset and the NBL dataset. The findings are summarised in Table 7.10. There were significant differences in the median values for seven of the major ions (including Si) between the full holy well samples and the NBL dataset, with the medians for Ca, Na, K, $SO_4$, Cl and $NO_3$ being higher than the NBL values. The exceptions were Mg, $HCO_3$ and Si, where the medians were lower than the NBLs, but the differences were not statistically significant except in the case of Si. When the low nitrate well samples were compared with the NBL data, there were statistical differences for all the major ions except Ca and Mg. The median values of Na, K, $SO_4$ and Cl were all significantly higher than the NBL values, whilst the median Ca, Mg, $HCO_3$ and Si values were lower than the NBL median values (albeit not significantly so for Ca or Mg). The median nitrate concentration for the low nitrate wells was 0.74 mg $l^{-1}$, compared to 0.62 mg $l^{-1}$ for the NBL dataset. This difference was found to be statistically significant in the Mann-Whitney U tests (p = 0.019), but only weakly significant (p = 0.049) when the comparison was repeated using an ANOVA test.

Table 7.10 Comparison of holy well data with the dataset used in the NBL study by Tedd *et al*. (2017). The table indicates whether or not (Y or N) there was a significant difference in the data groups

| Comparisons | pH | EC | Ca | Mg | Na | K | $HCO_3$[1] | $SO_4$ | Cl | $NO_3$ | Si |
|---|---|---|---|---|---|---|---|---|---|---|---|
| All holy wells and NBL dataset | Y 167, 480 | Y 167, 500 | Y 167, 464 | N 167, 464 | Y 167, 464 | Y 167, 464 | N 167, 606 | Y 167, 604 | Y 167, 613 | Y 167, 421 | Y 98, 3000 |
| Low N holy wells and NBL dataset | Y 80, 480 | N 80, 500 | N 80, 464 | N 80, 464 | Y 80, 464 | Y 80, 464 | Y 80, 606 | Y 80, 604 | Y 80, 613 | Y 80, 421 | Y 53, 3000 |

Note: [1] The first n value is the number of holy well water samples and the second n is the NBL dataset number

There was a significant difference in the median pH values between the holy wells and NBL datasets: 6.5 (full holy well dataset, or 6.45 for the low nitrate wells) compared to 7.2, respectively. The much lower pH in the holy wells probably reflects the larger representation of

more siliceous, less calcareous poorly productive aquifers. Groundwaters in shallow spring wells in poorly productive aquifers have shorter flow paths, with less opportunity for buffering from carbonate minerals.

Additional important points to note when comparing the chemical results from the holy wells with the NBL dataset are:

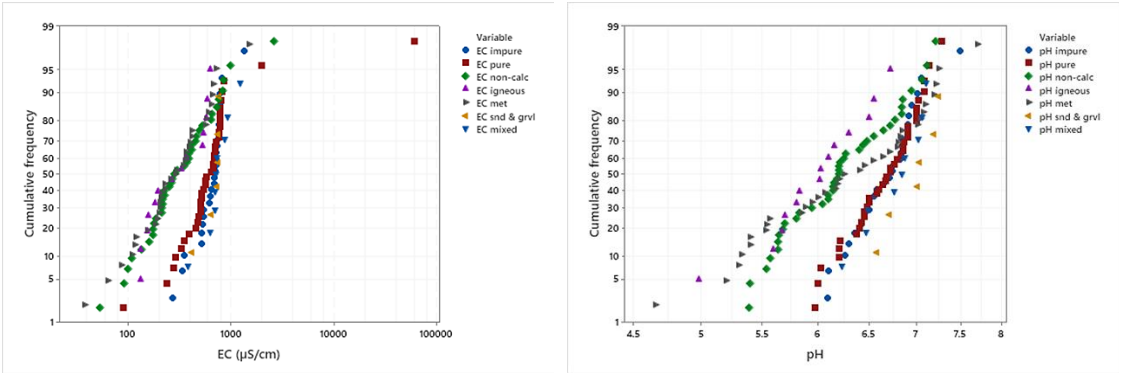
a) The NBL dataset were from EPA monitoring data for boreholes and springs.
b) The full dataset was used, including for confined as well as unconfined monitoring points (albeit the number of sites where the aquifer is confined was small – and even fewer in the case of the holy wells sampled).
c) For parameters potentially affected by anthropogenic activities (which included EC and all the major ions), the zones of contribution for all the monitoring points were screened for land use pressures, and only those points with low pressures and with maximum nitrate of less than 10 mg $l^{-1}$ (as $NO_3$) were selected. Further details of the screening process can be found in Tedd *et al*. (2017).
d) Although the number of data values for major ions exceeded 400 in the NBL dataset, these were mostly from only 21 monitoring points.
e) As monitoring data, the NBL records reflect seasonal variations for monitoring wells whereas the holy well data in this comparison are from one-off samples.
f) The EPA monitoring network (at the time of the NBL study) comprised 223 monitoring points, including 76 springs.
g) These 223 monitoring points are mainly in productive aquifers, and so there is a bias in the NBL results towards these aquifers. (Six sets of monitoring wells established in poorly productive aquifers by the EPA [Moe *et al*., 2010] were not used for the NBL dataset).
h) The EPA monitoring wells generally tap deeper aquifer zones than the shallow spring wells that make up the majority of holy wells. Flow paths and hence groundwater residence times can be expected to be longer in many of the monitoring wells. Moreover, the springs in the monitoring network will generally be larger, and hence have larger zones of contribution than the holy well springs and seeps.

### 7.5.4 Summary statistics by main lithological groupings

This section begins by looking at the cumulative probability distributions of the main physico-chemical parameters and major ion results for the seven lithological groups. Summary descriptive statistics are then presented in a series of tables, including comparisons with natural background levels (including the NBLs specific to the particular lithological grouping, where established). Concerning physico-chemical parameters, only pH and EC data are included in the cumulative probability diagrams and summary tables; temperature values were not broken down according to lithological groups in view of seasonal differences in measurements and hence potentially large biases in these smaller datasets. After the summary tables, the outcomes of statistical tests (using ANOVA) are given at the end of this section: these show whether differences in the means of individual parameters between lithological groups are significant.

#### 7.5.4.1 Cumulative probability distributions by lithological group

Cumulative probability diagrams for EC and pH for the seven lithological groups are shown in Figure 7.16. It is clear that, for both parameters, the distributions fall broadly into two groups, with distributions for the igneous, metamorphic and non-calcareous lithologies (i.e. those groups dominated by silicate mineralogies) being distinct from the four remaining groups, all of which are influenced by carbonate mineralogies.

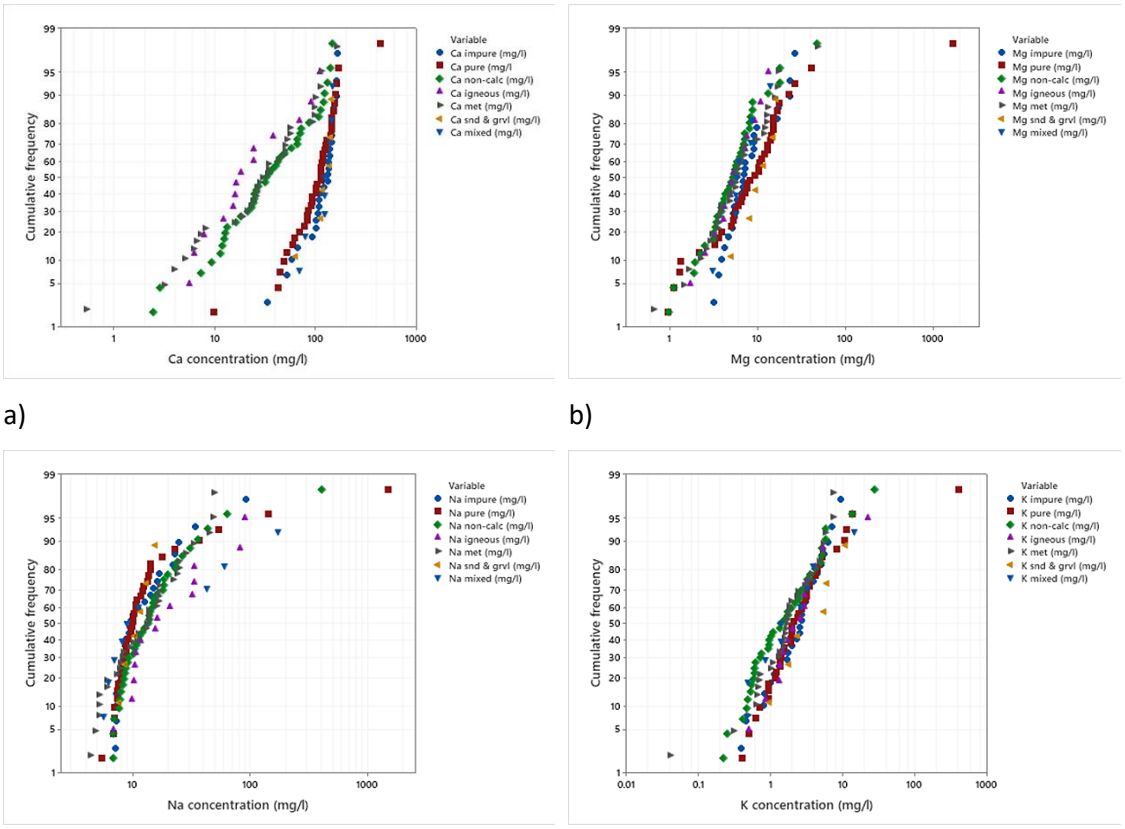



a) b)

Figure 7.16 Cumulative probability diagram for a) EC and b) pH for the seven lithological groups

Figures 7.17 and 7.18 show the cumulative probability plots for the major cations and major anions, respectively. The same differences by lithology observed for EC and pH are also apparent in the distributions of the Ca and $HCO_3$ ions, with higher concentrations in the limestone, sand

and gravel and mixed bedrock and gravel lithologies. However, the curves rise steeply to a similar upper limit for all the lithologies, suggesting solubility controls. The Na and Cl plots show a positive skew for most groups (especially the pure and impure limestone and non-calcareous sedimentary groups), suggesting the influence of brackish water and the absence of mineral solubility controls. There is one especially high data value on most of the graphs in Figures 7.17 and 7.18: this is the saltwater well, St Brendan's at Roskeen in Co Mayo. Mg, K and $SO_4$ concentrations follow (approximately) a log-normal distribution, with no clear differences between the lithological groups. Nitrate values also show a more or less linear (i.e. log-normal) distribution across most of their range, albeit with some extreme values (see below).




a) b)

c) d)

Figure 7.17 Cumulative probability diagram for the major cations: a) Ca, b) Mg, c) Na and d) K for the seven lithological groups

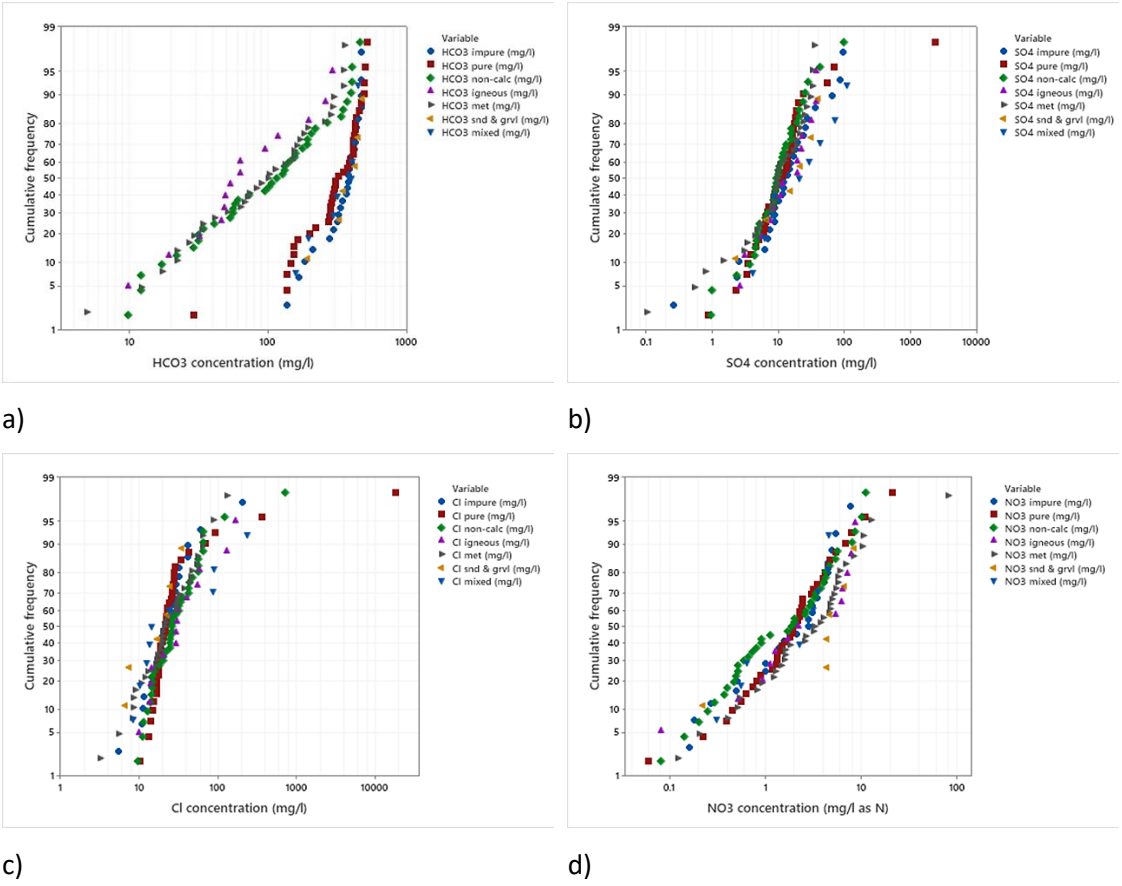



Figure 7.18 Cumulative probability diagram for the major anions: a) $HCO_3$, b) $SO_4$, c) Cl and d) $NO_3$ for the seven lithological groups

The cumulative probability diagram for Si in Figure 7.19 shows some differences between lithologies, with the lowest values occurring in the pure limestones, in line with the finding by Tedd *et al*. (2017). The relatively narrow range of Si values for all lithologies probably reflects the low solubility of quartz (MacDonald *et al*., 2017).

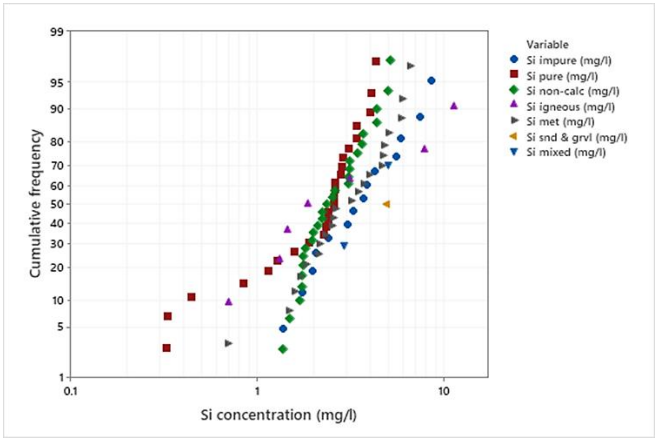



Figure 7.19 Cumulative probability diagram for Si for the seven lithological groups

#### 7.5.4.2 Descriptive statistics for each lithological group

Descriptive statistics for the impure limestone group are included in Table 7.11. The median values of EC, Ca, K, $HCO_3$ and Cl for the impure limestone wells exceed the NBLs (or provisional NBLs), whilst the 95$^{th}$ percentile values of all ionic species exceed the NBLs. The 95$^{th}$ percentile for Si is less than the NBL. Although the median nitrate value is less than the NBL, 13 of the 26 samples (i.e. 50%) had nitrate values above the NBL, indicating that the values of other parameters are likely to have been influenced by anthropogenic pollution. The maximum recorded pH value (7.49) is less than the provisional NBL of 8.3.

Table 7.11 Summary statistics of EC and major ion values for holy wells sampled in the impure limestone lithological grouping (n = 26)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 26 | 6.09 | 6.14 | 6.73 | 6.67 | 7.04 | 7.49 | (8.3)[a,b] |
| EC (μS cm$^{-1}$) | 26 | 271 | 344 | 704 | 668 | 812 | 1352 | (554)[a,b] |
| Ca (mg l$^{-1}$) | 26 | 33.2 | 54.0 | 133.0 | 119.4 | 162.6 | 165.8 | (113)[a,b] |
| Mg (mg l$^{-1}$) | 26 | 3.2 | 3.7 | 6.9 | 9.3 | 23.2 | 26.8 | 17[c] |
| Na (mg l$^{-1}$) | 26 | 7.1 | 7.2 | 9.6 | 15.6 | 31.7 | 91.5 | 13[c] |
| K (mg l$^{-1}$) | 26 | 0.39 | 0.54 | 2.64 | 3.01 | 6.86 | 9.57 | 2.1[c] |
| $HCO_3$ (mg l$^{-1}$) | 26 | 137.0 | 172.7 | 382.6 | 359.6 | 474.6 | 476.0 | (354)[a,b] |
| $SO_4$ (mg l$^{-1}$) | 26 | 0.3 | 2.4 | 12.8 | 21.5 | 82.1 | 96.2 | 13[c] |
| Cl (mg l$^{-1}$) | 26 | 5.5 | 11.0 | 21.7 | 30.6 | 55.4 | 203.0 | 21[d] |
| $NO_3$ (mg l$^{-1}$ as N) | 26 | 0.0 | 0.0 | 1.8 | 2.3 | 5.3 | 7.6 | 2.0[c] |
| Si (mg l$^{-1}$) | 14 | 1.4 | 1.6 | 3.5 | 3.9 | 7.8 | 8.6 | (7.9)[b] |

Notes [a] NBL values in brackets are based on limited data, and are only included for illustration

[b] NBL for this particular lithological group

[c] National NBL values for unconfined aquifers

[d] National NBL value

The descriptive statistics for the pure limestone grouping are given in Table 7.12. The maximum EC, Ca, Mg, Na, K, $SO_4$ and Cl values were all recorded in St Brendan's well at Roskeen in Co Mayo, a coastal well that is clearly inundated by sea water (see Sections 5.10.3 and 7.5.5). The 95$^{th}$ percentiles for EC, Ca, Mg, Na, K, $HCO_3$, $SO_4$, Cl, and $NO_3$ are all higher than the NBLs, although the median values for Ca, Mg, Na, K, $HCO_3$ and $SO_4$ are all below the NBL (as are the 95$^{th}$ percentile and median values of pH and Si).

Eighteen of the 38 wells (47%) sampled in pure limestones had nitrate values above the NBL, and the median nitrate was equal to the NBL. The highest nitrate concentration of 21.2 mg $l^{-1}$ (as N) was recorded in St John's well at Toberboe in Co Laois, and likely reflects the impacts of cattle grazing near this karst spring (Section 7.5.2).

Table 7.12 Summary statistics of EC and major ion values for holy wells sampled in the pure limestone lithological grouping (n = 38)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 38 | 5.97 | 6.03 | 6.70 | 6.66 | 7.09 | 7.28 | 7.9[a] |
| EC (µS $cm^{-1}$) | 38 | 90 | 271 | 615 | 2213 | 1032 | 61150 | 601[a] |
| Ca (mg $l^{-1}$) | 38 | 9.7 | 44.6 | 113.3 | 113.6 | 165.1 | 440.7 | 117[a] |
| Mg (mg $l^{-1}$) | 38 | 0.9 | 1.3 | 8.8 | 54.3 | 28.4 | 1688 | 17[b] |
| Na (mg $l^{-1}$) | 38 | 5.4 | 6.9 | 9.9 | 54.2 | 67.0 | 1476.1 | 13[b] |
| K (mg $l^{-1}$) | 38 | 0.40 | 0.60 | 2.04 | 13.8 | 11.8 | 408.4 | 2.1[b] |
| $HCO_3$ (mg $l^{-1}$) | 38 | 29.3 | 136.6 | 314.8 | 327.2 | 498.7 | 524.6 | 393[a] |
| $SO_4$ (mg $l^{-1}$) | 38 | 0.9 | 3.2 | 11.0 | 76.2 | 57.8 | 2394.8 | 13[b] |
| Cl (mg $l^{-1}$) | 38 | 10.4 | 14.0 | 21.6 | 513.8 | 133.1 | 18271.1 | 21[c] |
| $NO_3$ (mg $l^{-1}$ as N) | 38 | 0.1 | 0.4 | 2.0 | 3.0 | 8.3 | 21.2 | 2.0[b] |
| Si (mg $l^{-1}$) | 25 | 0.3 | 0.4 | 2.6 | 2.3 | 4.1 | 4.3 | 4.7[a] |

Notes [a] NBL for this particular lithological group

[b] National NBL values for unconfined aquifers

[c] National NBL value

The summary data for the non-calcareous sedimentary well samples in Table 7.13 show that the median values of Na and Cl slightly exceed the NBLs, whilst the 95$^{th}$ percentile values of all parameters except pH and Si exceed the NBLs (although in the case of Mg the 95$^{th}$ percentile is only marginally above the NBL: 17.8 mg $l^{-1}$ compared to an NBL of 17 mg $l^{-1}$). The 95$^{th}$ percentile for pH is similar to the NBL at approximately 7.1, and the median value is 6.20, noticeably lower than the median pH values for the carbonate lithologies in Tables 7.11 and 7.12 (see discussion in Section 7.5.1). Seventeen of the 39 well samples (44%) in this lithological group had nitrate values above the NBL.

Table 7.13 Summary statistics of EC and major ion values for holy wells sampled in the non-calcareous sedimentary lithological grouping (n = 39)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 39 | 5.39 | 5.53 | 6.20 | 6.23 | 7.08 | 7.22 | 7.1[a] |
| EC (µS $cm^{-1}$) | 39 | 53 | 99 | 284 | 424 | 865 | 2650 | 392[a] |
| Ca (mg $l^{-1}$) | 39 | 2.4 | 6.8 | 33.0 | 49.4 | 133.3 | 148.6 | 64[a] |
| Mg (mg $l^{-1}$) | 39 | 1.0 | 1.8 | 5.3 | 6.9 | 17.8 | 47.9 | 17[b] |
| Na (mg $l^{-1}$) | 39 | 6.8 | 6.9 | 13.5 | 26.2 | 45.7 | 408.0 | 13[b] |
| K (mg $l^{-1}$) | 39 | 0.22 | 0.40 | 1.40 | 2.96 | 6.7 | 28.6 | 2.1[b] |
| $HCO_3$ (mg $l^{-1}$) | 39 | 9.8 | 12.2 | 117.1 | 151.4 | 407.5 | 468.0 | 264[a] |
| $SO_4$ (mg $l^{-1}$) | 39 | 1.0 | 2.2 | 9.5 | 13.9 | 30.2 | 98.6 | 13[b] |
| Cl (mg $l^{-1}$) | 39 | 9.7 | 11.4 | 26.2 | 50.6 | 71.5 | 724.0 | 21[c] |
| $NO_3$ (mg $l^{-1}$ as N) | 39 | 0.1 | 0.2 | 1.9 | 2.7 | 8.9 | 11.2 | 2.0[b] |
| Si (mg $l^{-1}$) | 27 | 1.4 | 1.5 | 2.4 | 2.7 | 4.8 | 5.2 | 6.6[a] |

Notes [a] NBL for this particular lithological group

[b] National NBL values for unconfined aquifers

[c] National NBL value

The median values of most chemical parameters for the igneous well samples exceed the NBLs (Table 7.14), whilst nitrate is at the NBL (2 mg $l^{-1}$) and the median pH, Mg and Si values are less than the NBLs. The maximum pH of 6.72 is appreciably lower than the provisional NBL, suggesting that the NBL should be set at a lower value. Similarly, all the igneous well samples exceed the provisional NBL for EC, suggesting that the NBL of 60 µS $cm^{-1}$ is too low.

In interpreting these data, it should be remembered that only 14 igneous wells were sampled. Moreover, six of these wells are on islands or are located at or close to the coast of the mainland, which at least partly explains the elevated values of ions like Na and Cl, whilst half of the wells have nitrate values about the NBL, indicating some anthropogenic influences.

Table 7.14 Summary statistics of EC and major ion values for holy wells sampled in the igneous lithological grouping (n = 14)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 14 | 4.98 | 5.38 | 6.03 | 6.00 | 6.61 | 6.72 | (7.5)[a,b] |
| EC (µS $cm^{-1}$) | 14 | 132 | 133 | 297 | 342 | 602 | 627 | (60)[a,b] |
| Ca (mg $l^{-1}$) | 14 | 5.6 | 6.0 | 17.4 | 32.8 | 99.3 | 112.4 | (8.2)[a,b] |
| Mg (mg $l^{-1}$) | 14 | 1.7 | 2.2 | 5.1 | 6.0 | 11.5 | 13.1 | 17[c] |
| Na (mg $l^{-1}$) | 14 | 6.8 | 8.7 | 15.8 | 27.3 | 84.4 | 89.5 | 13[c] |
| K (mg $l^{-1}$) | 14 | 0.50 | 0.73 | 2.33 | 3.82 | 11.5 | 22.8 | 2.1[c] |
| $HCO_3$ (mg $l^{-1}$) | 14 | 9.8 | 16.0 | 58.4 | 96.6 | 272.1 | 292.8 | (52)[a,b] |
| $SO_4$ (mg $l^{-1}$) | 14 | 2.6 | 3.0 | 15.4 | 17.1 | 37.2 | 37.4 | 13[c] |
| Cl (mg $l^{-1}$) | 14 | 9.8 | 12.3 | 29.8 | 45.8 | 142.0 | 167.0 | 21[d] |
| $NO_3$ (mg $l^{-1}$ as N) | 14 | 0.0 | 0.1 | 2.0 | 3.5 | 8.2 | 8.7 | 2.0[c] |
| Si (mg $l^{-1}$) | 7 | 0.7 | 0.9 | 1.9 | 4.0 | 10.3 | 11.4 | (8.9)[a,b] |

Notes [a] NBL values in brackets are based on limited data, and are only included for illustration

[b] NBL for this particular lithological group

[c] National NBL values for unconfined aquifers

[d] National NBL value

For the metamorphic bedrock well samples (Table 7.15), the median values of all parameters except Na and nitrate are less than the NBLs (although Na is approximately the same as the NBL: 13.1 mg $l^{-1}$ compared to an NBL of 13 mg $l^{-1}$). The 95$^{th}$ percentiles for EC, Na, K, $SO_4$, Cl, and $NO_3$ exceed the NBLs, whilst the maximum recorded pH of 7.7 (at Ladywell in Dundalk) is at the NBL. Twenty-one of the 35 wells (60%) have nitrate values above the NBL, and the median nitrate value for all metamorphic wells of 3.2 mg $l^{-1}$ (as N) is 60% above the NBL. The metamorphic wells include St Colman's well at Salterstown, which has the exceptionally high $NO_3$ value of 81.5 mg $l^{-1}$ as N (or 361 mg $l^{-1}$ as $NO_3$) – see discussion of nitrate in Section 7.5.2.

There were only six wells sampled in the sand and gravel lithological grouping (Table 7.16), so the statistics should be regarded with caution. Moreover, five of the six well samples had nitrate values above the NBL - the median value of nitrate for the six wells is more than twice the NBL - indicating that the values for other parameters are likely to be influenced by anthropogenic effects. This may at least partly explain why the median values of EC, Ca, K and $SO_4$ are all above the NBLs.

Table 7.15 Summary statistics of EC and major ion values for holy wells sampled in the metamorphic lithological grouping (n = 35)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 35 | 4.65 | 5.27 | 6.25 | 6.29 | 7.23 | 7.70 | (7.7)[a,b] |
| EC (µS $cm^{-1}$) | 35 | 38 | 79 | 292 | 355 | 695 | 1500 | (546)[a,b] |
| Ca (mg $l^{-1}$) | 35 | 0.5 | 3.7 | 29.6 | 43.3 | 112.3 | 164.0 | (114)[a,b] |
| Mg (mg $l^{-1}$) | 35 | 0.6 | 1.6 | 5.8 | 7.9 | 16.7 | 47.4 | 17[c] |
| Na (mg $l^{-1}$) | 35 | 4.3 | 5.0 | 13.1 | 16.0 | 45.4 | 48.8 | 13[c] |
| K (mg $l^{-1}$) | 35 | 0.04 | 0.43 | 1.71 | 2.34 | 6.2 | 7.4 | 2.1[c] |
| $HCO_3$ (mg $l^{-1}$) | 35 | 4.9 | 15.6 | 100.0 | 130.3 | 351.8 | 361.0 | (378)[a,b] |
| $SO_4$ (mg $l^{-1}$) | 35 | 0.0 | 0.7 | 9.7 | 13.1 | 32.7 | 34.7 | 13[c] |
| Cl (mg $l^{-1}$) | 35 | 3.1 | 7.4 | 20.6 | 30.3 | 71.1 | 131.0 | 21[d] |
| $NO_3$ (mg $l^{-1}$ as N) | 35 | 0.1 | 0.3 | 3.2 | 6.0 | 11.1 | 81.5 | 2.0[c] |
| Si (mg $l^{-1}$) | 22 | 0.7 | 1.5 | 2.9 | 3.3 | 5.9 | 6.5 | (7.5)[a,b] |

Notes [a] NBL values in brackets are based on limited data, and are only included for illustration

[b] NBL for this particular lithological group

[c] National NBL values for unconfined aquifers

[d] National NBL value

Table 7.16 Summary statistics of EC and major ion values for holy wells sampled in the sand and gravel lithological grouping (n = 6)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL* |
|---|---|---|---|---|---|---|---|---|
| pH | 6 | 6.58 | 6.61 | 7.02 | 6.96 | 7.24 | 7.25 | (7.5)[a,b] |
| EC (µS $cm^{-1}$) | 6 | 420 | 476 | 739 | 679 | 768 | 772 | (583)[a,b] |
| Ca (mg $l^{-1}$) | 6 | 63.9 | 76.3 | 128.8 | 120.9 | 146.0 | 146.7 | (111)[a,b] |
| Mg (mg $l^{-1}$) | 6 | 5.0 | 5.8 | 10.5 | 10.9 | 15.8 | 16.0 | 17[c] |
| Na (mg $l^{-1}$) | 6 | 7.6 | 7.9 | 11.1 | 11.1 | 14.9 | 15.5 | 13[c] |
| K (mg $l^{-1}$) | 6 | 0.96 | 1.17 | 3.99 | 4.65 | 9.9 | 11.1 | 2.1[c] |
| $HCO_3$ (mg $l^{-1}$) | 6 | 195.2 | 228.7 | 390.2 | 372.8 | 473.6 | 481.0 | (427)[a,b] |
| $SO_4$ (mg $l^{-1}$) | 6 | 2.3 | 3.4 | 18.8 | 19.8 | 38.4 | 40.7 | 13[c] |
| Cl (mg $l^{-1}$) | 6 | 6.7 | 6.9 | 19.7 | 18.9 | 32.2 | 34.6 | 21[d] |
| $NO_3$ (mg $l^{-1}$ as N) | 6 | 0.2 | 1.2 | 4.5 | 4.8 | 8.0 | 8.5 | 2.0[c] |
| Si (mg $l^{-1}$) | 1 | | | (5.0) | | | | (6.1)[a,b] |

Notes [a] NBL values in brackets are based on limited data, and are only included for illustration

[b] NBL for this particular lithological group

[c] National NBL values for unconfined aquifers

[d] National NBL value

Six of the nine wells in the mixed bedrock and gravel grouping had nitrate levels above the NBL (Table 7.17). Note that comparisons are only possible for those parameters for which NBLs have been defined nationally, or nationally for unconfined aquifers, because a mixed lithological grouping was not included in the NBL study (see Table 6.4). Where comparisons can be made, the median values for $SO_4$ and $NO_3$ exceeded the NBLs, whilst the 95$^{th}$ percentile values for Na, K and Cl also exceeded the NBLs. However, as with the sand and gravel lithology dataset, there were relatively few water samples (9) for the mixed bedrock and gravel lithology, so the results should again be regarded with caution.

Table 7.17 Summary statistics of EC and major ion values for holy wells sampled in the mixed bedrock and gravel lithological grouping (n = 9)

| | N | Min | 5%ile | Median | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|
| pH | 9 | 6.23 | 6.33 | 6.85 | 6.76 | 7.09 | 7.11 | N/A[a] |
| EC (µS cm$^{-1}$) | 9 | 388 | 486 | 717 | 769 | 1111 | 1234 | N/A[a] |
| Ca (mg l$^{-1}$) | 9 | 69.8 | 73.8 | 125.5 | 122.8 | 149.3 | 151.1 | N/A[a] |
| Mg (mg l$^{-1}$) | 9 | 3.0 | 3.6 | 5.8 | 6.8 | 11.7 | 13.8 | 17[b] |
| Na (mg l$^{-1}$) | 9 | 5.7 | 5.9 | 8.9 | 35.7 | 127.3 | 172 | 13[b] |
| K (mg l$^{-1}$) | 9 | 0.47 | 0.48 | 1.41 | 3.25 | 10.4 | 14.8 | 2.1[b] |
| $HCO_3$ (mg l$^{-1}$) | 9 | 161.0 | 176.0 | 405.0 | 347.3 | 451.0 | 451.0 | N/A[a] |
| $SO_4$ (mg l$^{-1}$) | 9 | 4.1 | 5.0 | 20.8 | 33.9 | 96.1 | 111.6 | 13[b] |
| Cl (mg l$^{-1}$) | 9 | 8.2 | 9.0 | 14.3 | 55.1 | 177.5 | 236.0 | 21[c] |
| $NO_3$ (mg l$^{-1}$ as N) | 9 | 0.3 | 0.4 | 2.8 | 2.5 | 4.6 | 4.6 | 2.0[b] |
| Si (mg l$^{-1}$) | 2 | 2.9 | 3.0 | 4.0 | 4.0 | 4.9 | 5 | N/A[a] |

Notes [a] Not applicable - NBL have not been established for this particular lithological group

[b] National NBL values for unconfined aquifers

[c] National NBL value

### 7.5.4.3 ANOVA tests on major ion data for lithological groups

The results of the pH, EC and major ion chemical analyses for the seven lithological groups were analysed using one-way analysis of variance (ANOVA) along with the Fisher least significant difference test. The tests were carried out on both the raw data and log-transformed data, the latter to better satisfy the assumption of normality underlying the ANOVA method (see Section 7.4). ANOVA with Fisher LSD post hoc testing on the non-transformed data showed that pH, Ca and $HCO_3$ were significantly different between the impure limestone, pure limestone, sand and

gravel, and mixed bedrock and gravel groups on the one hand, and the non-calcareous sedimentary, igneous and metamorphic groups on the other. There were no significant differences in the means between the seven groups for EC, Mg, Na, K, $SO_4$ or Cl. For $NO_3$, the test showed significant differences between the metamorphic group and the non-calcareous sedimentary and impure limestone groups. For Si, ANOVA tests were carried out for five lithological groups only as there were insufficient data for the sand and gravel and the mixed bedrock and gravel groupings. The Si mean was significantly different between the pure limestone and the impure limestone lithologies.

When the ANOVA with Fisher LSD post hoc testing was repeated with log-transformed data (Table 7.18), generally the same relationships were observed e.g. pH, Ca and $HCO_3$ were significantly different in the impure limestone, pure limestone, sand and gravel, and mixed bedrock and gravel groups compared to the other three lithological groups, whereas there were no significant differences in the means between the seven groups for Na, $SO_4$ and Cl. (In Table 7.18, the means of a parameter that do not share a letter across the lithological groups are significantly different). For $NO_3$, the test showed a significant difference between the metamorphic group and the non-calcareous sedimentary group: this difference could possibly relate to land use influences rather than directly to geology (with more intensive farming in areas of the south of the country that are underlain by sandstone formations).

Table 7.18 ANOVA tests for differences of means of pH, EC and major ions for the seven lithological groups (log-transformed data)

| Parameter | Impure lst | Pure lst | Non-calc sed | Igneous | Met | Sand & gravel | Mixed bedrock & gravel |
|---|---|---|---|---|---|---|---|
| pH | A | A | B | B | B | A | A |
| EC | A | A | B | B | B | A | A |
| Ca | A | A | B | B | B | A | A |
| Mg | A B C | A | B C | A B C | C | A B C | A B C |
| Na | A | A | A | A | A | A | A |
| K | A B | A | B | A B | A B | A B | A B |
| $HCO_3$ | A | A | B | B | B | A | A |
| $SO_4$ | A | A | A | A | A | A | A |
| Cl | A | A | A | A | A | A | A |
| $NO_3$ | A B | A B | B | A B | A | A B | A B |
| Si | A | B | A B | A B | A | - | - |

Note: means that do not share a letter across the lithological groups are significantly different

However, the tests with the log-transformed data did show some differences not shown by the earlier tests. Similar to pH, Ca and $HCO_3$, EC was also found to be significantly different between the impure limestone, pure limestone, sand and gravel, and mixed bedrock and gravel groups on the one hand, and the non-calcareous sedimentary, igneous and metamorphic groups on the other. For Mg, there was a significant difference between the pure limestones compared to the non-calcareous sedimentary and metamorphic groups, whilst K showed a significant difference between the pure limestones and the non-calcareous sedimentary groups. For $NO_3$, the test showed a significant difference between the metamorphic group and the non-calcareous sedimentary group – but not with the impure limestone group (as had been shown by the test with the non-transformed data). With Si, there were insufficient data to perform ANOVA tests for the sand and gravel and the mixed bedrock and gravel groups; the results for the remaining five groups showed significant differences between the pure limestone and the impure limestone and metamorphic groups.

The other thing to note in the table is that the ANOVA results for the sands and gravels and the mixed bedrock and gravel are similar to each other, and broadly similar to those for the impure and pure limestones, indicating the calcareous nature of the gravels.

### 7.5.5 Summary statistics for wells in coastal settings

As noted in Section 6.2.1, rainfall in coastal areas contains elevated concentrations of Mg, Na, K, $SO_4$ and, especially Cl (Jordan, 1997; Shand *et al*., 2007; MacDonald *et al*., 2017), and hence recharge waters near the coast often have increased concentrations of these ions. Furthermore, the water chemistry in coastal wells may be affected by aquifer saline intrusion or, for wells near the shoreline, by periodic inundation with seawater during high tides or storms (e.g. St Colman's well at Salterstown, Co Louth – see Section 5.10.2).

Summary descriptive statistics of physico-chemical parameters and major ions for wells within 500 m of the coastline are included in Table 7.19. The 31 coastal wells are distributed in the main lithological groups as follows: impure limestones (3), pure limestones (8), non-calcareous sedimentary (9), igneous (5), metamorphic (6); there were no coastal wells sampled in the sand and gravel or mixed bedrock and gravel groupings. Iodide data would be useful for future studies

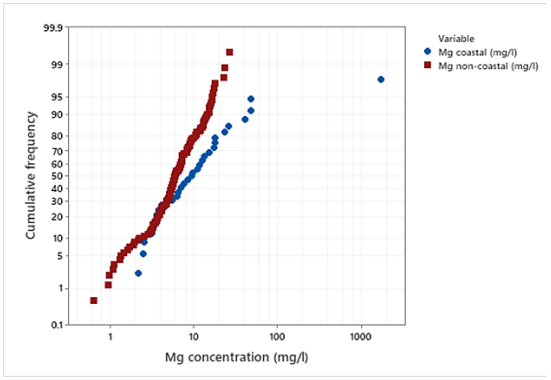
of coastal groundwaters. Of the coastal wells, 14 (45.2%) had nitrate above the NBL of 2 mg $l^{-1}$ as N.

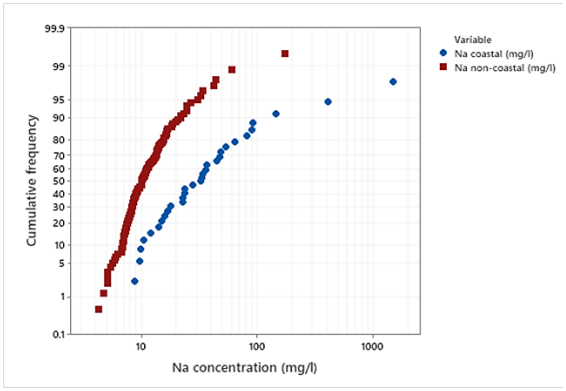
Table 7.19 Summary statistics of EC and major ion values for holy wells within 500 m of the coast (n = 31)

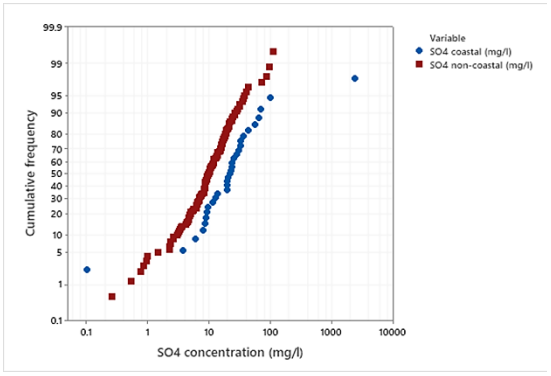
| | N | Min | 5%ile | Median | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|
| pH | 31 | 5.53 | 5.59 | 6.40 | 6.33 | 6.91 | 7.08 |
| EC (µS $cm^{-1}$) | 31 | 215 | 225 | 589 | 2662 | 2327 | 61150 |
| Ca (mg $l^{-1}$) | 31 | 3.2 | 9.4 | 69.7 | 87.0 | 167.6 | 440.7 |
| Mg (mg $l^{-1}$) | 31 | 2.1 | 2.5 | 9.3 | 67.0 | 47.7 | 1688 |
| Na (mg $l^{-1}$) | 31 | 8.7 | 9.8 | 32.2 | 95.9 | 275.8 | 1476.1 |
| K (mg $l^{-1}$) | 31 | 0.48 | 0.58 | 2.63 | 16.53 | 13.71 | 408.4 |
| $HCO_3$ (mg $l^{-1}$) | 31 | 9.8 | 19.5 | 197.6 | 211.6 | 424.6 | 524.6 |
| $SO_4$ (mg $l^{-1}$) | 31 | 0.0 | 4.9 | 22.2 | 102.6 | 84.0 | 2394.8 |
| Cl (mg $l^{-1}$) | 31 | 16.7 | 23.8 | 55.7 | 682.8 | 541.8 | 18271.1 |
| $NO_3$ (mg $l^{-1}$ as N) | 31 | 0.1 | 0.3 | 1.9 | 5.7 | 11.5 | 81.5 |
| Si (mg $l^{-1}$) | 24 | 0.3 | 0.7 | 2.1 | 2.4 | 4.1 | 7.4 |

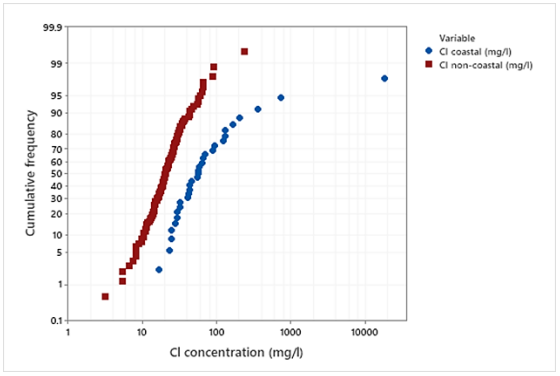
Cumulative probability diagrams for four selected ions are illustrated in Figure 7.20. These compare the distributions between wells near the coast (n= 31) and the remaining holy wells (n = 136). The influence of the coastal setting is most marked in the distributions of Na and Cl, but is also apparent for Mg and $SO_4$. Although not included in Figure 7.20, some enrichment in K was also observed in the coastal wells, but not in the distributions of Ca , $HCO_3$ or $NO_3$. In the case of Si, the distributions of the coastal and non-coastal wells were different, but with the Si concentrations elevated in the inland as opposed to the coastal wells.

The significance of the coastal setting for each of the major ions and EC was tested using ANOVA. Tests on both the raw data and log-transformed data gave similar results. The means of the following parameters were found to differ significantly ($p < 0.05$) between coastal and non-coastal settings: EC, Mg, Na, K, $SO_4$, Cl and Si, consistent with the observations from the cumulative probability plots. Calcium, bicarbonate and nitrate were found to be not significantly different between these two groups of samples, again in line with the frequency plots. The absence of a significant association between nitrate and coastal setting supports the use of the full dataset (i.e. all wells, including the well samples with elevated nitrate levels) in this analysis.




c) d)

Figure 7.20 Cumulative probability diagram comparing coastal and non-coastal wells for concentrations of a) Mg, b) Na, c) $SO_4$ and d) Cl

Repeating the statistical tests for coastal versus non-coastal wells using the Mann-Whitney U method for non-parametric data gave similar results. EC, Mg, Na, K, $SO_4$, Cl and Si were again significantly different between the two groups (in this method, it is the median values which are tested).

As mentioned previously, one of the holy wells contained highly saline water (61,150 µS $cm^{-1}$). This was St Brendan's well at Roskeen on the Mayo shoreline (Section 5.10.3 and Section 7.5.1). That the water had a composition similar to seawater is illustrated by the comparisons of the major ion concentrations in Table 7.20. All ionic concentrations for the well samples are similar to those for seawater with the exception of Na, where the well water value is an order of magnitude lower. This most likely reflects an error in the analysis, and is consistent with a very large negative ion balance error of -41%: a large negative IBE in this case suggests an underestimation of one of more of the cation concentrations. (It should be added here that the Geochemistry lab ICP-MS system [Section 7.2.1] was not set up to analyse such a high salinity

sample, and so errors for this sample result are likely – even though the analysis was repeated, and gave a similar Na value both times). The sample from St Brendan's well also had elevated concentrations of trace elements such as strontium (6.6 mg $l^{-1}$) and lithium (294 µg $l^{-1}$), again in line with seawater values.

Table 7.20 Comparison of major ion chemistry between St Brendan's well Roskeen (Co Mayo) and seawater (all values in mg $l^{-1}$)

| Parameter | St Brendan's well, Roskeen | North Atlantic seawater[a] | Average seawater[b] |
|---|---|---|---|
| Ca | 441 | 450 | 410 |
| Mg | 1688 | 1336 | 1350 |
| Na | 1476 | 11,120 | 10,500 |
| K | 408 | 400 | 390 |
| $HCO_3$ | 154 | 135 | 142 |
| $SO_4$ | 2395 | 2830 | 2700 |
| Cl | 18,271 | 20,100 | 19,000 |

Notes: [a] Data provided by Dr C Rocha, TCD

[b] From Hem (1985)

### 7.5.6 Distribution of major ions by lithology and hydrogeological setting

In considering the spatial distribution of water chemistry, several factors need to be borne in mind, including:

a) Groundwater chemistry depends on the age and experience of groundwater i.e. where the sample point is located along the flow system. The shallow springs typical of holy wells are at the discharge end of flow paths. In the poorly productive aquifers that contain nearly 70% of the Irish holy wells, the flow paths can be expected to be short, of the order of a few hundred metres (Fitzsimons *et al*., 2005; RPS, 2008 and Tedd *et al*., 2015 - see Section 3.2).
b) Shallow or deep samples from the same aquifer may exhibit different hydrochemistries – groundwater chemistry varies with depth, not just distance along horizontal flow path. In poorly productive aquifers, the majority of flow takes place in the transition zone between the subsoil and bedrock and within the upper fractured bedrock zones, whereas in regionally important aquifers, such as pure limestones, the flow paths are often deeper (Section 3.2).

c) Groundwater chemistry may vary seasonally and respond to short-term rainfall events. Although it was not possible to collect samples from all wells at all times of year, four wells were monitored for their major ion and trace element water chemistry over a 2-year period (the results are discussed in Section 7.7).

The distributions of major ions are illustrated here with the aid of trilinear Durov diagrams (Durov, 1948, as described in Lloyd and Heathcote, 1985). Cation and anion concentrations are calculated in milliequivalents per litre, and then expressed as percentages. These percentages are plotted in the appropriate triangle on the top (cations) and side (anions) of the diagram, and the resulting data points are then projected into the central square of the diagram. The software was provided by David Banks of Holymoor Consultants. Figure 7.21 shows the major ion distributions for the six main lithological groupings. The figure is somewhat crowded with data points and so, for greater clarity, just the median values of the major ions for the six groups are plotted in Figure 7.22.

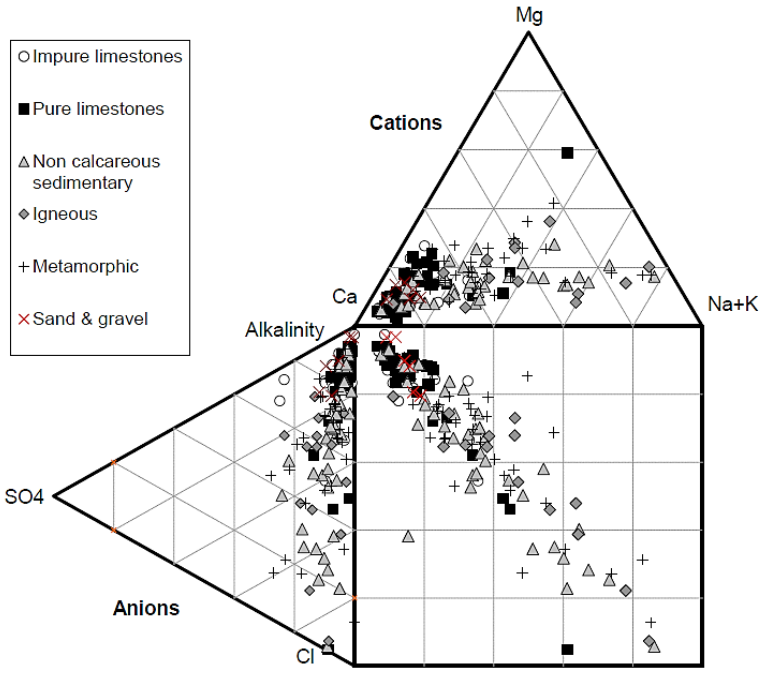



Figure 7.21 Durov plot for the six main lithological groupings (n = 158 wells; excludes the 9 wells in the Mixed aquifer category)

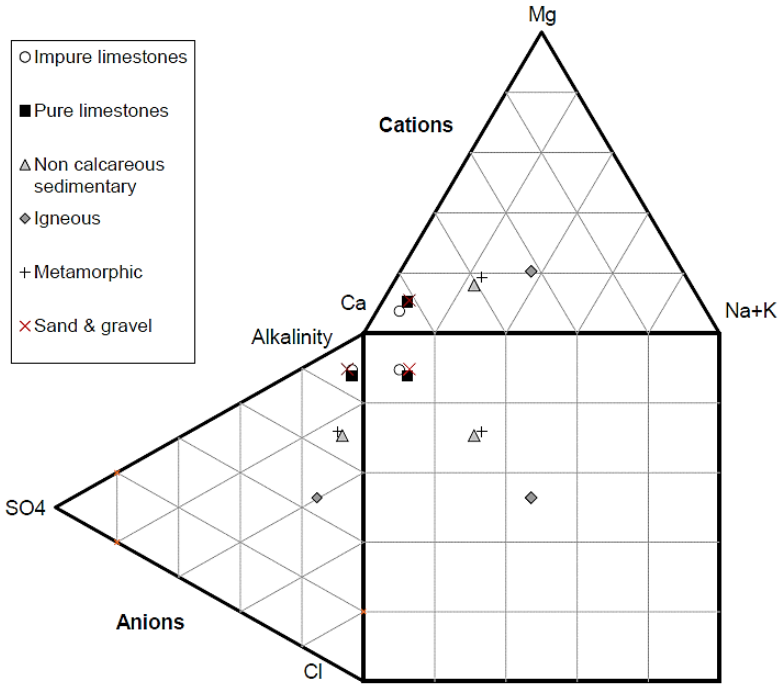



Figure 7.22 Durov plot for the median ionic concentrations of the six main lithological groupings

For the impure limestone, pure limestone and sand and gravel lithological groups, the majority of data points (and the median values) lie in the top left of the Durov diagrams indicating Ca-$HCO_3$ type groundwaters. This is to be expected with the limestone lithologies. For the sands and gravels, a Ca-$HCO_3$ hydrochemistry suggests that these deposits mainly derive from carbonate (limestone) parent materials. The other lithologies (non-calcareous sedimentary, igneous and metamorphic) show a stronger influence of Na and Cl in their hydrochemistries, and this is especially the case for the igneous grouping. Groundwaters in such lithologies are softer, with less buffering from $CaCO_3$ in their rock mineralogies.

As well as lithology, the major ion hydrochemistry will also be influenced by factors such as the aquifer condition (unconfined or confined) and proximity to the sea. These are illustrated by the Durov diagram in Figure 7.23, which also shows the distributions for the mixed bedrock and gravel lithology in comparison with the sand and gravel lithology. For all these groups the number of samples is small and so the results should be treated with circumspection. Comparing, firstly, the mixed with the sand and gravel lithological groupings, the mixed samples are also mostly characterised by a Ca-$HCO_3$ hydrochemistry. There is one noticeable exception, which exhibits an Na-Cl water type. This sample was taken from St Patrick's well in Trinity

College Dublin. The aquifer here is probably a combination of impure limestone bedrock and gravels laid down in an old alluvial channel (see Section 5.8.1). It is a city-centre site, and hence vulnerable to pollution. In support of likely pollution, the water EC is elevated (1234 µS $cm^{-1}$), as are the nitrate and phosphorus concentrations (3.6 mg $l^{-1}$ as N and 0.19 mg $l^{-1}$ as P, respectively) and those of several minor ions and trace elements (including Li, Ni and Mo).

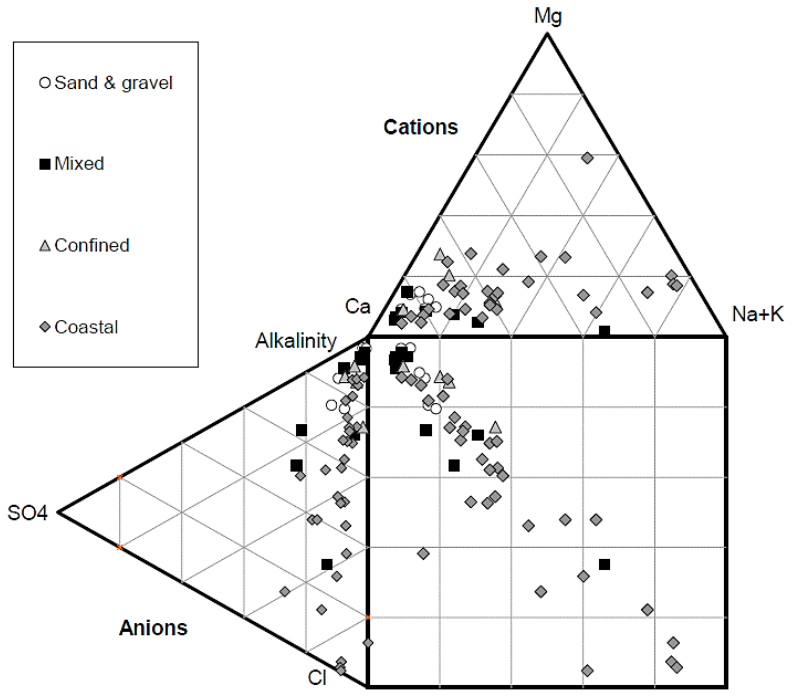



Figure 7.23 Durov plot for the sand and gravel (n = 6 wells) and mixed bedrock and gravel lithologies (n = 9), plus confined wells (n = 4) and wells in coastal settings (n = 31)

There are only four samples from confined aquifers and these all plot in the Ca-$HCO_3$ section of the Durov diagram. Two of the wells are in pure limestones (St Gorman's well Ballinakill, Co Meath and St Brigid's well Shangarry, Co Limerick), one in impure limestones (Bride's well Calgath, Co Meath) and the fourth – which is only locally confined – non-calcareous sediments (Holy well Shrone, Co Kerry); see Section 5.9 for descriptions of three of these wells. Consistent with the broad pattern observed in Figures 7.21 and 7.22 it is the latter well that has the softest water and the greater proportion of Na and Cl, and hence plots furthest from the top left in Figure 7.23.

Of most interest in Figure 7.23 is the clear depiction of the strong influence of a coastal setting in the major ion chemistry. All those wells with an Na-Cl water chemistry in this Durov diagram (excepting the mixed aquifer well already discussed above) have a coastal setting, here regarded as a location within 500 m of the shoreline (Section 5.10). In such areas the rainfall, and hence recharge waters, can be expected to contain elevated sodium and chloride especially, and also increased Mg, K and $SO_4$ (Section 7.5.5). In some areas, this influence is likely to extend further inland, but 500 m was chosen as a somewhat arbitrary distance to illustrate this effect.

### 7.5.7 Nitrate levels in relation to groundwater vulnerability

Nitrate results were discussed in Section 7.5.2, where it was reported that slightly more than 50% of wells sampled had $NO_3$ values in excess of the NBL. In this section, the nitrate results are compared with the groundwater vulnerability classification results.

Table 7.21 gives the median, mean and maximum nitrate values (as N) for water samples collected from wells within each vulnerability class. The numbers of values in excess of the NBL of 2.0 mg $l^{-1}$ are also included in the table. It was shown in Section 4.2.7 that 49% of the surveyed holy wells fall into the X or E Extreme vulnerability class, and a further 29% are in areas with a High vulnerability rating. Of the 167 wells that were sampled for major ions, 81 (49%) are located in areas with X/E Extreme vulnerability whilst 48 (29%) are in High vulnerability areas, hence matching the overall survey proportions. As with the analysis in Section 4.2.7, a well located at the boundary between two vulnerability classes was assigned to the higher category; for example, a well at the boundary between High and Moderate vulnerability was included under the High vulnerability category.

Table 7.21 Comparison of nitrate values with groundwater vulnerability class

| | X | E | H | M | L |
|---|---|---|---|---|---|
| Nr of samples | 51 | 30 | 48 | 27 | 11 |
| Median $NO_3$ (mg $l^{-1}$ as N) | 1.6 | 2.1 | 3.3 | 2.6 | 0.8 |
| Mean $NO_3$ (mg $l^{-1}$ as N) | 3.9 | 2.9 | 4.1 | 2.9 | 2.6 |
| Maximum $NO_3$ (mg $l^{-1}$ as N) | 81.5 | 10.1 | 21.2 | 10.8 | 10.2 |
| Nr samples with $NO_3$ > 2.0 mg $l^{-1}$ | 19 | 15 | 32 | 17 | 4 |

It is evident from the table that the mean $NO_3$ values across all five groundwater vulnerability classes exceeded the NBL, suggesting that there is little relation between groundwater

vulnerability class and nitrate pollution. This observation is borne out by the results of ANOVA tests (incorporating the Fisher least significant difference test). No significant differences between the mean nitrate concentrations were observed when the tests were performed on the untransformed nitrate data. When the data were log-transformed to achieve better normality (see Section 7.4), the only significant difference in the means was between that for the High vulnerability category compared to the Low vulnerability category i.e. between the categories with the highest and lowest mean values in Table 7.21.

At first sight, the general lack of correlation between nitrate distributions and the geological classification of groundwater vulnerability might seem surprising. However, it is important to bear in mind that these shallow spring wells may be impacted by nearby pollution sources which can bypass subsurface geological pathways (it is the characteristics of the subsurface pathways that largely determine the vulnerability classification – see Section 3.2). In this respect, a study of water quality in private wells in four areas in Ireland found that the incidences of pollution (in this case faecal bacteria) were as high or even higher in the one area with Low vulnerability compared to the other three areas which were characterised by High or Extreme groundwater vulnerability (Hynds *et al*., 2012; 2013). The likely explanation for this is that areas with Low vulnerability often have very low permeability clayey soils and subsoils, and so local pollutants may follow overland pathways and contaminate susceptible wells (wells lacking proper protective headworks), especially in periods following heavy rainfall.

### 7.5.8 Ion relationships

Insights into hydrochemistry can be obtained by examining the relationships between individual ions (Lloyd and Heathcote, 1985). Examples considered here are Mg:Ca, Na:Cl and K:Na: these ratios were selected because of the insights they can give into human dietary benefits (Mg:Ca), coastal aquifer influences (Na:Cl), and anthropogenic pollution impacts (K:Na).

#### 7.5.8.1 Mg and Ca

In a study of Mg and Ca in groundwater in Serbia, Papić *et al*. (2014) report that a Mg:Ca ratio (using units of meq $l^{-1}$) of 0.7 or less may indicate a limestone source, whereas a ratio in the range 0.7 to 0.9 is likely to indicate the influence of dolomitic limestones. Groundwaters with Mg:Ca ratios above 0.9 are associated with Mg-rich silicate rocks including ophiolites and

ultramafic rocks. Mezga and Urbanc (2014), on the other hand, relate the source rock composition in their study of aquifers in Slovenia to the Ca:Mg molar ratio (i.e. the inverse of the Mg:Ca ratio). They report mean Ca:Mg molar ratios for limestones and dolomites or dolomitic limestones of 6.3 and 1.8, respectively – equivalent to Mg:Ca ratios of approximately 0.2 and 0.6, respectively. For clastic sedimentary rocks the mean groundwater Ca:Mg values varied from 2.2 to 7.3 (0.1 to 0.5 Mg:Ca), whilst samples from igneous and metamorphic rocks produced Ca:Mg values of 6.2 and 6.8, respectively (0.2 and 0.1 Mg:Ca, respectively). These igneous and metamorphic water samples were characterised by low values of Mg in particular, with a maximum of only 1 mg $l^{-1}$ for the metamorphic rock waters (albeit there were only four samples). Apart from the composition of the source lithology, long residence times (and higher groundwater temperatures) can lead to greater dissolution of Mg-rich rocks and hence higher Mg:Ca ratios (Sappa *et al*., 2014). In a study of warm springs in Leinster and Munster in Ireland, Aldwell and Burdon (1980) found Ca:Mg ratios (in meq $l^{-1}$ units) to have a wide range of values from 1.79 to 10.25 (or 0.10 to 0.56 as Mg:Ca) for samples from 12 wells, all of which tap Dinantian limestones.

The relationships between Mg and Ca are summarised in Table 7.22 according to the following criteria: by lithological grouping, by location with respect to the coast, and according to whether or not the samples had elevated nitrate levels. The results are then illustrated graphically in Figure 7.24 to 7.26. It should be remembered when reviewing the results by lithology that the number of samples is small for the igneous, sand and gravel, and mixed bedrock and gravel groupings.

The summary statistics in Table 7.22 show that the median and mean Mg:Ca ratios are higher in the non-calcareous sedimentary group than for the pure or impure limestones (whilst noting that the maximum value for the pure limestones is for the saline water sample from St Brendan's well Roskeen, Co Mayo), and also that the water samples from igneous and metamorphic rocks have higher Mg:Ca ratios than the non-calcareous as well as the carbonate rocks. As such, this finding is broadly consistent with the trend reported by Papić *et al*. (2014) for Slovenian aquifers (where the Mg-rich silicate rock aquifers gave the highest Mg:Ca ratios, albeit the ratios were higher in the Slovenian study). One further point of interest in the Irish data in Table 7.22 is that the Mg:Ca ratios for the sand and gravel and the mixed bedrock and gravel groupings are low, and similar to those for the calcareous rock groups – suggesting that the gravels are dominated by carbonate rocks, consistent with the Durov plots and observations in the previous section.

Table 7.22 Mg:Ca ion ratios for a) the main lithological groupings, b) coastal and non-coastal wells; and c) well samples with elevated nitrate and wells with low nitrate. All ratios are based on meq $l^{-1}$ units

| | n | Min | 5%ile | Median | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|
| *a) Lithology* | | | | | | | |
| Impure limestone | 26 | 0.05 | 0.05 | 0.09 | 0.14 | 0.30 | 0.41 |
| Pure limestone | 38 | 0.03 | 0.04 | 0.13 | 0.32 | 0.38 | 6.30 |
| Non calcareous sedimentary | 39 | 0.06 | 0.09 | 0.25 | 0.38 | 1.0 | 3.13 |
| Igneous | 14 | 0.09 | 0.10 | 0.35 | 0.71 | 2.24 | 3.86 |
| Metamorphic | 35 | 0.09 | 0.12 | 0.32 | 0.54 | 1.95 | 2.84 |
| Sand and gravel | 6 | 0.11 | 0.11 | 0.15 | 0.15 | 0.19 | 0.19 |
| Mixed bedrock and gravel | 9 | 0.06 | 0.06 | 0.08 | 0.09 | 0.15 | 0.18 |
| *b) Coastal setting* | | | | | | | |
| Coastal wells | 31 | 0.05 | 0.07 | 0.25 | 0.77 | 3.49 | 6.30 |
| Non-coastal wells | 136 | 0.03 | 0.06 | 0.19 | 0.27 | 0.81 | 2.03 |
| *c) Nitrate* | | | | | | | |
| Wells with elevated nitrate | 87 | 0.05 | 0.06 | 0.20 | 0.28 | 0.79 | 1.92 |
| Wells with low nitrate | 80 | 0.03 | 0.05 | 0.20 | 0.46 | 2.07 | 6.30 |

The relationship between Ca and Mg for the main lithological groupings is illustrated in Figure 7.24. Note that the sample from St Brendan's well Roskeen is excluded (seawater). Linear trend lines (using the zero intercept option) are shown on the figure: the Mg to Ca relationship varies from y = 0.09x for the Mixed bedrock and gravel grouping, to y = 0.12x for the impure limestone group, and up to y = 0.28x for the metamorphic group. The linear trend lines for the four other lithological groups are very similar. $R^2$ values range from 0.0125 for the impure group up to 0.56 for the metamorphic group and 0.58 for sand and gravel.

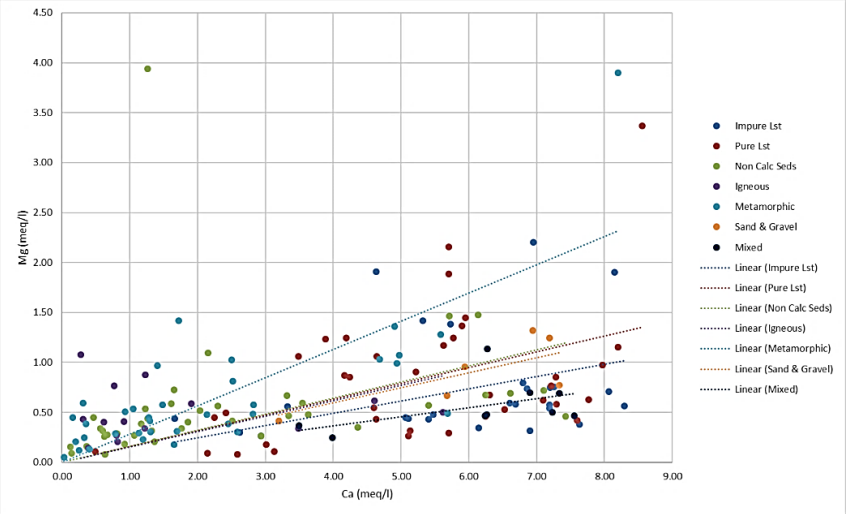



Figure 7.24 Mg versus Ca (in meq $l^{-1}$) for the main lithological groupings

In Figure 7.25, the Mg and Ca groundwater values are plotted for coastal and non-coastal wells. As explained in Section 5.10 and Section 7.5.5, coastal is here categorised (somewhat arbitrarily) as those wells within 500 m of the shoreline. The figure (which again excludes the seawater well St Brendan's well at Roskeen, Co Mayo) shows that Mg values are indeed elevated with respect to Ca in the coastal well samples (y = 0.25x compared to y = 0.13x). This is borne out by the summary statistics in Table 7.22 (these do include the sample from St Brendan's well), which show that the median and more especially the mean Mg:Ca ratios are higher in the coastal wells.

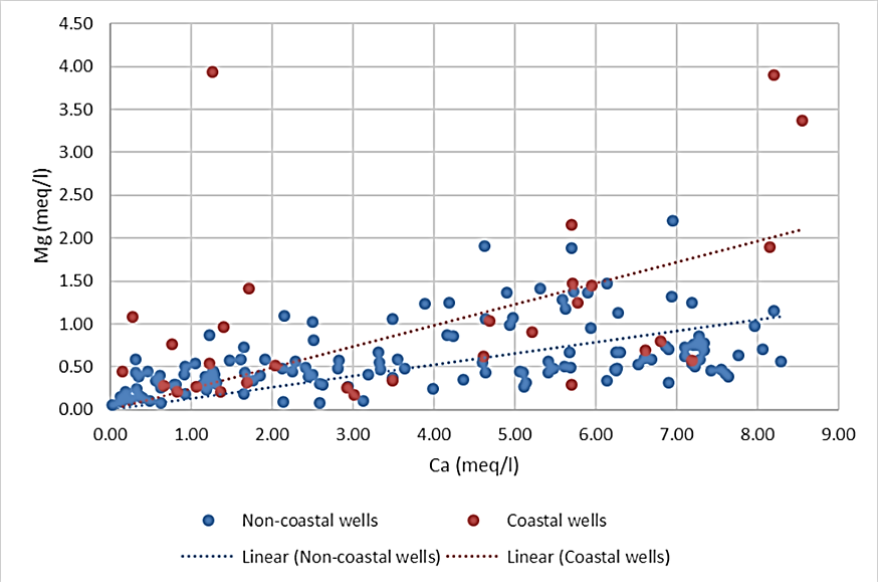



Figure 7.25 Mg versus Ca (in meq $l^{-1}$) in coastal versus non-coastal wells

Figure 7.26 indicates that there is no evident difference in the Mg:Ca trends for the water samples from wells with elevated nitrate compared to the wells with low nitrate. As before, elevated nitrate is here considered those samples with nitrate values above the natural background level of 2.0 mg $l^{-1}$ as N. The summary statistics in Table 7.22 indicate that the median Mg:Ca values are identical for both groups, but that the mean, 95$^{th}$ percentile and maximum Mg:Ca ratios are higher within the low nitrate well grouping, which includes St Brendan's well at Roskeen (again not included in Figure 7.26).

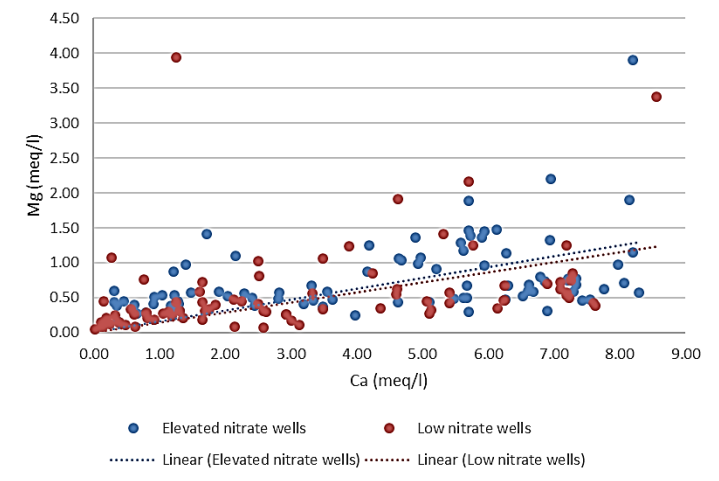



Figure 7.26 Mg versus Ca (in meq $l^{-1}$) in wells with elevated nitrate versus low nitrate wells

The relationship between Ca and Mg is considered to have some significance for human health, and is discussed further in Section 8.2.4.

### 7.5.8.2 Na and Cl

The relationships between Na and Cl are shown graphically for the different lithological groups, coastal versus non-coastal wells and for wells with elevated nitrate versus wells with low nitrate, in Figures 7.27 to 7.29, respectively. The Na:Cl ratio (in meq $l^{-1}$ units) should follow a trend line of 1:1 if halite dissolution is the main hydrochemical process governing their presence (Sappa *et al*., 2014). Whilst this is indeed the trend evident on all three graphs, halite is unlikely to be present in these lithologies and so a mixing line between fresh water and seawater compositions is the more likely hydrochemical process. The well sample with the highest Na and Cl values on all three figures is the seawater St Brendan's well at Roskeen, Co Mayo. It can be seen that this sample falls off the 1:1 trend – the likely reason for this is an underestimate of the Na

concentration, as discussed in Section 7.5.5. The sample with the second highest Na and Cl concentrations is from St Kee's well at Foohagh in Co Clare: a well with brackish water (EC = 2650 µS $cm^{-1}$) located in near horizontal beds of Namurian sandstones and shales, about 200 m from sea cliffs, and known for its eye cures (see Section 8.2.1).

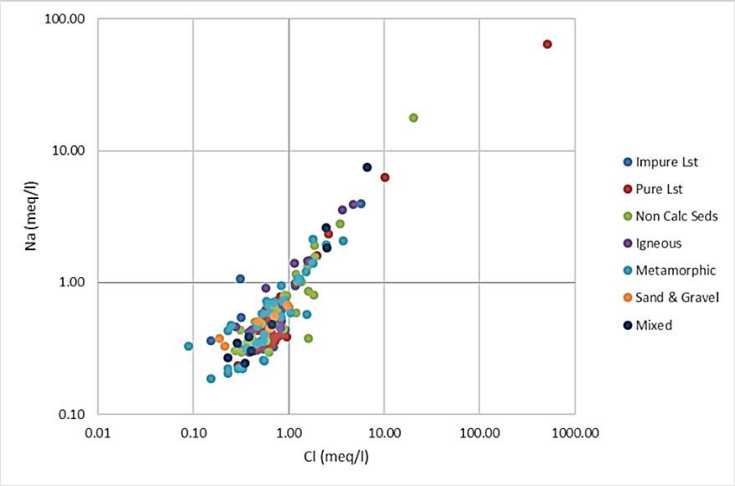



Figure 7.27 Na versus Cl (in meq $l^{-1}$, log-log scale) for the main lithological groupings

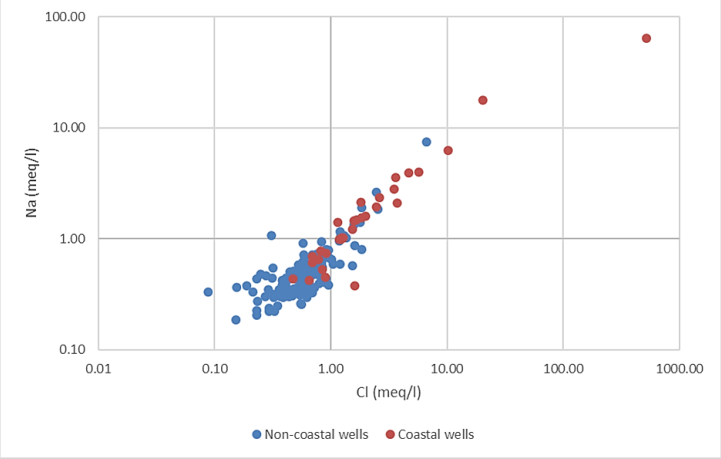



Figure 7.28 Na versus Cl (in meq $l^{-1}$, log-log scale) in coastal vs non-coastal wells

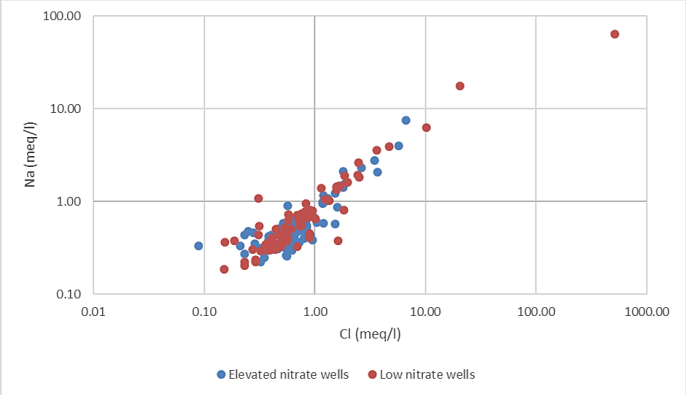



Figure 7.29 Na versus Cl (in meq $l^{-1}$, log-log scale) in wells with elevated nitrate versus low nitrate wells

In some samples, the Na:Cl ratios are greater than 1, suggesting an additional source of Na. However, the results in Figure 7.29 do not give a clear indication as to whether these are mainly high or low nitrate wells.

#### 7.5.8.3 K and Na

The ratio of K to Na has been used in several previous Irish studies as an indicator of groundwater pollution and its potential source. K and Na are both released into effluents as a result of the decomposition of vegetable organic matter, but K in higher proportion compared to Na. Groundwaters contaminated by such effluents therefore have elevated K and K:Na values. Daly and Daly (1982) suggested that K values greater than 5 mg $l^{-1}$ and K:Na ratios above 0.3 were indicative of pollution from farmyard runoff. Fitzsimons and Wright (2000) gave a threshold of 0.4 rather than 0.3 - albeit they emphasised that a K:Na ratio of less than 0.4 does not necessarily mean that farmyards wastes are *not* the source of contamination. Several studies have shown that K values in domestic wastewater are lower than in decaying vegetable matter, leading to K:Na ratios in affected groundwaters of less than 0.4, and sometimes nearer to 0.2 (Fennell, 2017; Gill *et al*., 2018). However, when attempting to use K:Na ratios to fingerprint the source of pollution, several limitations should be borne in mind: K may be derived from dissolution of K-rich rock minerals, K is preferentially adsorbed by clay particles in the soil and subsoil, and the K:Na ratios in groundwater can vary seasonally (Thorn and Hanna, 1989; Fennell, 2017).

The results of the K, Na and K:Na data from the holy well study are summarised in Table 7.23. The results are presented for the full dataset (n = 167 well samples), followed by the

values for coastal versus non-coastal wells and for the wells with elevated nitrate versus low nitrate wells. The median K and K:Na ratios for the full dataset are 1.94 mg $l^{-1}$ and 0.14 respectively, below the thresholds suggested by Daly and Daly (1982) as being indicative of pollution from vegetable matter. Although the median (and mean) K concentrations for coastal wells are higher than those for the other wells, the K:Na ratios are actually lower.

Table 7.23 K, Na and K:Na values for a) the full holy well dataset, b) coastal and non-coastal wells; and c) well samples with elevated nitrate and wells with low nitrate. All values and ratios are in mg $l^{-1}$

| | | N | Min | 5%ile | Median | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|
| *a) Full dataset* | | | | | | | | |
| | K | 167 | 0.04 | 0.47 | 1.94 | 5.45 | 10.3 | 408.4 |
| | Na | 167 | 4.3 | 6.1 | 10.9 | 28.8 | 58.2 | 1476 |
| | K:Na | 167 | 0.01 | 0.03 | 0.14 | 0.23 | 0.74 | 1.96 |
| *b) Coastal setting* | | | | | | | | |
| Coastal wells | K | 31 | 0.48 | 0.58 | 2.63 | 16.5 | 13.7 | 408.4 |
| | Na | 31 | 8.7 | 9.8 | 32.2 | 95.8 | 275.8 | 1476 |
| | K:Na | 31 | 0.03 | 0.03 | 0.09 | 0.10 | 0.22 | 0.28 |
| Non-coastal wells | K | 136 | 0.04 | 0.45 | 1.77 | 2.93 | 8.7 | 28.6 |
| | Na | 136 | 4.3 | 5.8 | 10.1 | 13.6 | 27.6 | 172 |
| | K:Na | 136 | 0.01 | 0.03 | 0.16 | 0.26 | 0.86 | 1.96 |
| *c) Nitrate* | | | | | | | | |
| Wells with elev nitrate | K | 87 | 0.39 | 0.55 | 2.33 | 3.24 | 10.0 | 22.8 |
| | Na | 87 | 5.1 | 6.4 | 10.7 | 16.9 | 48.5 | 172 |
| | K:Na | 87 | 0.03 | 0.05 | 0.16 | 0.27 | 0.74 | 1.96 |
| Wells with low nitrate | K | 80 | 0.04 | 0.39 | 1.76 | 7.85 | 9.77 | 408.4 |
| | Na | 80 | 4.3 | 5.4 | 12.2 | 41.8 | 82.1 | 1476 |
| | K:Na | 80 | 0.01 | 0.01 | 0.12 | 0.19 | 0.62 | 1.54 |

Of most interest in the table are the comparisons between the wells with elevated nitrate and those with low nitrate levels. The elevated nitrate wells have higher median K and K:Na ratios, as might be expected since anthropogenic influences are the likely cause of the high nitrate levels. The highest K:Na ratio (1.96) was from St Fiachra's well in Ullard in Co Kilkenny. This well is in a field where grazing cattle were observed near the well. The aquifer is weathered granite (i.e. igneous lithological group), and the groundwater

vulnerability is rated as Extreme. The K concentration was 22.8 mg $l^{-1}$, and the $NO_3$ was 8.7 mg $l^{-1}$ as N, both indicative of pollution. The well sample with the highest K and Na concentrations was the seawater well at Roskeen in Co Mayo (note that the Na value is likely an underestimate - see Section 7.5.5 – and hence the true K:Na ratio is likely lower than the value calculated (0.28).

K:Na and K values are plotted (log-log scale) for the elevated nitrate versus the low nitrate well samples in Figure 7.30. The K:Na to K relationships are similar for the two groups. Of the 87 wells with elevated nitrate (i.e. $NO_3$ above 2.0 mg $l^{-1}$ as N), 10 samples (i.e. 11%) satisfied the Daly and Daly (1982) criteria for agricultural contamination of having K:Na ratios above 0.3 and K concentrations above 5 mg $l^{-1}$. For the low nitrate wells, seven samples (9%) exceeded the Daly and Daly threshold values i.e. a similar proportion, suggesting that there was very little relationship between K:Na ratio and nitrate concentration.

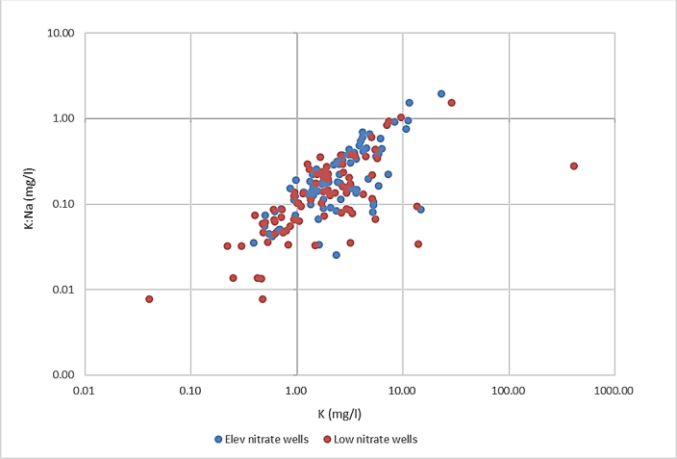



Figure 7.30 K:Na versus K (mg $l^{-1}$) for elevated and low nitrate wells

## 7.6 Minor ion and trace element results

### 7.6.1 Background equivalent concentration and limit of detection

When dealing with minor ions and, most especially, trace elements the minimum reporting limit is particularly important. In the statistical summaries that follow in this section, three analytical limits are given for each parameter: the background equivalent concentration (BEC), the limit of detection (LoD) and the limit of quantification (LoQ). In spectrochemistry, the BEC is defined

as 'the analyte concentration that produces a net signal (peak minus background) equal to the background' (Spectroscopy, 2012). In the TCD Geochemistry lab, the BEC was based on calibrating the background signal in each individual experiment.

This account of the procedures was provided by Cora McKenna: taking the 2% $HNO_3$ solution used as a carrier acid, which was spiked with an internal standard to account for any addition from that, and calibrating the raw counts in that solution using the calibration value for each element in the experiment - which took account of the ICP-MS machine's sensitivity on that day - gave a basic background for the entire set-up used for that day. The LoD was based on 3.3 times the standard deviation on the raw blank counts (International Council for Harmonisation, 2005). For a more stringent view of the results, a factor of 10 on the standard deviation was also used, and referred to as the limit of quantification (LoQ). In the results tables that follow, the BEC, LoD and LoQ values are the averages over the experimental period.

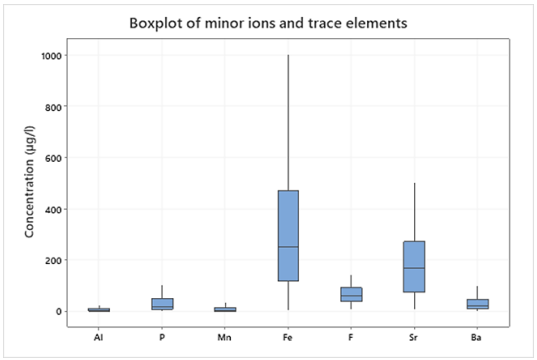
It should be noted that values recorded in the TCD Geochemistry lab results spreadsheet as "#N/A" were either minus values, zeros, or elements that could not be calibrated in a particular experiment (i.e. not determined). These are not included in the summary statistics. Therefore, the statistics are for those samples where a positive value was recorded, even if this value was below the LoD or the BEC.

Much has been written about how best to incorporate values below detection limits ('nondetects') into the statistical treatment of data. Methods include substituting zero values or half the value of the LoD, to approaches involving more sophisticated statistical treatments such as maximum likelihood estimate (MLE) and regression analysis on a probability plot. In a review of methods, Helsel (2010) argued against using substitution methods, although he pointed out that different authors have come to different conclusions about the relative performance of MLE and probability distribution approaches. In their study of arsenic in Irish groundwaters (Section 6.3.3), McGrory *et al*. (2017) used many datasets collected over a 20-year period, with many different detection limits. They therefore applied a statistical method involving the calculation of empirical distribution functions, which can cope with multiple detection limits. In contrast, in their NBL study (see Section 6.3.2), Tedd *et al*. (2017) adopted a simple substitution approach (i.e. 0.5 x LoD). This approach likely had a large impact on the statistics of those parameters with a high proportion of values below the LoD.

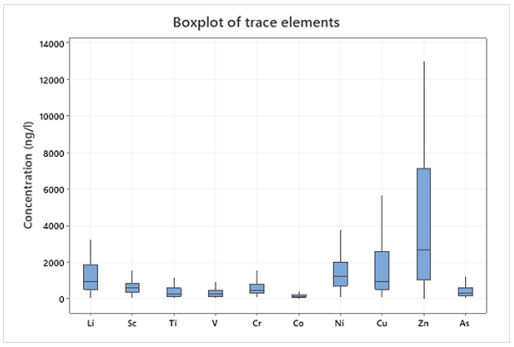
For the current research, it was decided to avoid substitution, but to follow the simple approach whereby positive values below the LoD were retained when calculating the descriptive statistics. It was not considered justified to apply methods such as MLE or regression analysis for the large number of different parameters involved in this research, especially when there are differences of opinion in the literature as to the best method to follow.

### 7.6.2 Summary descriptive statistics for minor ions and trace elements

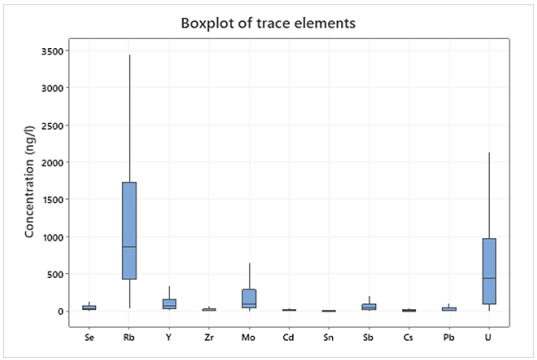
Box and whisker plots for 37 minor ions and trace elements are shown in Figure 7.31, whilst the plot for the 14 lanthanide rare earth elements analysed is included in Figure 7.32. These two figures, together with the box plot for major ions presented previously in Figure 7.14 (see Section 7.5.3), provide statistical summaries for all the chemical parameters analysed (n = 60) except for iodide. Iodide was analysed for in only 10 samples, and in every case the result was less than the reporting value of 0.1 mg $l^{-1}$.



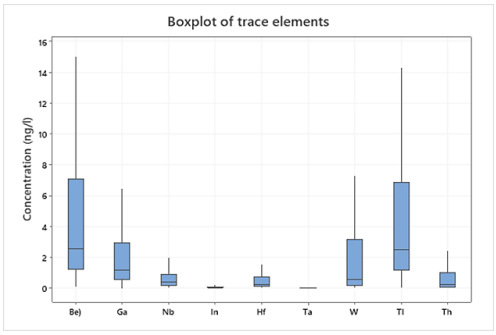

a)




b)




c)




d)

Figure 7.31 Box and whisker plots for 37 minor ions and trace elements. (The number of determinations for the different elements varies – see the relevant tables).

For convenience of scaling, the elements in the box plots in Figures 7.31a to 7.31d are grouped approximately according to concentration values (rather than by chemical characteristic e.g. alkali metal, alkali earth element, transition metal, etc). In 7.31a, the concentrations are in µg $l^{-1}$ (ppb) and it can be seen that Fe and Sr have the highest median values and the greatest ranges in values. The other three plots in the Figure 7.31 (b, c and d) all show concentrations in ng $l^{-1}$. Amongst the REEs in Figure 7.32, the lighter elements, especially La and Nd, are the most abundant and show the largest variation in concentrations.

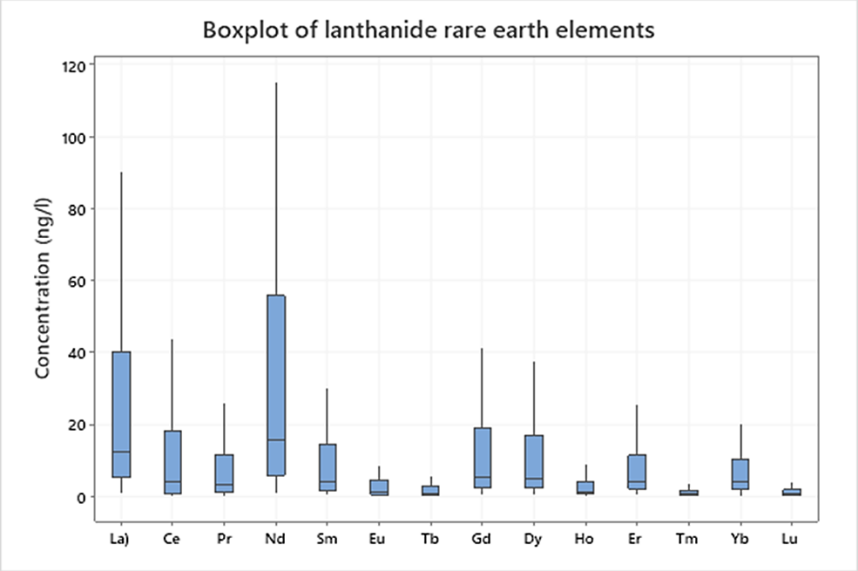



Figure 7.32 Box and whisker plots for the 14 lanthanide rare earth elements

Descriptive statistics for the minor ions and trace elements are included in Table 7.24 and Table 7.25, the latter containing the results for the lanthanide rare earth elements (REEs). NBL values are included in the right-hand column of Table 7.24 (NBLs have not been established for the REEs in Table 7.25). The NBLs are national, or national unconfined aquifer values. Trace element analyses were performed on up to 156 different well samples of the total 167 holy wells sampled (Section 7.2).

Table 7.24 Summary descriptive statistics for minor ions and trace elements, listed in alphabetical order (but excluding the REEs, which are shown in Table 7.25)

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 147 | 0.165 | 0.533 | 1.279 | 0.006 | 0.032 | 1.62 | 21.4 | 79.5 | 622.6 | |
| Antimony (Sb) | ng $l^{-1}$ | 155 | 0.75 | 1.83 | 4.03 | 1.039 | 5.209 | 46.89 | 110.2 | 283.2 | 4642 | 500 |
| Arsenic (As)[a] | µg $l^{-1}$ | 156 | 0.013 | 0.018 | 0.027 | 0.027 | 0.076 | 0.30 | 0.75 | 2.36 | 23.5 | 2.0 |
| Barium (Ba) | µg $l^{-1}$ | 156 | 0.011 | 0.016 | 0.027 | 0.728 | 1.653 | 19.62 | 42.4 | 149.5 | 538.3 | |
| Beryllium (Be) | ng $l^{-1}$ | 156 | 0.165 | 0.391 | 0.851 | 0.099 | 0.441 | 2.53 | 11.8 | 51.8 | 313.6 | <1000 |
| Cadmium (Cd) | ng $l^{-1}$ | 155 | 0.1 | 0.29 | 0.67 | 0.167 | 1.282 | 10.21 | 39.5 | 55.5 | 2725 | <400 |
| Caesium (Cs) | ng $l^{-1}$ | 156 | 0.06 | 0.1 | 0.19 | 0.142 | 0.526 | 6.41 | 32.1 | 194.1 | 488.8 | |
| Chromium (Cr)[a] | µg $l^{-1}$ | 133 | 0.158 | 0.194 | 0.269 | 0.089 | 0.146 | 0.46 | 1.25 | 1.89 | 63.4 | |
| Cobalt (Co)[a] | µg $l^{-1}$ | 156 | 0.006 | 0.008 | 0.011 | 0.010 | 0.023 | 0.13 | 0.20 | 0.43 | 3.25 | <1 |
| Copper (Cu) | µg $l^{-1}$ | 156 | 0.015 | 0.023 | 0.039 | 0.064 | 0.138 | 0.94 | 3.24 | 13.41 | 58.3 | 16 |
| Fluoride (F) | µg $l^{-1}$ | 151 | | 100 | | 9.1 | 20.0 | 58.8 | 75.4 | 164.0 | 520.0 | 200[b] |
| Gallium (Ga) | ng $l^{-1}$ | 150 | 0.25 | 0.45 | 0.86 | 0.0000 | 0.167 | 1.153 | 4.42 | 23.3 | 68.5 | |
| Hafnium (Hf) | ng $l^{-1}$ | 131 | 0.070 | 0.140 | 0.300 | 0.006 | 0.029 | 0.24 | 0.80 | 2.82 | 15.0 | |
| Indium (In) | ng $l^{-1}$ | 128 | 0.050 | 0.140 | 0.320 | 0.001 | 0.008 | 0.04 | 0.67 | 0.359 | 74.0 | |
| Iron (Fe) | µg $l^{-1}$ | 156 | 8.761 | 9.046 | 9.624 | 1.97 | 20.41 | 251.7 | 380.3 | 988.3 | 5154 | 268[b] |
| Lead (Pb) | ng $l^{-1}$ | 130 | 4.320 | 15.99 | 39.68 | 0.068 | 0.975 | 14.19 | 82.7 | 475.3 | 2094 | 2900 |
| Lithium (Li) | µg $l^{-1}$ | 156 | 0.122 | 0.137 | 0.167 | 0.017 | 0.143 | 0.95 | 4.05 | 5.10 | 293.7 | |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 150 | 0.046 | 0.063 | 0.10 | 0.01 | 0.04 | 2.09 | 27.9 | 86.6 | 1062 | 23[b] |
| Molyb'num (Mo) | ng $l^{-1}$ | 156 | 0.50 | 1.44 | 3.33 | 0.474 | 3.417 | 96.1 | 589.3 | 1235.3 | 23600 | <1000 |
| Nickel (Ni) | µg $l^{-1}$ | 156 | 0.007 | 0.014 | 0.028 | 0.048 | 0.255 | 1.24 | 1.69 | 5.26 | 11.3 | 2.1[b] |
| Niobium (Nb) | ng $l^{-1}$ | 142 | 0.110 | 0.210 | 0.400 | 0.005 | 0.072 | 0.37 | 1.30 | 4.105 | 22.4 | |
| Phosphorus (P) | µg $l^{-1}$ | 132 | 22.38 | 23.96 | 27.18 | 0.04 | 2.15 | 17.21 | 85.5 | 295.8 | 3299 | 17 |
| Rubidium (Rb) | µg $l^{-1}$ | 156 | 0.001 | 0.001 | 0.002 | 0.044 | 0.138 | 0.86 | 2.27 | 4.89 | 108.2 | |
| Scandium (Sc) | µg $l^{-1}$ | 156 | 0.046 | 0.049 | 0.055 | 0.041 | 0.137 | 0.58 | 0.63 | 1.22 | 2.04 | |
| Selenium (Se) | ng $l^{-1}$ | 100 | 7.421 | 10.62 | 17.13 | 4.383 | 10.38 | 36.13 | 63.5 | 185.0 | 845.8 | |
| Strontium (Sr) | µg $l^{-1}$ | 156 | 0.039 | 0.049 | 0.067 | 5.496 | 23.43 | 169.9 | 262.3 | 670.8 | 6647.0 | |
| Tantalum (Ta) | ng $l^{-1}$ | 98 | 0.020 | 0.050 | 0.100 | 0.000 | 0.001 | 0.02 | 0.04 | 0.174 | 0.71 | |
| Thallium (Tl) | ng $l^{-1}$ | 156 | 0.230 | 0.350 | 0.600 | 0.027 | 0.669 | 2.50 | 11.07 | 27.15 | 626.9 | |
| Thorium (Th) | ng $l^{-1}$ | 155 | 0.030 | 0.130 | 0.340 | 0.002 | 0.034 | 0.21 | 2.35 | 8.69 | 94.5 | |
| Tin (Sn) | ng $l^{-1}$ | 123 | 2.780 | 4.900 | 9.200 | 0.003 | 0.279 | 2.36 | 7.07 | 25.36 | 152.5 | |
| Titanium (Ti)[a] | µg $l^{-1}$ | 156 | 0.056 | 0.095 | 0.174 | 0.038 | 0.071 | 0.25 | 0.68 | 1.57 | 29.0 | |
| Tungsten (W) | ng $l^{-1}$ | 106 | 1.010 | 1.490 | 2.460 | 0.005 | 0.047 | 0.58 | 9.45 | 19.36 | 467.5 | |
| Uranium (U) | ng $l^{-1}$ | 156 | 0.330 | 0.440 | 0.660 | 3.515 | 8.212 | 445.3 | 786.4 | 2480.8 | 11150 | |
| Vanadium (V)[a] | µg $l^{-1}$ | 132 | 0.042 | 0.053 | 0.074 | 0.003 | 0.014 | 0.25 | 0.62 | 1.38 | 23.7 | |
| Yttrium (Y) | ng $l^{-1}$ | 156 | 0.105 | 0.421 | 1.064 | 7.716 | 13.33 | 68.08 | 210.1 | 788.4 | 6047 | |
| Zircon (Zr) | ng $l^{-1}$ | 149 | 0.800 | 1.400 | 2.630 | 0.123 | 1.254 | 11.26 | 31.1 | 97.3 | 622.0 | |
| Zinc (Zn)[a] | µg $l^{-1}$ | 77 | 0.088 | 0.287 | 0.692 | 0.016 | 0.172 | 2.67 | 15.3 | 58.8 | 350.8 | |

Notes: [a] Results prone to chloride interferences

[b] NBL for unconfined aquifer

Table 7.25 Summary descriptive statistics for lanthanide rare earth elements, listed in order of increasing atomic mass. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 156 | 0.080 | 0.340 | 0.880 | 1.040 | 2.092 | 12.45 | 108.2 | 417.6 | 3704 |
| Cerium (Ce) | 154 | 0.130 | 0.610 | 1.580 | 0.011 | 0.240 | 4.11 | 108.2 | 353.8 | 5121 |
| Praseodymium (Pr) | 156 | 0.020 | 0.100 | 0.260 | 0.179 | 0.515 | 3.39 | 32.2 | 130.8 | 1131 |
| Neodymium (Nd) | 156 | 0.090 | 0.390 | 0.980 | 0.934 | 2.519 | 15.89 | 151.5 | 624.6 | 6818 |
| Samarium (Sm) | 156 | 0.050 | 0.160 | 0.390 | 0.490 | 0.748 | 4.25 | 40.5 | 152.6 | 2495 |
| Europium (Eu) | 137 | 0.020 | 0.050 | 0.130 | 0.024 | 0.154 | 1.23 | 11.0 | 38.5 | 636.7 |
| Gadolinium (Gd) | 156 | 0.040 | 0.110 | 0.250 | 0.400 | 0.814 | 5.49 | 45.4 | 158.3 | 2902 |
| Terbium (Tb) | 156 | 0.010 | 0.020 | 0.050 | 0.050 | 0.122 | 0.77 | 5.59 | 19.07 | 300.6 |
| Dysprosium (Dy) | 156 | 0.040 | 0.110 | 0.270 | 0.528 | 0.912 | 4.98 | 29.6 | 104.2 | 1303 |
| Holmium (Ho) | 156 | 0.010 | 0.030 | 0.070 | 0.150 | 0.262 | 1.24 | 6.24 | 22.32 | 230.2 |
| Erbium (Er) | 156 | 0.030 | 0.080 | 0.180 | 0.393 | 0.785 | 4.05 | 17.06 | 58.07 | 554.8 |
| Thulium (Tm) | 156 | 0.010 | 0.020 | 0.040 | 0.046 | 0.113 | 0.64 | 2.41 | 7.78 | 71.7 |
| Ytterbium (Yb) | 156 | 0.030 | 0.070 | 0.170 | 0.257 | 0.790 | 4.22 | 14.98 | 46.93 | 420.2 |
| Lutetium (Lu) | 156 | 0.010 | 0.030 | 0.060 | 0.053 | 0.144 | 0.71 | 2.45 | 7.96 | 66.5 |

In examining the data in these tables, the following should be noted:

a) Concentration values are often very low, with minima and 5 percentiles often below the BEC value: for example, the minimum values of 24 of the parameters in Table 7.24 were below the BEC, whilst 11 of the 5%ile values were also less than the BEC. In the case of Sn (tin) and P the median concentrations are less than the BEC (with P, there is a high background noise signal when using ICP-MS, which results in a high BEC). Of the lanthanide REEs in Table 7.25, only the minimum value for Ce is less than the BEC.
b) The determinations for elements such as Ti, V, Cr, Co, Zn and As can be prone to interferences from chlorine (Section 7.2.1).
c) Sb values can be affected by leaching from PET sample containers (Reimann and Birke, 2010).

In relation to NBLs, the 95%ile values for As, Fe, Mn, Mo, Ni and P all exceed the national (or national unconfined aquifer) NBL, whilst the median value for Fe is close to the NBL and that for P is greater. For iron, 44% of the values exceeded the NBL. In the case of P it may be a case of not comparing like with like. The NBL is based on molybdenate reactive phosphorus (as P), whereas the determinations in this project were of total dissolved P (again the results expressed as P).

The highest Fe concentration of more than 5 mg $l^{-1}$ was taken from St Menaghan's well in Co Westmeath; this is an overgrown spring / seepage in a boggy field (the aquifer is impure limestone, and the groundwater vulnerability is rated as High) which would be susceptible to pollution (concentrations of K, Mn, Ni and As exceeded the NBLs, although the recorded $NO_3$ value was low, at 0.5 mg $l^{-1}$ as N).

The maximum value of antimony (Sb) was recorded in St Patrick's well in Trinity College Dublin. This mixed gravel and bedrock well is in the heart of the city and is vulnerable to pollution from a variety of sources, including leaking sewers, traffic and other urban activities. Na, K, Cl, Mo, Ni and As were also above the NBLs, as was the $NO_3$ at 3.6 mg $l^{-1}$ as N. The highest As concentration was found in the seawater St Brendan's well at Roskeen in Co Mayo. The value of 23.5 µg $l^{-1}$ is greater than the average concentration reported elsewhere for seawater of 3 µg $l^{-1}$ (Hem, 1985). The maximum concentration of Mo (23.6 µg $l^{-1}$) was detected in St Enda's well at Barna, Co Galway. This is a granite well, close to the sea, with X Extreme groundwater vulnerability. The nitrate concentration was below the NBL, but values of Na, K, $SO_4$, Cl, Fe, Mn and U were all above the NBLs.

Whilst NBLs for U have been established for different lithological groups rather than at a national level (Section 6.3.2) - and so an NBL value is not included in Table 7.24 - it is worth noting here that that the NBLs for the relevant lithologies were exceeded in five of the 156 wells sampled: four of these wells are in igneous aquifers (including St Enda's well at Barna), where elevated U might be expected, and the other is an impure limestone well (St Finian's well at Clonard in Co Meath), where the highest concentration of 11.15 µg $l^{-1}$ was determined (the NBL is 3.1 µg $l^{-1}$).

In terms of numbers of samples that exceeded the national (or national unconfined aquifer) NBL, there were 69 exceedances for Fe (44% of samples), 32 for Ni (21%), 26 for Mn (17%), 13 for Mo (8%), 8 for As (5%), 7 for Cu (4%), 5 for U (3%), 3 for Sb (2%), 2 for Co (1%) and 2 for Cd (1%). There were no exceedances of national NBLs for either Be or Pb.

Fluoride is one of the minor ions of special health significance (see Section 6.2.3). Importantly, none of the F concentrations approached levels where F would be a health concern. Only six of the values (n = 151) exceeded the NBL (for unconfined aquifers) of 0.2 mg $l^{-1}$. The maximum concentration of 0.52 mg $l^{-1}$ was matched in two samples: one from Tullowphelim in Co Carlow,

which probably has a mixed gravel and igneous bedrock source, and the other from St Hugh's well at Cleighran Beg in Co Leitrim, which is sourced from an impure limestone aquifer. The Tullowphelim sample had high nitrate (4.5 mg $l^{-1}$ as N), and the $SO_4$, Cl and Fe values also exceeded the NBLs. In contrast, the sample from St Hugh's well showed low nitrate (less than the NBL), but had Na, $SO_4$, Fe, Mn, and Mo values above the NBLs. In particular, the iron-rich (chalybeate) nature of the water at this spring well is evident from the ochreous staining of the well lining and overflow (see Section 5.2.2.2).

In Table 7.25, where the REE elements are presented in order of increasing atomic mass, the lighter REEs are more abundant, with higher median and mean concentrations. NBLs have not been established for any of the REEs, so are not shown in Table 7.25. However, comparisons can be made between concentrations in individual wells and the 95%ile values for the full dataset. Wells with elevated REEs (i.e. several REE concentrations above the 95%ile) include:

a) Our Lady's well and Lady's Island well in Co Wexford. In Lady's Island well, all 14 of the lanthanide REEs were above the 95%ile, plus yttrium, whilst 11 of the lanthanide REEs plus Y were elevated in Our Lady's well. Both are coastal wells probably tapping the transition zone of metamorphic bedrock.
b) St Colmcille's well at Glencolmcille, Co Donegal: all 14 lanthanide REEs and Y were elevated, as were concentrations of several other trace elements including Fe, Mn, Ti, Ga, Zr, Nb, In, Hf, Ta and Th. The aquifer is metamorphic bedrock, and the well is within 500 m of the coast (Section 5.6.4).
c) St Patrick's well at Cartron, Co Longford, where 10 of the 14 lanthanide REEs had elevated concentrations. This well is also sourced from a metamorphic bedrock aquifer (but is in an inland setting; Section 5.6.1).
d) Toberpatrick at Cornacullew in Co Longford: values for nine of the lanthanide REEs plus Y were above the 95%iles. Several other trace elements exceeded the NBLs, including Al, Mn, Ni and Cu. The main lithology is metamorphic.
e) St Kilian's well at Mullagh in Co Cavan: six of the lanthanide REEs had concentrations above the 95%ile, and the aquifer lithology is again metamorphic.
f) St Kevin's well at Glendalough Co Wicklow: 10 of the lanthanide REEs plus Y were present in concentrations above the 95%ile. The groundwater source is likely to be metamorphic bedrock (although the local river alluvium may also contribute; see Section 5.6.2).

g) St Patrick's well Knockpatrick in Co Limerick: concentrations of all 14 lanthanide REEs plus Y were elevated. The bedrock aquifer here is non-calcareous sedimentary (Namurian sandstones).
h) St Colmcille's well at Disert in Co Donegal: all 14 lanthanide REEs and Y had concentrations above the 95%ile. The groundwater source of this well is non-calcareous sedimentary bedrock (Dinantian sandstones; Section 5.4.3.1).

Of the nine wells mentioned above, seven are in metamorphic bedrock whilst the remaining two have a non-calcareous sedimentary groundwater source (see Section 7.6.3.1 below for further discussion in relation to lithology, illustrated by cumulative probability plots and normalised values relative to crustal REE concentrations). Three of the wells are located in a coastal environment. With regard to potential anthropogenic impacts, only three of the nine well samples had elevated nitrate values.

The potential influence of anthropogenic activities can be examined by removing those well samples with elevated nitrate concentrations. Tables 7.26 and 7.27 include the minor ion and trace element descriptive statistics for the well samples with low nitrate (<2 mg $l^{-1}$ as N), with the second table again comprising the lanthanide REEs.

When the median concentrations of trace elements are compared between the low nitrate wells in Table 7.26 with the full well dataset in Table 7.24, over half of the 37 trace elements (54%) have higher median values in the low nitrate wells, with 30% higher in the full well dataset (with the medians being approximately equal in the remaining 16%). The 95%ile values are higher in the low nitrate wells for 65% of the 37 parameters compared to the full well dataset.

The situation is even more striking in the lanthanide REEs: here, the median values for all 14 elements (and the 95%iles for 13 out of 14 of these REE elements) are higher in the low nitrate wells (Table 7.27) than in the full dataset (Table 7.25). This finding is consistent with the earlier observation that the majority of wells with elevated REEs did not have high nitrate concentrations.

Overall, these comparisons suggest that anthropogenic activities – or at least those associated with elevated nitrate values – have *not* resulted in elevated trace element concentrations in this holy wells dataset, and that the dominant influence is lithology (see Section 7.6.3 below).

Table 7.26 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table 7.27) for wells with low nitrate concentrations (< 2 mg $l^{-1}$ as N)

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max | NBL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 73 | 0.165 | 0.533 | 1.279 | 0.02 | 0.09 | 3.76 | 39.7 | 255.0 | 622.6 | |
| Antimony (Sb) | ng $l^{-1}$ | 76 | 0.75 | 1.83 | 4.03 | 1.039 | 4.653 | 47.34 | 94.8 | 281.9 | 1299 | 500 |
| Arsenic (As)[a] | µg $l^{-1}$ | 76 | 0.013 | 0.018 | 0.027 | 0.038 | 0.073 | 0.30 | 0.77 | 1.69 | 23.5 | 2.0 |
| Barium (Ba) | µg $l^{-1}$ | 76 | 0.011 | 0.016 | 0.027 | 0.728 | 1.607 | 13.85 | 30.4 | 88.6 | 281.6 | |
| Beryllium (Be) | ng $l^{-1}$ | 76 | 0.165 | 0.391 | 0.851 | 0.155 | 0.653 | 2.95 | 10.2 | 36.0 | 132.3 | <1000 |
| Cadmium (Cd) | ng $l^{-1}$ | 75 | 0.1 | 0.29 | 0.67 | 0.167 | 1.206 | 11.07 | 19.8 | 55.5 | 302.7 | <400 |
| Caesium (Cs) | ng $l^{-1}$ | 76 | 0.06 | 0.1 | 0.19 | 0.302 | 0.498 | 4.03 | 19.8 | 53.7 | 340 | |
| Chromium (Cr)[a] | µg $l^{-1}$ | 70 | 0.158 | 0.194 | 0.269 | 0.089 | 0.140 | 0.42 | 1.79 | 2.08 | 63.4 | |
| Cobalt (Co)[a] | µg $l^{-1}$ | 76 | 0.006 | 0.008 | 0.011 | 0.010 | 0.025 | 0.13 | 0.25 | 0.94 | 3.25 | <1 |
| Copper (Cu) | µg $l^{-1}$ | 76 | 0.015 | 0.023 | 0.039 | 0.094 | 0.158 | 0.95 | 4.30 | 20.07 | 58.3 | 16 |
| Fluoride (F) | µg $l^{-1}$ | 72 | | 100 | | 9.1 | 18.6 | 59.1 | 79.7 | 180.3 | 520.0 | 200[b] |
| Gallium (Ga) | ng $l^{-1}$ | 72 | 0.25 | 0.45 | 0.86 | 0.122 | 0.301 | 1.36 | 6.74 | 30.38 | 68.5 | |
| Hafnium (Hf) | ng $l^{-1}$ | 69 | 0.070 | 0.140 | 0.300 | 0.013 | 0.075 | 0.34 | 1.25 | 5.71 | 15.0 | |
| Indium (In) | ng $l^{-1}$ | 68 | 0.050 | 0.140 | 0.320 | 0.002 | 0.010 | 0.04 | 1.20 | 0.628 | 74.0 | |
| Iron (Fe) | µg $l^{-1}$ | 76 | 8.761 | 9.046 | 9.624 | 1.97 | 17.28 | 208.3 | 382.8 | 1028.8 | 5154 | 268[b] |
| Lead (Pb) | ng $l^{-1}$ | 67 | 4.320 | 15.99 | 39.68 | 0.068 | 1.353 | 15.00 | 80.9 | 359.4 | 1131 | 2900 |
| Lithium (Li) | µg $l^{-1}$ | 76 | 0.122 | 0.137 | 0.167 | 0.017 | 0.119 | 0.66 | 5.47 | 4.31 | 293.7 | |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 75 | 0.046 | 0.063 | 0.10 | 0.03 | 0.04 | 7.65 | 48.7 | 212.9 | 1062 | 23[b] |
| Molyb'num (Mo) | ng $l^{-1}$ | 76 | 0.50 | 1.44 | 3.33 | 0.474 | 6.646 | 136.9 | 778.5 | 2850.3 | 23600 | <1000 |
| Nickel (Ni) | µg $l^{-1}$ | 76 | 0.007 | 0.014 | 0.028 | 0.048 | 0.240 | 1.26 | 1.96 | 6.32 | 11.3 | 2.1[b] |
| Niobium (Nb) | ng $l^{-1}$ | 66 | 0.110 | 0.210 | 0.400 | 0.066 | 0.091 | 0.70 | 2.24 | 14.25 | 22.4 | |
| Phosphorus (P) | µg $l^{-1}$ | 65 | 22.38 | 23.96 | 27.18 | 0.04 | 1.34 | 13.58 | 56.0 | 301.0 | 710.9 | 17 |
| Rubidium (Rb) | µg $l^{-1}$ | 76 | 0.001 | 0.001 | 0.002 | 0.086 | 0.146 | 0.79 | 2.71 | 4.98 | 108.2 | |
| Scandium (Sc) | µg $l^{-1}$ | 76 | 0.046 | 0.049 | 0.055 | 0.041 | 0.087 | 0.38 | 0.45 | 1.00 | 1.38 | |
| Selenium (Se) | ng $l^{-1}$ | 50 | 7.421 | 10.62 | 17.13 | 4.383 | 8.492 | 27.10 | 55.7 | 136.3 | 845.8 | |
| Strontium (Sr) | µg $l^{-1}$ | 76 | 0.039 | 0.049 | 0.067 | 5.496 | 19.980 | 150.2 | 313.4 | 796.5 | 6647 | |
| Tantalum (Ta) | ng $l^{-1}$ | 50 | 0.020 | 0.050 | 0.100 | 0.001 | 0.002 | 0.02 | 0.07 | 0.273 | 0.71 | |
| Thallium (Tl) | ng $l^{-1}$ | 76 | 0.230 | 0.350 | 0.600 | 0.217 | 0.777 | 3.29 | 7.36 | 18.75 | 103.2 | |
| Thorium (Th) | ng $l^{-1}$ | 76 | 0.030 | 0.130 | 0.340 | 0.038 | 0.050 | 0.67 | 4.36 | 19.70 | 94.5 | |
| Tin (Sn) | ng $l^{-1}$ | 61 | 2.780 | 4.900 | 9.200 | 0.058 | 0.441 | 2.90 | 9.27 | 34.73 | 152.5 | |
| Titanium (Ti)[a] | µg $l^{-1}$ | 76 | 0.056 | 0.095 | 0.174 | 0.038 | 0.063 | 0.25 | 1.01 | 2.97 | 29.0 | |
| Tungsten (W) | ng $l^{-1}$ | 56 | 1.010 | 1.490 | 2.460 | 0.005 | 0.029 | 0.67 | 11.88 | 20.33 | 467.5 | |
| Uranium (U) | ng $l^{-1}$ | 76 | 0.330 | 0.440 | 0.660 | 3.515 | 10.153 | 237.6 | 708.6 | 2075.8 | 11150 | |
| Vanadium (V)[a] | µg $l^{-1}$ | 63 | 0.042 | 0.053 | 0.074 | 0.006 | 0.027 | 0.28 | 0.93 | 2.71 | 23.7 | |
| Yttrium (Y) | ng $l^{-1}$ | 76 | 0.105 | 0.421 | 1.064 | 7.716 | 13.55 | 71.83 | 244.6 | 817.8 | 6047 | |
| Zircon (Zr) | ng $l^{-1}$ | 75 | 0.800 | 1.400 | 2.630 | 0.773 | 1.443 | 12.15 | 47.2 | 191.7 | 622.0 | |
| Zinc (Zn)[a] | µg $l^{-1}$ | 38 | 0.088 | 0.287 | 0.692 | 0.016 | 0.048 | 2.83 | 9.1 | 31.1 | 77.6 | |

Notes: [a] Results prone to chloride interferences

[b] NBL for unconfined aquifer

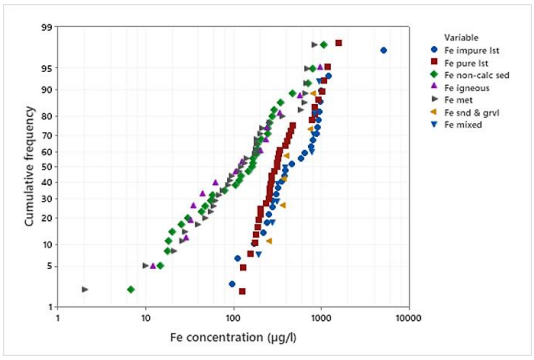
Table 7.27 Summary descriptive statistics for the lanthanide rare earth elements for wells with low nitrate concentrations (<2 mg $l^{-1}$ as N). All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 76 | 0.080 | 0.340 | 0.880 | 1.210 | 2.619 | 19.06 | 168.2 | 729.4 | 3704 |
| Cerium (Ce) | 76 | 0.130 | 0.610 | 1.580 | 0.213 | 0.520 | 9.39 | 190.2 | 834.4 | 5121 |
| Praseodymium (Pr) | 76 | 0.020 | 0.100 | 0.260 | 0.327 | 0.815 | 5.02 | 48.3 | 201.5 | 1131 |
| Neodymium (Nd) | 76 | 0.090 | 0.390 | 0.980 | 1.625 | 3.814 | 24.46 | 223.5 | 866.8 | 6818 |
| Samarium (Sm) | 76 | 0.050 | 0.160 | 0.390 | 0.511 | 1.012 | 6.09 | 60.4 | 186.9 | 2495 |
| Europium (EU) | 71 | 0.020 | 0.050 | 0.130 | 0.065 | 0.285 | 1.64 | 15.4 | 41.6 | 636.7 |
| Gadolinium (Gd) | 76 | 0.040 | 0.110 | 0.250 | 0.582 | 1.235 | 6.84 | 67.2 | 189.4 | 2902 |
| Terbium (Tb) | 76 | 0.010 | 0.020 | 0.050 | 0.094 | 0.203 | 0.95 | 7.93 | 26.78 | 300.6 |
| Dysprosium (Dy) | 76 | 0.040 | 0.110 | 0.270 | 0.708 | 1.233 | 6.37 | 39.5 | 145.4 | 1303 |
| Holmium (Ho) | 76 | 0.010 | 0.030 | 0.070 | 0.173 | 0.259 | 1.53 | 7.77 | 26.94 | 230.2 |
| Erbium (Er) | 76 | 0.030 | 0.080 | 0.180 | 0.430 | 0.758 | 4.85 | 20.17 | 67.29 | 554.8 |
| Thulium (Tm) | 76 | 0.010 | 0.020 | 0.040 | 0.073 | 0.112 | 0.70 | 2.74 | 9.04 | 71.7 |
| Ytterbium (Yb) | 76 | 0.030 | 0.070 | 0.170 | 0.449 | 0.749 | 4.48 | 16.43 | 51.29 | 420.2 |
| Lutetium (Lu) | 76 | 0.010 | 0.030 | 0.060 | 0.059 | 0.136 | 0.79 | 2.59 | 7.58 | 66.5 |

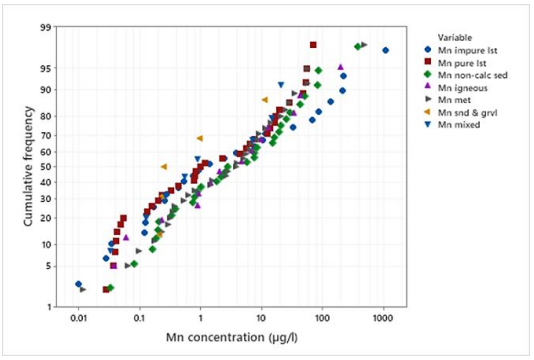
### 7.6.3 Minor ions and trace elements by lithological groups

#### 7.6.3.1 Cumulative probability distributions for lithological groups

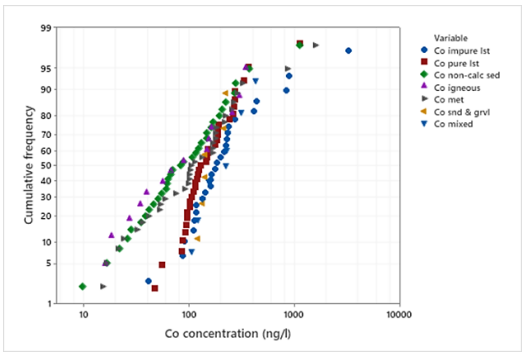
Tables with summary descriptive statistics for minor ions and trace elements for each of the seven lithological groups are included in Appendix C. The cumulative probability distributions for selected parameters are illustrated in Figures 7.33 to 7.37. Figure 7.33 shows the probability plots for Fe, Mn and four of the other transition metals whose solubility is often controlled by the presence of Fe and Mn i.e. Co, Mo, Cd and Cr (see Section 7.6.5). Fe and Mn are common minor ions in Irish groundwaters, occurring in silicate minerals and as oxyhydroxides in most rock types. Their solubility, and that of other transition metals, is strongly controlled by redox conditions (Section 7.6.5).



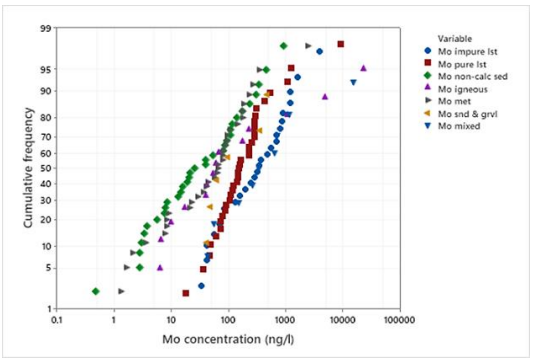

a)



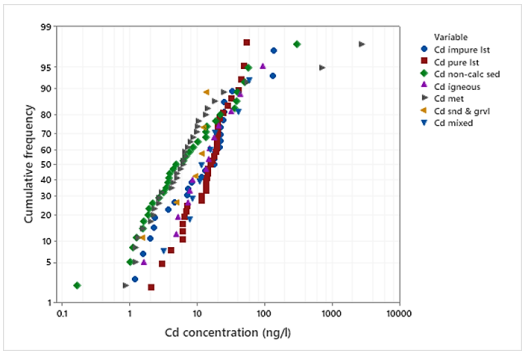

b)



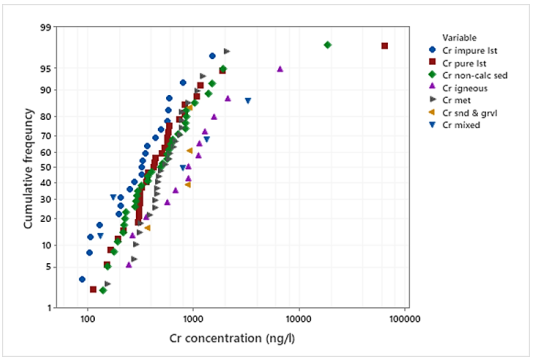

c)




d)




e)



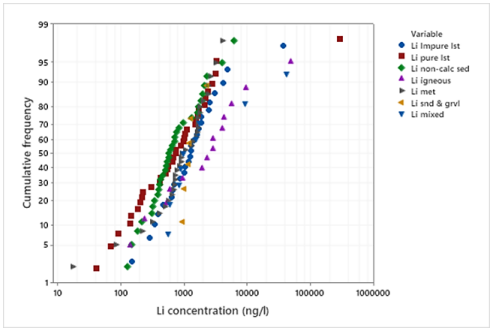

f)

Figure 7.33 Cumulative probability diagrams of selected transition metals for each of the seven lithological groups: a) Fe, b) Mn, c) Co, d) Mo, e) Cd and f) Cr

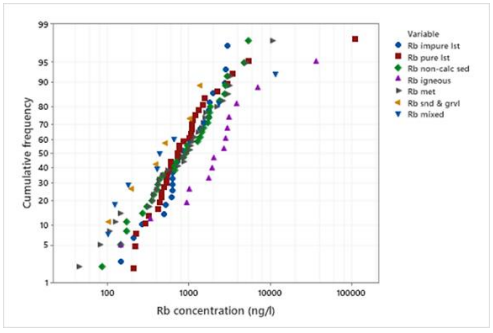
It can be seen in Figure 7.33 that the distributions of Fe, Co and Mo are influenced by lithology, with higher concentrations (especially in the lower percentiles ranges) in the impure and pure limestones and, although the number of samples is small, also in the sand and gravel and mixed bedrock and gravel groups. For Mo, a study in England and Wales found that the highest concentrations occurred in anoxic and reducing groundwaters, across a range of lithologies (Smedley *et al*., 2014a). Lithological differences are not so clear in Figure 7.33 for Mn, Cd or Cr. In the case of Cr, it is the igneous lithology, as well as the sands and gravels and mixed group, that show the highest distributions. The elevated Cr values in the igneous lithology is somewhat

surprising because Cr mineral concentrations are low in granitic rocks (MacDonald *et al*., 2017) and the NBL study found lower levels of Cr in the igneous group (Tedd *et al*., 2017).

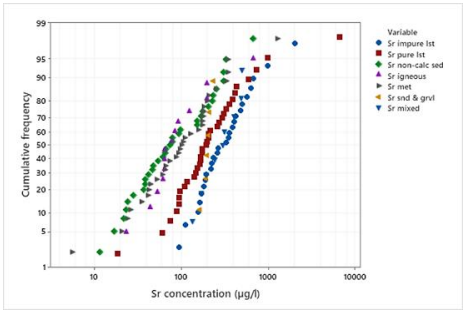
Figure 7.34 includes the cumulative probability plots for the alkali metals Li and Rb, and for the alkali earth elements Sr and Ba. The concentrations of Li found in this study are lower than those reported by Kavanagh *et al*. (2017) in a recent study in Co Carlow (Section 6.3.4), with a mean concentration in the holy well samples of 4 µg $l^{-1}$ (Table 7.24), compared to a mean in the Carlow groundwater samples of 23 µg $l^{-1}$. Two-thirds of Co Carlow is underlain by igneous granites, which include some pegmatites with Li-rich spodumene minerals, and the bedrock in the remaining area includes Carboniferous limestones. However, that study did not find any statistically-significant differences in Li mean values across the county. The ANOVA tests carried out on the holy well dataset (Section 7.6.3.2 below) does show some statistically-significant differences between lithologies e.g. igneous compared to pure limestones and metamorphic, whilst the cumulative probability plot in Figure 7.34a indicates a higher Li distribution in the igneous lithology.



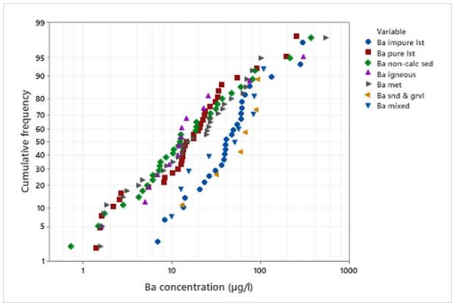

a)




b)




c)




d)

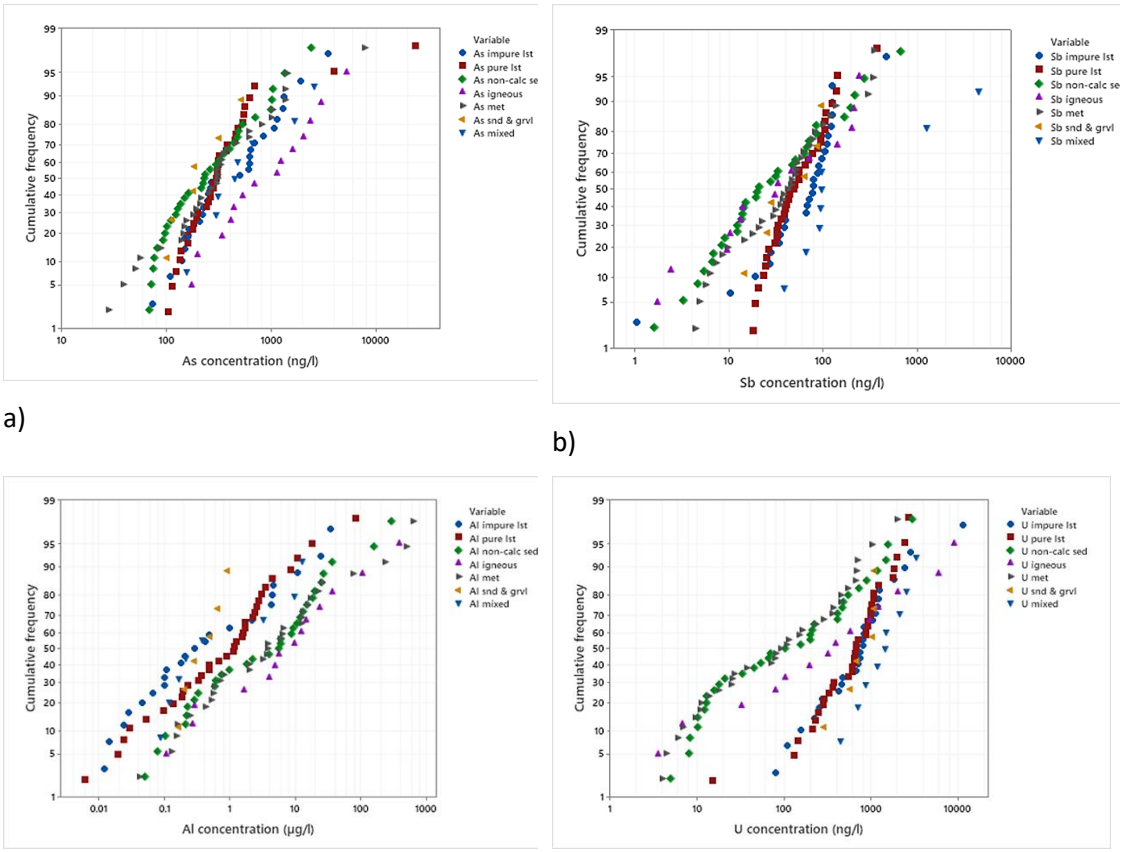
Figure 7.34 Cumulative probability diagrams of: a) Li, b) Rb, c) Sr and d) Ba, for each of the seven lithological groups

The distribution of Rb is also higher in the igneous lithology (Figure 7.34b). Rb often substitutes for potassium in mica and feldspar minerals, and so can be enriched in granites (Reimann and Birke, 2010). Sr concentrations are higher in the limestone lithologies than the non-carbonate rocks (Figure 7.34c). Sr is an alkaline earth metal, with common mineral sources including strontianite and celestine. It is intermediate in size between Ca and K and often substitutes for these elements in rock-forming minerals such as calcite, dolomite and feldspars (Reimann and Birke, 2010). The solubility limits of Sr are seldom reached in fresh waters, and therefore Sr concentrations are a good indicator of groundwater residence times. The higher concentrations in the pure and impure limestone lithologies therefore probably reflect both the mineral geochemistry and the likely longer groundwater flow paths, especially where they form the more productive aquifers (see Section 3.2).

Barium is commonly sourced from the minerals barite (barium sulphate) and witherite (barium carbonate). Tedd *et al*. (2017) found that there were wide variations in Ba concentrations, and that these reflected not only lithological influences, but also the specifics of the location, with e.g. elevated values in sandstones associated with the Rathdowney structural trend known for mineral occurrences including barite. Its solubility is mainly controlled by its saturation in relation to barite, with high Ba concentrations generally found where $SO_4$ values are low (Hem, 1985; Tedd *et al*., 2017). In the holy wells dataset, the Ba values tended to be highest in the impure limestones and in the sands and gravels (Figure 7.34d).

Figure 7.35 includes the cumulative probability plots for the metalloids As and Sb plus Al and U. The As distribution is highest in the igneous group, albeit all values are generally low (with a median value of 0.3 µg $l^{-1}$). As noted in Section 7.6.2, the highest As value was recorded in a seawater well (St Brendan's well at Roskeen in Co Mayo), where the bedrock is a pure limestone. The most common mineral sources of As are sulphides (e.g. pyrite) and iron oxyhydroxides. The study of As data across the country by McGrory *et al*. (2017) concluded that elevated values of As in groundwaters were more likely to occur in sandstones and shales (including Ordovician and Silurian metasediments), rhyolites and impure limestones (see Section 6.3.3). Rhyolites would fall within the igneous group as defined in this holy wells study. In this respect, it is interesting to note that a water sample taken from one of the three holy wells at Kilrossanty in Co Waterford – these are springs which issue from an Ordovician rhyolite aquifer (Section 5.5.3) - gave an 'elevated' As value of 2.0 µg $l^{-1}$, which is close to the 95%ile value for the full holy wells dataset of 2.36 µg $l^{-1}$, albeit 2.0 µg $l^{-1}$ is also the NBL for As (Table 7.24).

An ongoing study by Russell is investigating high As levels at three metamorphic lithology sites in the east and southeast of Ireland, with As groundwater concentrations of up to 60 µg $l^{-1}$ (Russell *et al.*, 2019). Although the probability plot in Figure 7.35a does not show generally elevated As concentrations within the metamorphic group, it is worth noting that the second highest As value in this holy wells research (7.8 µg $l^{-1}$) was detected in a sample from a metamorphic well close to one of the three areas being studied by Russell: St Brigid's well at Faughart in Co Louth.




a) b)

c) d)

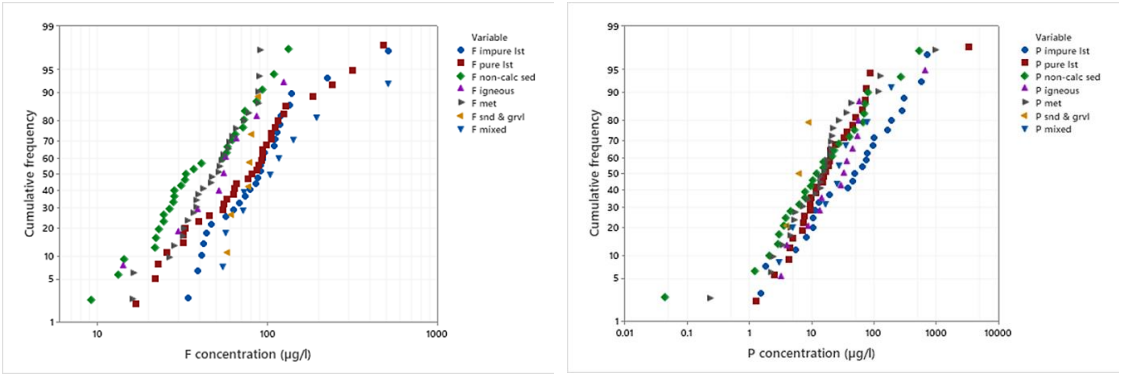
Figure 7.35 Cumulative probability diagrams of: a) As, b) Sb, c) Al and d) U, for each of the seven lithological groups

Antimony values in Figure 7.35b show some scatter, without a clear pattern in relation to lithology. Aluminium concentrations (Figure 7.35c) tend to show more consistent log-normal distributions, with higher values in the non-calcareous sandstone, igneous and metamorphic lithologies, consistent with its relative abundance in silicate minerals like feldspars and micas (Shand *et al.*, 2007). The NBL study found Al to be especially elevated in groundwater samples

from the igneous lithological group (Tedd *et al*., 2017). The radionuclide uranium is particularly associated with crystalline rock terrains (see Section 6.2.4), but also occurs in association with iron hydroxides in sedimentary environments, and can be mobile under oxic conditions (Shand *et al*., 2007). Figure 7.35d shows that U concentrations tend to be less in the non-calcareous and metamorphic groundwaters, and highest in the limestone and sand and gravel and mixed bedrock and gravel groups. The igneous lithological grouping shows the greatest spread, with some of the lowest as well as some of the highest concentrations.

The probability distribution for the minor ions fluoride and phosphorus are shown in Figure 7.36. As mentioned in the previous section F concentrations are low in all samples, with a maximum of only 0.52 mg $l^{-1}$. There were certainly no values to match the 3.8 mg $l^{-1}$ recorded in a study of a confined limestone aquifer in Co Monaghan (Misstear *et al*., 2008). The solubility of F is controlled by saturation with respect to fluorite, so high F values mainly occur when Ca levels are low, but other factors influencing F concentrations include the presence of fluorapatite (a phosphate mineral), a long groundwater residence time, and a Na-$HCO_3$ major ion chemistry. In Figure 7.36a, it can be seen that the non-calcareous sandstone, metamorphic and igneous groundwater samples generally had the lowest F levels, whilst the highest concentrations generally occurred within the carbonate lithologies.

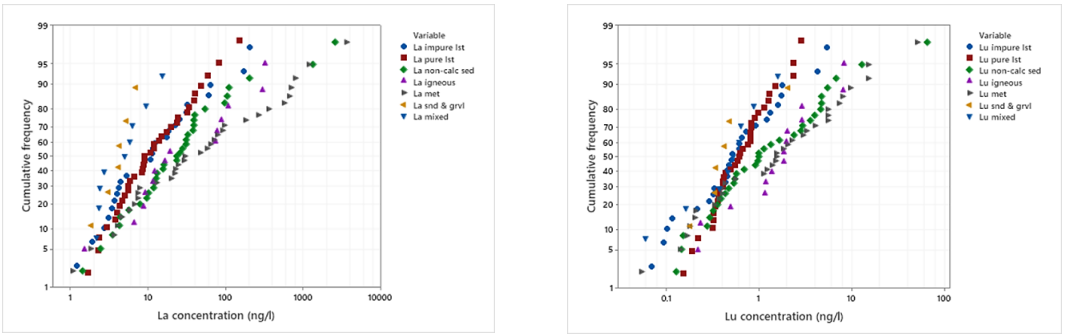
The main mineral source of phosphorus is apatite, but P can also be derived from anthropogenic activities, especially agriculture and waste disposal. However, P is usually relatively immobile in groundwater systems as it sorbs easily onto carbonate and iron oxide minerals. An exception is in karstic aquifer systems, where P can be more mobile and hence Tedd *et al*. (2017) distinguished between intergranular and karstified flow regimes (and poorly productive aquifers) when setting NBLs. However, in Figure 7.36b the lithological group with the highest P distribution is the impure limestone rather than pure limestone, even though the latter is more likely to contain karstified flow regimes.




a) b)

Figure 7.36 Cumulative probability diagrams of the minor ions a) F and b) P, for each of the seven lithological groups

Cumulative probability plots for two of the lanthanide rare earth elements are included in Figure 7.37. Lanthanum is the lightest (i.e. lowest atomic mass) and lutetium the heaviest of these REEs. As noted in Section 7.6.2, the groundwaters generally had higher concentrations of the lighter REEs. It was also remarked in Section 7.6.2 that of the nine examples given of wells with the highest REE concentrations, seven of these were located in metamorphic bedrock, whilst the remaining two tapped a non-calcareous sedimentary aquifer. The cumulative frequency plots for La and Lu in Figure 7.37 also indicate the relative enrichment in samples from metamorphic and non-calcareous sedimentary aquifers, but the plots also show a high frequency in the igneous lithology. In igneous and metamorphic rocks, REEs are found in accessory minerals such as apatite, monazite and sphene (Shand *et al.*, 2007). REEs can be sorbed onto iron oxides and clays, and so sorption/desorption processes affect their mobility, as does the groundwater pH, with increased solubility under acidic conditions (MacDonald *et al.*, 2017; see Section 7.6.5).




a) b)

Figure 7.37 Cumulative probability diagrams of the lanthanides a) La and b) Lu, for each of the seven lithological groups

Whereas the baseline groundwater chemistry studies in Britain found low concentrations of REEs in sandstones (Shand *et al*., 2007; MacDonald *et al*., 2017), the relatively high concentrations in the Irish holy well samples taken from non-calcareous sedimentary aquifers may reflect the presence of shales (the samples with the highest concentrations were collected from Namurian and Dinantian sandstone and shale lithologies). REEs were not included in the natural background levels study of Irish groundwaters, owing to insufficient data (Tedd *et al*., 2017). However, REEs were used in a recent investigation to finger print recharge sources to a karst lowland aquifer in the west of Ireland (Gill *et al*., 2018). For that study, insights into water sources and pathways were gained from normalising the abundances of lanthanide REEs (plus yttrium) in both water and rock/sediment samples relative to Mud of Queensland (MuQ) values, which are considered as being indicative of the composition of young weathered continental crust (Kamber *et al*., 2005; Lawrence *et al*., 2006b).

The mean REE concentrations from this research normalised to MuQ are shown in Figure 7.38. The higher relative abundances of REEs in the non-calcareous, metamorphic and igneous lithologies compared to the carbonate lithologies are apparent. In their study in the west of Ireland, Gill *et al*. (2018) also found that waters draining sandstone bedrock were enriched in REEs relative to limestone groundwaters. In Figure 7.38, a slight depletion of light REEs relative to the heavier REEs is evident. This trend has been observed in other studies, and has been explained by a greater stability in solution of heavier REE-carbonate complexes (Smedley and Allen, 2004). A negative Ce anomaly is also evident in the figure, for groundwaters in all seven lithological groups. Negative Ce anomalies have been linked with precipitation of Ce oxides in oxic groundwaters, and loss by adsorption (MacDonald *et al*., 2017).

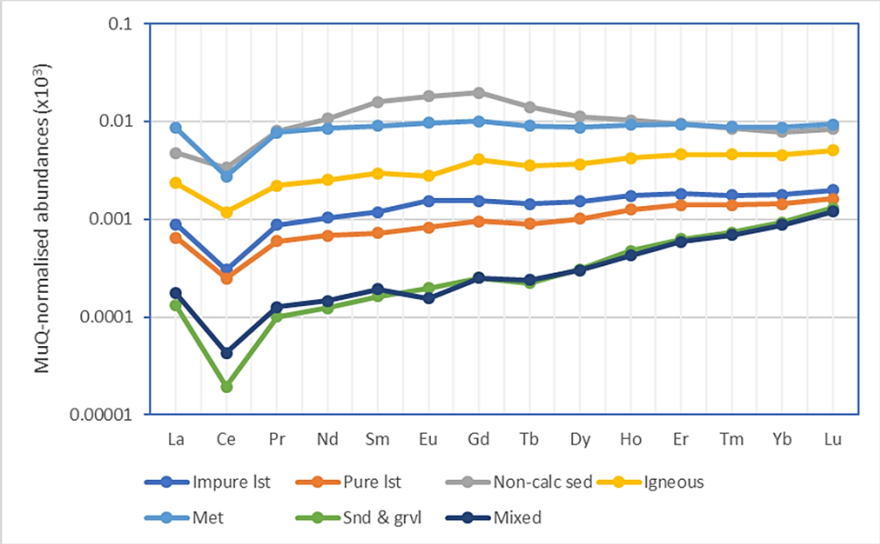



Figure 7.38 REE abundances relative to Mud of Queensland

### 7.6.3.2 ANOVA tests on minor ions and trace elements by lithological group

One-way analysis of variance (ANOVA) using the Fisher least significant difference test was carried out on the minor ion and trace element results to see if there were significant differences in the mean values of individual parameters between lithological groups. The tests were undertaken after log-transformations of the data to better satisfy the assumption of normal distributions in the datasets (log transformations resulted in 88% of the data for the 51 minor ions and trace elements achieving normal distributions; see Section 7.4). The outcomes of the ANOVA tests are summarised in Tables 7.28 and 7.29 (the latter containing the results for the 14 lanthanide REEs). In the tables, means that do not share a letter across the lithological groups are significantly different.

Table 7.28 presents a somewhat complicated picture of relationships; nevertheless, a number of observations can be made. For four of the 37 parameters in the table (Hf, In, Mn and Zn), no significant differences were found in the mean concentrations across any of the seven lithological groups. NBLs have been established for two of these parameters: a national value for unconfined aquifers for Mn (and therefore consistent with the finding here), but for Zn the NBL was defined by lithological group (albeit that there were sufficient data to establish values for only two groups, i.e. pure limestones and non-calcareous sedimentary; see Section 6.3.2).

Table 7.28 ANOVA tests for differences of means of minor ions and trace elements (excluding the lanthanide REEs, which are shown in Table 7.29) for the seven lithological groups (log-transformed data)

| | Impure lst | Pure lst | Non-calc sed | Igneous | Met | Sand & gravel | Mixed bedrock & gravel |
|---|---|---|---|---|---|---|---|
| Aluminium (Al) | C | C | A B | A | A B | C | B C |
| Antimony (Sb) | B | B | C | B C | B C | B C | A |
| Arsenic (As) | B | B | B | A | B | B | A B |
| Barium (Ba) | A | C | C | B C | B C | A | A B |
| Beryllium (Be) | C D | C D | B | A | B C | D | D |
| Cadmium (Cd) | A B | A | B | A B | B | A B | A B |
| Caesium (Cs) | C | C | A B | A | B C | C | B C |
| Chromium (Cr) | C | B C | B C | A | A B | A B C | A B C |
| Cobalt (Co) | A | A B | D | C D | B C D | A B C D | A B |
| Copper (Cu) | B | B | B | A | A B | B | A B |
| Fluoride (F) | A | A B | D | B C D | C D | A B C | A |
| Gallium (Ga) | B | A B | B | A | B | A B | A B |
| Hafnium (Hf) | A | A | A | A | A | A | A |
| Indium (In) | A | A | A | A | A | A | A |
| Iron (Fe) | A | A | B | B | B | A | A |
| Lead (Pb) | A B C | C | B C | A | A B | A B C | A B C |
| Lithium (Li) | A B C | C | C | A | B C | A B C | A B |
| Manganese (Mn) | A | A | A | A | A | A | A |
| Molybdenum (Mo) | A | A B | D | B C | C D | A B C D | A |
| Nickel (Ni) | A | A B | C | A B C | B C | A B C | A |
| Niobium (Nb) | A B | B | B | A | B | A B | A B |
| Phosphorus (P) | A | A B | B | A B | B | A B | A B |
| Rubidium (Rb) | B | B | B | A | B | B | B |
| Scandium (Sc) | A | C | C | B C | A B | A | A B |
| Selenium (Se) | A B | A B | A B | A B | B | A B | A |
| Strontium (Sr) | A | A | C | B C | B C | A B | A |
| Tantalum (Ta) | B C | B C | B C | A | B | B C | C |
| Thallium (Tl) | A B | A | C | B C | C | C | A |
| Thorium (Th) | C | B C | B C | A | A B | C | C |
| Tin (Sn) | A B | A B | B | A B | A B | A B | A |
| Titanium (Ti) | A | A B | B | A B | A B | A B | A |
| Tungsten (W) | A B | A B | B | A | A B | A B | A B |
| Uranium (U) | A B | A B | C | B | C | A B | A |
| Vanadium (V) | A B | A B | A B | A | A B | A B | B |
| Yttrium (Y) | B C D | C D | A | A B C | A | D | D |
| Zircon (Zr) | A | A B | A B | A B | B | A B | A B |
| Zinc (Zn) | A | A | A | A | A | A | A |

Table 7.29 ANOVA tests for differences of lanthanide rare earth elements for the seven lithological groups (log-transformed data)

| | Impure lst | Pure lst | Non-calc sed | Igneous | Met | Sand & gravel | Mixed bedrock & gravel |
|---|---|---|---|---|---|---|---|
| Lanthanum (La) | B C D | C D | A B | A B C | A | D | D |
| Cerium (Ce) | C | B C | A B | A | A | C | C |
| Praseodymium (Pr) | B | B | A | A | A | B | B |
| Neodymium (Nd) | B | B C | A | A | A | B C | C |
| Samarium (Sm) | B | B C | A | A | A | B C | C |
| Europium (EU) | B C | C D | A | A B | A | C D | D |
| Gadolinium (Gd) | B | B C | A | A | A | B C | C |
| Terbium (Tb) | B | B C | A | A | A | B C | C |
| Dysprosium (Dy) | B | B | A | A | A | B | B |
| Holmium (Ho) | B | B | A | A | A | B | B |
| Erbium (Er) | B | B | A | A | A | B | B |
| Thulium (Tm) | B | B | A | A | A | B | B |
| Ytterbium (Yb) | C | C | A B | A | A | B C | C |
| Lutetium (Lu) | C | C | A B | A | A | B C | C |

For most parameters, significant differences in means between one or more lithological groups were highlighted by the ANOVA tests. It is especially noticeable in Table 7.28 that one or more of the three non-carbonate bedrock lithologies (i.e. non-calcareous sedimentary, igneous and metamorphic groups) are often significantly different from the impure limestone and pure limestone groups. In the case of Al, Fe and Sr, all three non-carbonate bedrock lithologies differ significantly from the impure and pure limestones. For other parameters such as Be, Cs, Co, F, Mo, Tl and U the significant differences apply between two of the non-carbonate lithologies and the impure and pure limestones, whilst for elements such as Sb, Rb, Ta and Th only one of the non-carbonate bedrock groups shows a significant difference with the carbonate lithologies.

The sand and gravel and the mixed bedrock and gravel groups generally give similar results, i.e. they share a letter in each row of Table 7.28 indicating that the mean value of each parameter is not significantly different between the two groups. Two exceptions are antimony (Sb) and thallium (Tl). When the minor ions and trace elements in the sand and gravel and mixed bedrock and gravel groups are compared with the bedrock groups, no clear general patterns are apparent, although some relationships are apparent for individual parameters e.g. Be and Fe

significantly differ between these two groups and the three non-calcareous bedrock lithologies, but not with the impure and pure limestones.

In Table 7.29, containing the ANOVA test results for the 14 lanthanide REEs, the most common finding is that the means for the non-calcareous sedimentary, igneous and metamorphic lithologies are significantly different from those for the impure and pure limestones, and from those for the sand and gravel and mixed bedrock and gravel groups i.e. that there are differences between the more silicate groups compared to the carbonate lithologies.

NBLs have been established for several of the parameters in Table 7.24, but for none of the lanthanide REEs in Table 7.25 (Section 6.3.2). NBLs were defined by lithology for six of the parameters in Table 7.28: Al, Ba, Cr, Sr, U and, as mentioned above, for Zn. For each of the parameters apart from Zn the ANOVA tests here showed some differences between lithological groups. However, the ANOVA tests also indicated that the means for some parameters for which NBLs were defined on a national basis (including national unconfined aquifer values) also differed significantly between some of the lithological groups: Sb, As, Be, Cd, Co, F, Fe, Pb, Mo, Ni an P. These findings probably reflect the different nature of the datasets used in the two studies – more than 150 one-off samples from the shallow holy wells versus, for many of the parameters, multiple samples from 21 monitoring points (mainly boreholes) in the NBL study (Tedd *et al*., 2017; see Section 6.3.2). As highlighted in Section 7.5.3, the majority of wells and springs used in the NBL analysis were from the more productive (regionally important) aquifers, and so poorly productive aquifers were under-represented. It should be added that the statistical treatment of the data, including transformations and posthoc analysis, might also have a bearing on the test outcomes (Section 7.4).

### 7.6.4 Minor ions and trace elements for wells in coastal settings

Non-parametric Mann-Whitney U tests (Section 7.4) were performed on the minor ion and trace element results (non-transformed data) to see if there were significant differences in the median concentrations between samples from those wells in a coastal setting (less than 500 m from the coast; see Sections 5.10 and 7.5.5) and samples from the remaining wells. For the tests, the maximum number of coastal well values was 27, compared to a maximum n of 129 for the other wells (giving a maximum total n of 156: see Tables 7.24 and 7.25).

The Mann-Whitney U tests showed significant differences between the median values for coastal and non-coastal wells for 15 of the 37 trace elements in Table 7.24, comprising Sc, Ti, V, Cr, Cu, Zn, Ga, Se, Sr, Y, Zr, In, Hf, W and Th, and for 11 of the 14 lanthanide rare earths in Table 7.25 i.e., La, Pr, Nd, Sm, Tb, Gd, Dy, Ho, Tm, Yb and Lu. For 25 of these 26 parameters, the median values for the coastal wells were higher than those for the non-coastal wells; the exception was Sc, where the median value was lower in the coastal wells. Whilst studies have shown that sea spray is a major source of major ions such as Mg, Na, Cl and $SO_4$, any elevated values of trace elements in coastal rainfall (and hence recharge) are more likely to come from crustal or anthropogenic sources (Heaton *et al*., 1990; Al Momani, 2003).

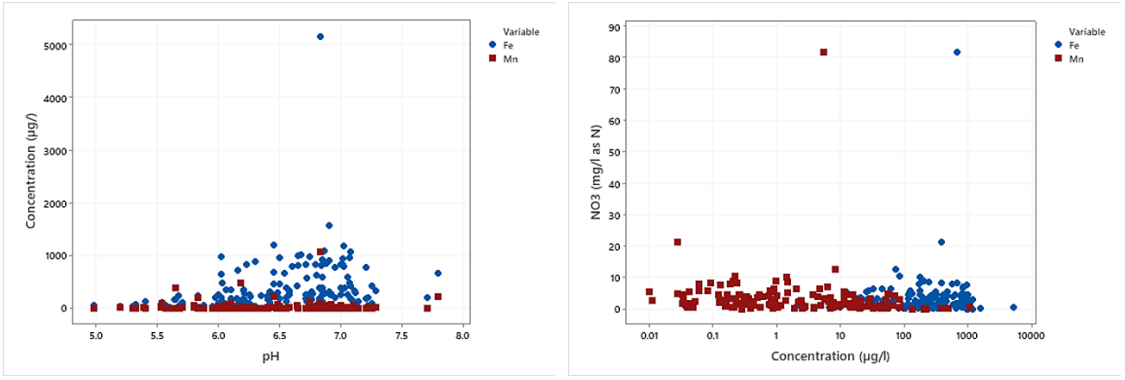
In a recent study of seawater intrusion into a coastal sedimentary aquifer in Mexico, Mora *et al*. (2020) found that some trace elements (such as V, Co and Se) were mobilised during saline intrusion, others were not mobilised (including Ni, Cr and Mo), whilst a third group (including As, Sb and U) showed more complex behaviour, being mobilised in some situations and not in others. With the holy wells dataset, aquifer seawater intrusion is unlikely to be a major influence on trace elements near the coast, since abstractions are low and the hydraulic connection between the sea and the well will often be restricted.

### 7.6.5 Minor ion and trace element relationships

The mobility of many trace elements is controlled by redox reactions and by the presence of iron and manganese oxyhydroxides (Shand *et al*., 2007; MacDonald *et al*., 2017; see Section 6.2.1). In this section, the relationships between some of the relevant parameters will be investigated. However, the water samples were collected from shallow open spring wells, involving generally oxic conditions, and although pH was recorded, redox potential (Eh) was not. Moreover, pH measurements – although made with an instrument which was calibrated prior to use in the field each day (Section 7.1.3) – can be unreliable owing to release or absorption of carbon dioxide from the sample, or because of instrumental drift. Therefore, any discussion of solubility controls will be somewhat limited.

The solubilities of Fe and Mn are largely controlled by pH-Eh conditions (Hem, 1985). Both elements are soluble in a reducing environment (as $Fe^{2+}$ and $Mn^{2+}$ ions, respectively). Fe, which is the more abundant of these two elements, is normally poorly soluble in oxic conditions around neutral pH, but dissolved Mn can be more stable under these conditions (Shand *et al*.,

2007). Figure 7.39a shows the relationship between pH and Fe and Mn concentrations for the holy wells dataset (n = 156 for Fe vs pH; n = 150 for Mn vs pH). This illustrates, firstly, that Fe is indeed more abundant than Mn in the holy well samples and, secondly, that there is not a strong association between the concentrations of these elements and pH – for example, elevated Fe values occur over a wide range of pH, from 6 to 7.7.

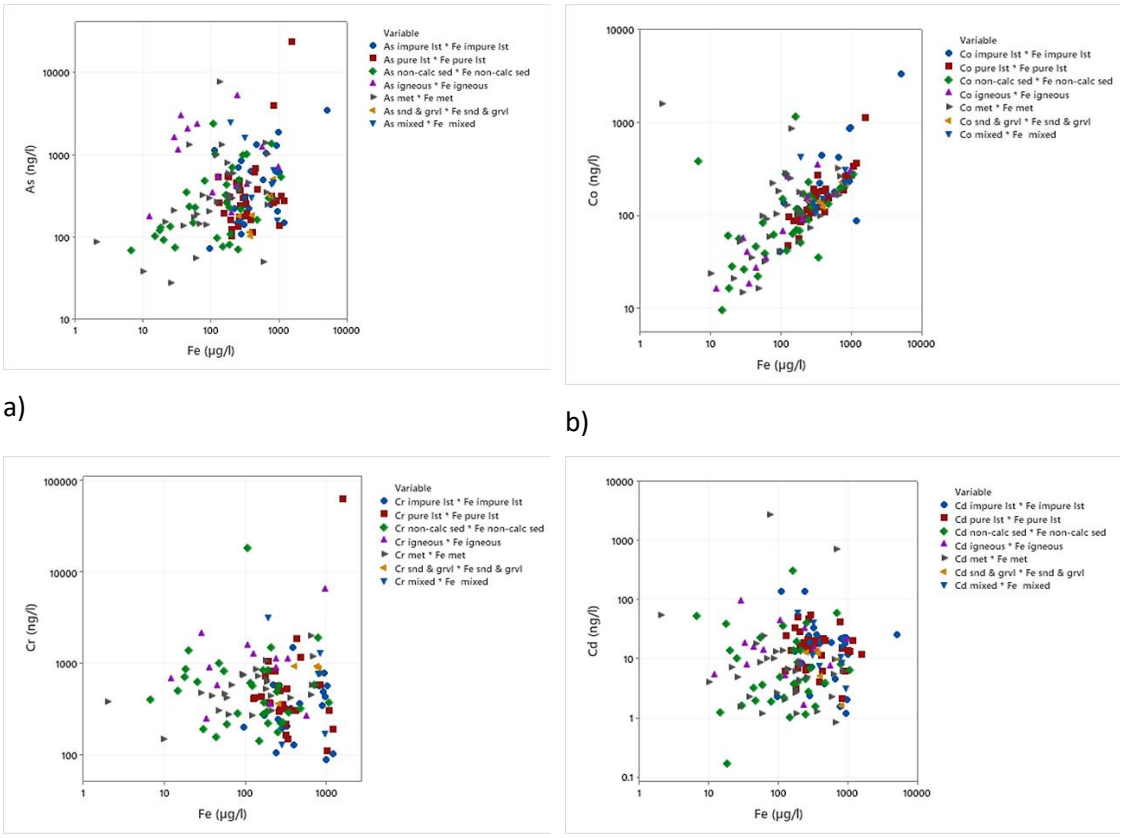



a) b)

Figure 7.39 Fe and Mn concentrations in relation to a) pH and b) $NO_3$ for all holy wells

Figure 7.39b shows the relationship between Fe and Mn concentrations with $NO_3$. The presence of nitrate is an indicator of oxic conditions and so low Fe concentrations would normally be expected where nitrate levels are elevated (Shand *et al*., 2005). However, the data in Figure 7.39b do not exhibit a strong association between these metal ions and $NO_3$.

The mobility of trace elements such as As, Cd, Cr, Co, Mo is often controlled by the presence of Fe and Mn oxyhydroxides, which can adsorb these elements under oxidising conditions, or release them under reducing conditions. Elevated values of these elements in groundwaters may therefore be associated with elevated Mn and, especially, Fe concentrations (MacDonald *et al*., 2017). Figure 7.40 shows the relationship between Fe concentrations with As, Co, Cr and Cd, for all samples in all the lithological groups. Although there is some scatter, a positive relationship is apparent between Fe and As and especially between Fe and Co, but not between Fe and Cr or Fe and Cd.




a) b)

c) d)

Figure 7.40 Fe concentrations in relation to a) As, b) Co, c) Cr and d) Cd, for all lithological groups

In other comparisons (not illustrated), there were positive associations between Fe and Mo, Ni, Sb and U, but not between Fe and Al, Be, Cu, Li, Pb, Se, V or Zn. In relation to Li, it is worth noting that Kavanagh *et al*. (2017), in their Li study in Co Carlow, did not find any correlation between Li concentrations and concentrations of other trace elements, including Fe. A final relationship may be worth mentioning here. In the ongoing study of As in groundwaters in three areas of metamorphic lithology, Russell *et al*. (2019) have reported that As is mainly derived from weathering of sulphide minerals, and that there is an association between As and Co in two of the study areas relating to the presence of sulphide mineral phases enriched in Co-As. A positive association between As and Co is also apparent in the holy wells dataset (Figure 7.41), although linear regression suggests this relationship is strongest for the impure and pure limestone lithologies.

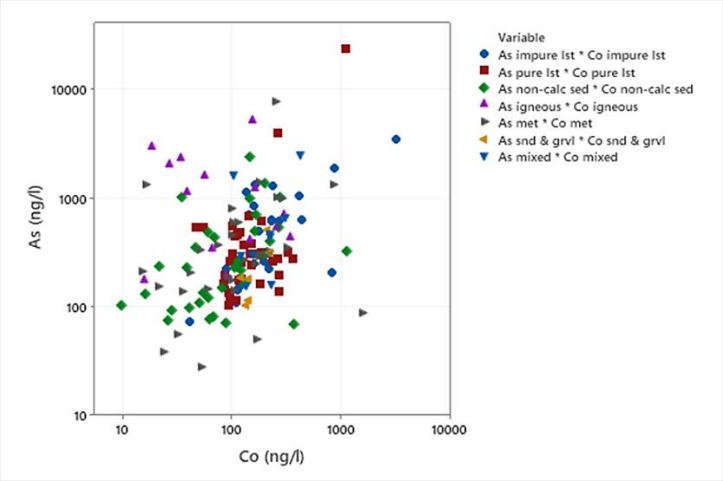



Figure 7.41 Relationship between As and Co in the main lithological groups

One important controlling factor on the solubility of various minor ions and trace metals is aquifer confinement, since this strongly influences the availability of oxygen and the pH-Eh relationships. This has not been discussed here owing to the very small number of samples collected from confined aquifers (only three of the 167 holy wells sampled were definitely located in confined aquifers – see Section 5.9). However, one of the monitoring wells discussed in the next section tapped a confined aquifer, and therefore some observations of the influence of this aquifer condition on the water chemistry are included in that section.

## 7.7 Temporal variations in major ions and trace elements: Monitoring well results

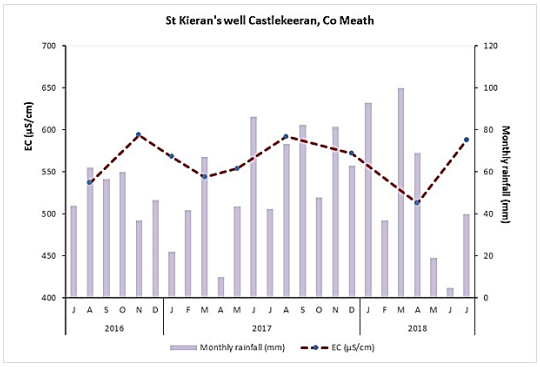
As discussed in Section 4.1.4, four holy wells were selected for monitoring over a 2-year period, from August 2016 to July 2018. The monitoring wells were: St Kieran's well at Castlekeeran in Co Meath (pure limestone lithological group; the well hydrogeology is described in Section 5.3.3.2); Bride's well at Calgath in Co Meath (impure limestone; Section 5.9.1); St Moling's well at St Mullins in Co Carlow (igneous; Section 5.5.1); and St Brigid's well at Tully in Co Kildare (sand and gravel; Section 5.7.1.1). Three of the wells are in unconfined aquifers, whereas Bride's well Calgath has a confined (artesian) groundwater source. Physico-chemical parameters including EC were measured on site during each visit, and samples were collected for ionic and trace element analyses in the laboratories. Eight samples were collected for major ion analyses from three of the wells, and seven samples from St Brigid's well Tully. Seven samples from three of the wells - and six samples from St Brigid's well - were analysed for minor ions and trace elements (the Geochemistry lab being out of commission for one of the sampling rounds;

Section 7.1.2). The samples for lab analyses were collected between November 2016 and July 2018.

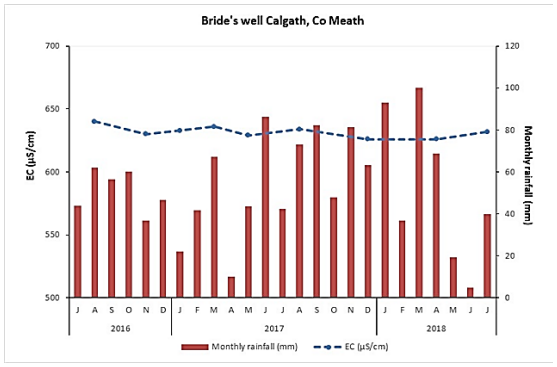
### 7.7.1 Physico-chemical parameters

Figure 7.42 shows the variation of EC at the four monitoring well sites. Monthly rainfall values are also included (Dublin airport data for the two wells in Co Meath; Casement aerodrome data for St Brigid's well Tully; Oak Park Carlow data for St Moling's well). There was relatively little variation in EC at Bride's well Calgath and St Brigid's well Tully. The constant EC (varying only from 626 to 640 µS $cm^{-1}$ in nine measurements over two years) at the former well would be expected, given that the aquifer is confined at this location and hence there is probably a relatively long groundwater flow path. That the EC in a sand and gravel well was also relatively constant (varying only from 760 to 785 µS $cm^{-1}$; nine measurements) also suggests that the groundwater is sufficiently experienced to be in equilibrium with its aquifer geochemistry. St Brigid's well is located towards the western edge of the extensive Curragh sand and gravel aquifer (which covers an area of more than 200 $km^2$; see Figure 5.42) and there may be a relatively long flow path. It should be added that the water levels at both of these wells are controlled by outlet pipes, and so do not give much of an indication of seasonal variations.

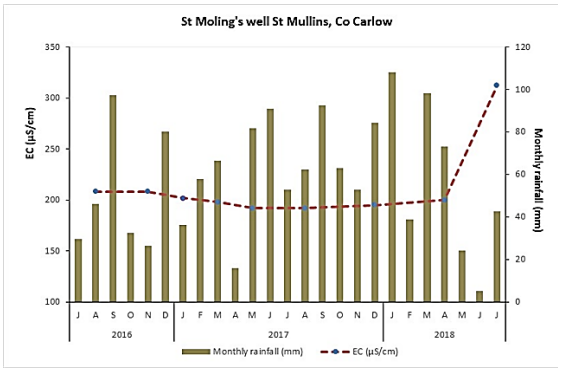
The EC at St Kieran's well Castlekeeran showed larger variations over the 2-year period, ranging from 513 to 594 µS $cm^{-1}$ (9 measurements). The relationship with monthly rainfall is not clear-cut. The three highest EC values occurred in November 2016, August 2017 and July 2018. Whilst November 2016 and July 2018 were relatively dry months (37 mm and 40 mm rainfall, respectively, compared to a monthly average rainfall of 53 mm for the 25-month period shown in Figure 7.42) - and the lowest water level was recorded in July 2018; see Figure 5.21) - this was not the case for August 2017 (73 mm); however, the EC measurement was taken quite early in the month (10$^{th}$ August), and the previous month had been dry (42 mm). The lowest EC value of 513 µS $cm^{-1}$ was recorded in early April 2018, following a very wet March when the rainfall was almost twice the monthly average for this 2-year period. The highest water level measurement was also made on that date. These observations suggest that the higher EC values are associated with lower recharge and hence less 'dilution' of the groundwater, whilst low EC values occur following recent recharge events.



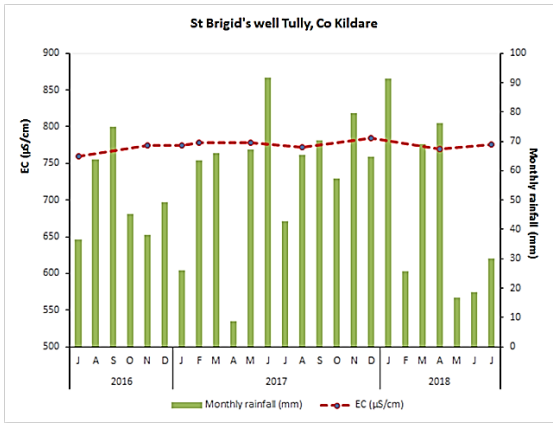

a)




b)




c)



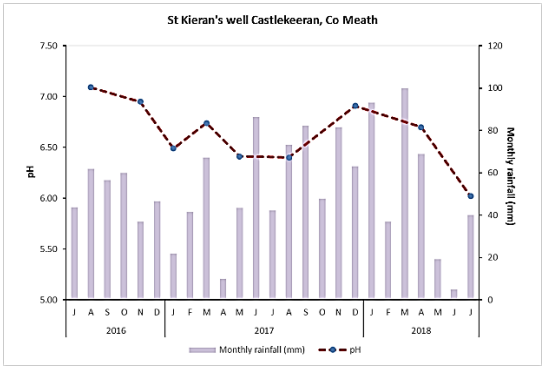

d)

Figure 7.42 Plots of EC against monthly rainfall for the four monitoring wells: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); c) St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare). Monthly rainfall data were obtained from Met Éireann

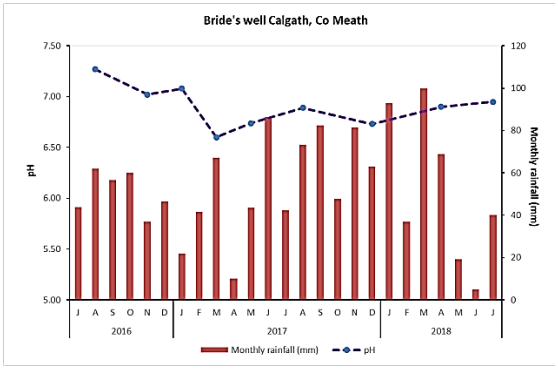
At St Moling's well, the EC measurements were relatively constant between August 2016 and April 2018 (values ranged between 192 and 208 µS $cm^{-1}$; 8 measurements). However, a sharp increase in EC to 312 µS $cm^{-1}$ was observed in July 2018 (see Figure 7.42c). As explained in Section 5.5.1, this coincided with draining of the spring pond by the landowner earlier that day (as part of periodic cleaning of the pond). The inflows to this spring may derive from more than one depth – perhaps, a less mineralised inflow from a shallow transition zone and a more mineralised inflow from the deeper, less weathered, granite bedrock. Alternatively, the water remaining in the pond after the partial cleaning out may have been relatively stagnant.

Seasonal variations in pH are shown in Figure 7.43. A caveat should be noted here: although the pH meter was calibrated each morning prior to use in the field (Section 7.1.3), pH readings can

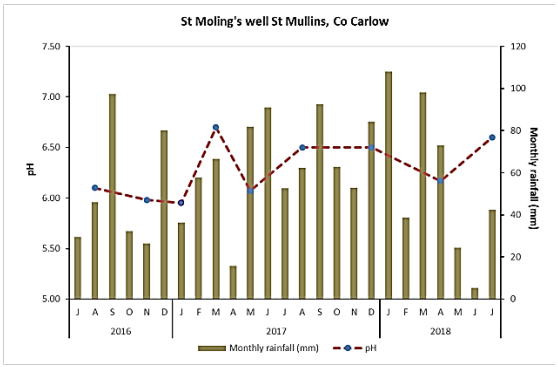
be subject to instrumental drift and to the effects of degassing or absorption of carbon dioxide in the samples.



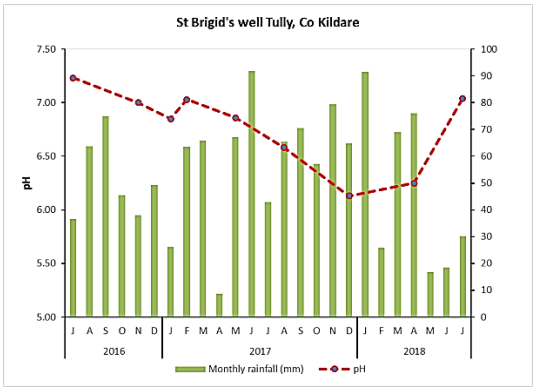

a)




b)




c)




d)

Figure 7.43 Plots of pH against monthly rainfall for the four monitoring wells: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); c) St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare). Monthly rainfall data were obtained from Met Éireann

Patterns in the pH values over the 2-year monitoring period are difficult to discern, possibly influenced by the issues mentioned above. Nevertheless, a couple of observations are worth making. Firstly, the pH values in the confined aquifer well (Bride's well Calgath) are more stable (ranging from 6.6 to 7.27) than those in the three wells in unconfined aquifers, which would be expected to exhibit greater seasonal variations. Secondly, the well in the igneous lithology (St Moling's well) had a lower pH than the two limestone wells (Bride's well and St Kieran's well) and the sand and gravel well (St Brigid's well). Again, this is as expected, since the limestone and gravel lithologies contain carbonate minerals that will buffer the pH. The mean pH value for the St Moling's well samples was 6.29, compared to mean pH values of 6.91, 6.63 and 6.77 for Bride's well, St Kieran's well and St Brigid's well, respectively.

The variations in water temperature in the four monitoring wells are shown in Figure 7.44. Again, the confined aquifer well (Bride's well) exhibits the smallest seasonal variation. As discussed in Section 5.9.1, Bride's well has a reputation of being a warm water well, with a plaque at the well enclosure indicating that temperatures can reach 70 °F (21 °C) in winter. Whilst the maximum temperature recorded in this research project was only 14.6 °C, it is interesting that the winter temperatures (which ranged between 12.3 and 13 °C) were elevated when compared with the winter temperatures recorded in the other three wells (typically between 8 and 10 °C). As with the pH and especially the EC results, the elevated water temperature in winter at Bride's well is consistent with a relatively deep groundwater source.

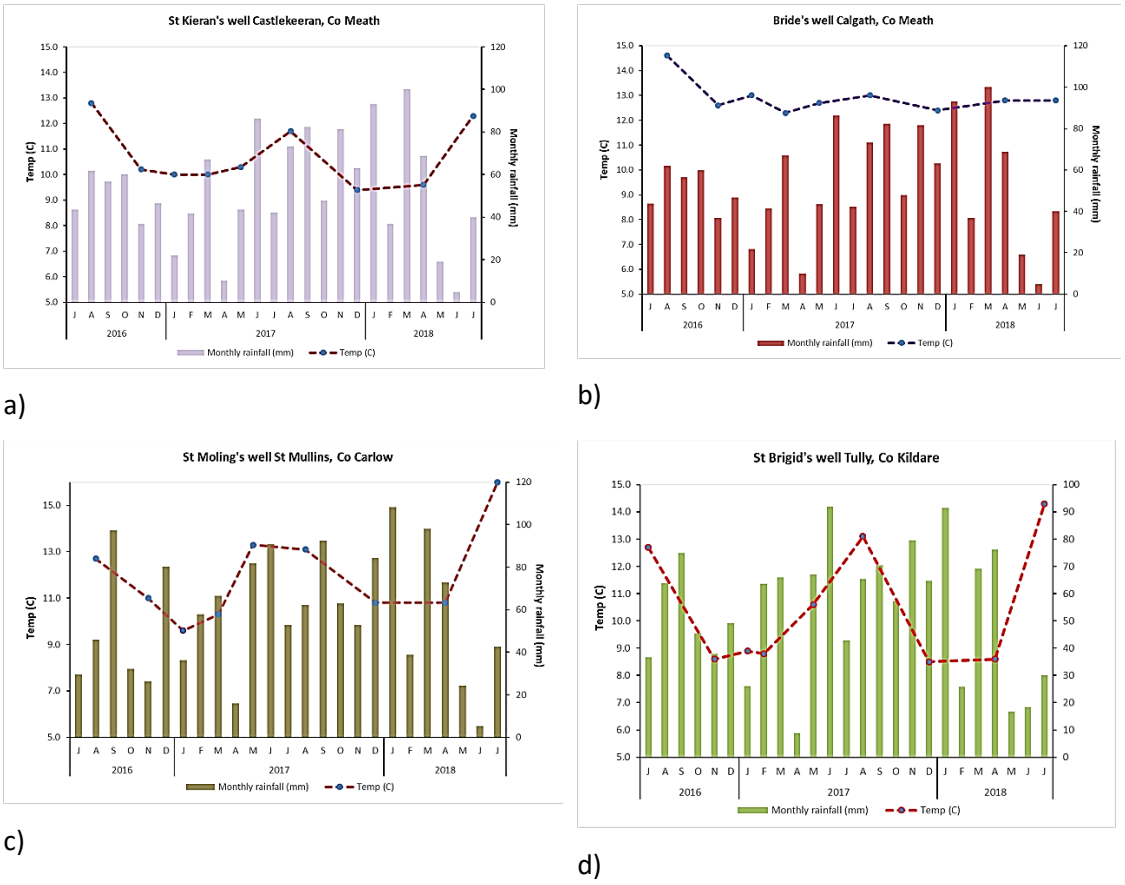



Figure 7.44 Plots of temperature (°C) against monthly rainfall for the four monitoring wells: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); c) St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare). Monthly rainfall data were obtained from Met Éireann

The highest water temperature measured at any of the monitoring wells was at St Moling's well on 18th July 2018. However, this temperature of 16 °C was recorded after the pond fed by the

spring had been partially drained, giving an opportunity for the remaining water to be warmed by the sun (the air temperature in the shade that day was 20 °C).

### 7.7.2 Major ions

Variations in major ion concentrations for the four monitoring wells over the 2-year sampling period are shown as a series of stacked bar graphs in Figure 7.45. Seven samples were collected from St Brigid's well at Tully, and eight from the other three wells. The results are presented in meq $l^{-1}$. (Silicon is not included, as few data were available, and it does not behave as a charged species in water).

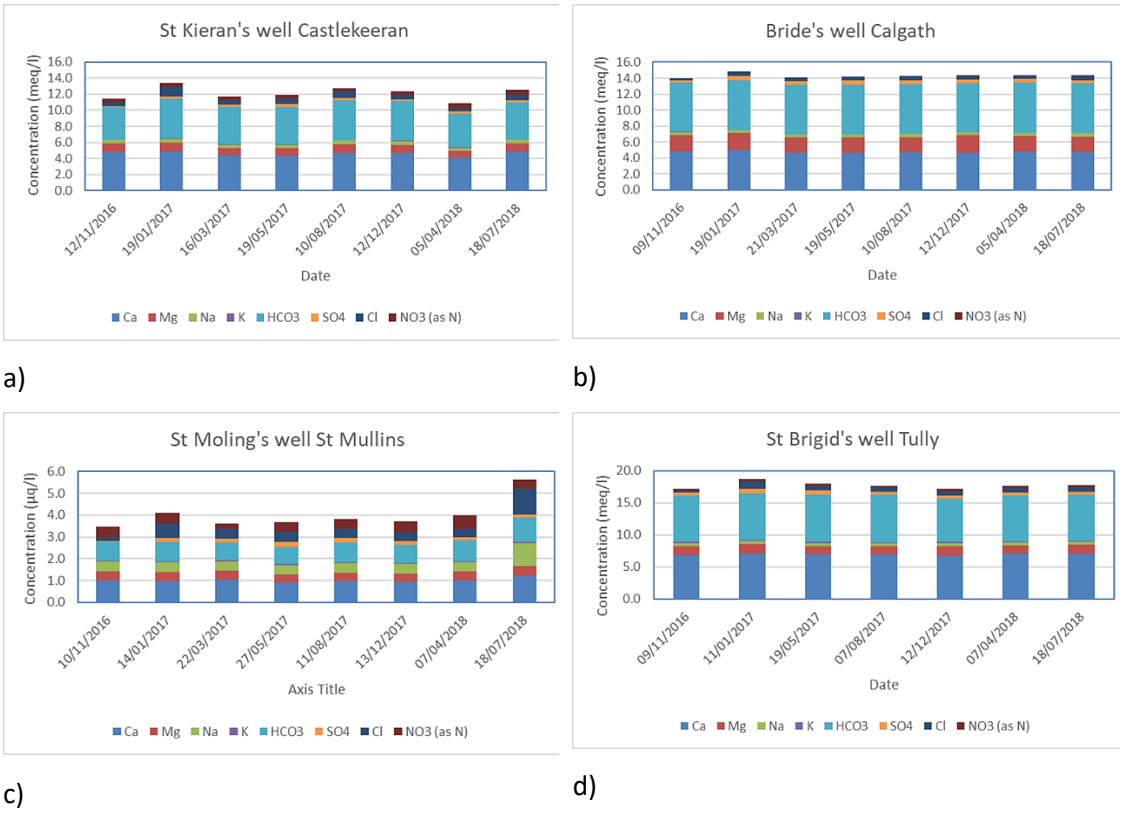



Figure 7.45 Major ion concentrations (in meq $l^{-1}$) for the four monitoring wells over a 2-year sampling period: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); c) St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare)

It can be seen from the figure that St Kieran's well, Bride's well and St Brigid's well have a Ca-$HCO_3$ major ion chemistry, in line with the overall findings for holy wells in limestone and sand and gravel lithologies discussed in Section 7.5.6. St Moling's well, on the other hand, contains

greater proportions of Mg, $SO_4$ and Cl, which again is in line with other results for a granite (igneous) lithology.

Bride's well and St Brigid's well showed least variation in major ion chemistry over the monitoring period. This is consistent with these wells showing the least variation in EC over the same period (Figure 7.42). Bride's well likely has a deep groundwater source, whilst the relatively stable water chemistry in St Brigid's well (and the fact that it contains water even during prolonged dry periods – Section 5.7.1.1) suggests a relatively long groundwater flow path, and chemical equilibrium with the surrounding aquifer material.

In line with the observations from the EC and pH results, St Kieran's well showed the largest seasonal variations in its major ion chemistry. The most mineralised sample was collected in January 2017, a relatively dry month (with 40% of the average monthly rainfall for the 2-year period), whilst the sample with the lowest ionic concentration was taken in early April 2018, following a very wet March (with almost twice the average monthly rainfall for the monitoring period – see Figure 7.42), suggesting some dilution by recent recharge waters.

St Moling's well also gave one of its most mineralised samples in the dry month of January 2017, but the sample with the highest EC and major ion concentration was collected in July 2018. As explained above, this was when the pond fed by the spring had been partially dewatered.

The nitrate concentrations measured in the four wells over the monitoring period are shown in Figure 7.46, along with monthly rainfall figures. Even though the first samples were not collected until November 2016, the graphs commence in July 2016 to facilitate easy comparison with the graphs of the physico-chemical parameters described in the previous section. Note also that the same vertical axis scale (0-10 mg $l^{-1}$ as N) has been used for all wells except Bride's well, where a narrower range (0-5 mg $l^{-1}$ as N) was used owing to the lower concentrations.

Nitrate values were consistently low in the confined aquifer well (Bride's well), but exceeded the NBL of 2 mg $l^{-1}$ (as N) throughout the monitoring period in the three other wells. The highest nitrate concentration in St Brigid's well occurred in April 2018 (and the second highest was recorded in St Kieran's well the same month). As noted above, this was a wet period and it was also a time when the effects of fertiliser applications on groundwater quality might be expected. The highest nitrate values in St Kieran's well and at St Moling's well were recorded in July 2018,

which followed a very dry June (with only 5 mm of rainfall measured at Dublin airport and at Oak Park). The nitrate concentration at St Kieran's well in that month's sample was only slightly greater than that in April 2018 (8.8 compared to 8.5 mg $l^{-1}$ as N). It is also noticeable that there is an overall trend of rising nitrate levels in this well during this 2-year period. At St Moling's well the July 2018 nitrate value was 7.5 mg $l^{-1}$ (as N), only slightly elevated compared to the 2-year mean of 6.5 mg $l^{-1}$ (as N). It can be seen in Figure 7.46 that the nitrate levels at St Moling's well were fairly constant over this period, except for a low value (3.6 mg $l^{-1}$ as N) in March 2017.

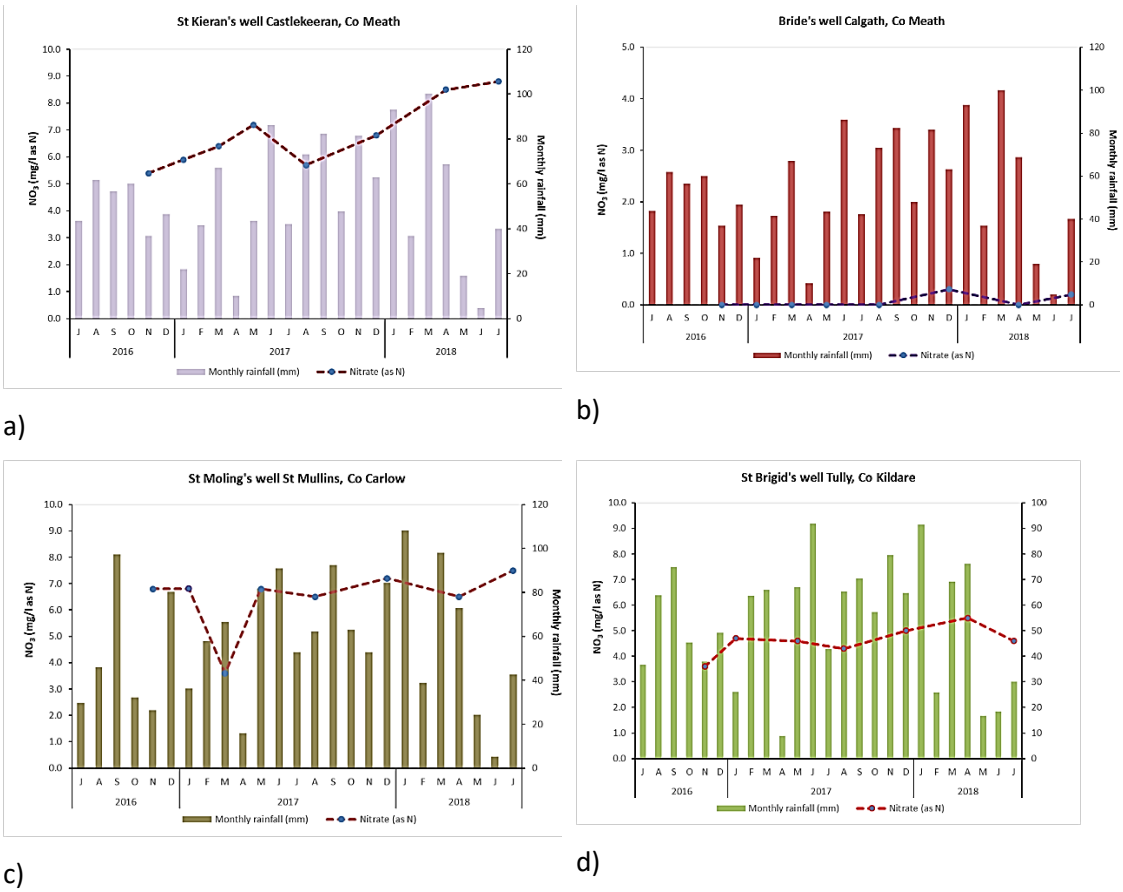



Figure 7.46 Plots of nitrate (mg $l^{-1}$ as N) against monthly rainfall for the four monitoring wells: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); c) St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare). Monthly rainfall data were obtained from Met Éireann

### 7.7.3 Minor ions and trace elements

The monitoring data for all 51 minor ions and trace elements are plotted in Appendix D. Six water samples were analysed for trace elements in St Brigid's well Tully, and seven samples in each of the other three wells. Figure 7.47 shows the monitoring data for 10 of the minor ions

and trace elements, but the reader should also refer to the full dataset in the discussion that follows.

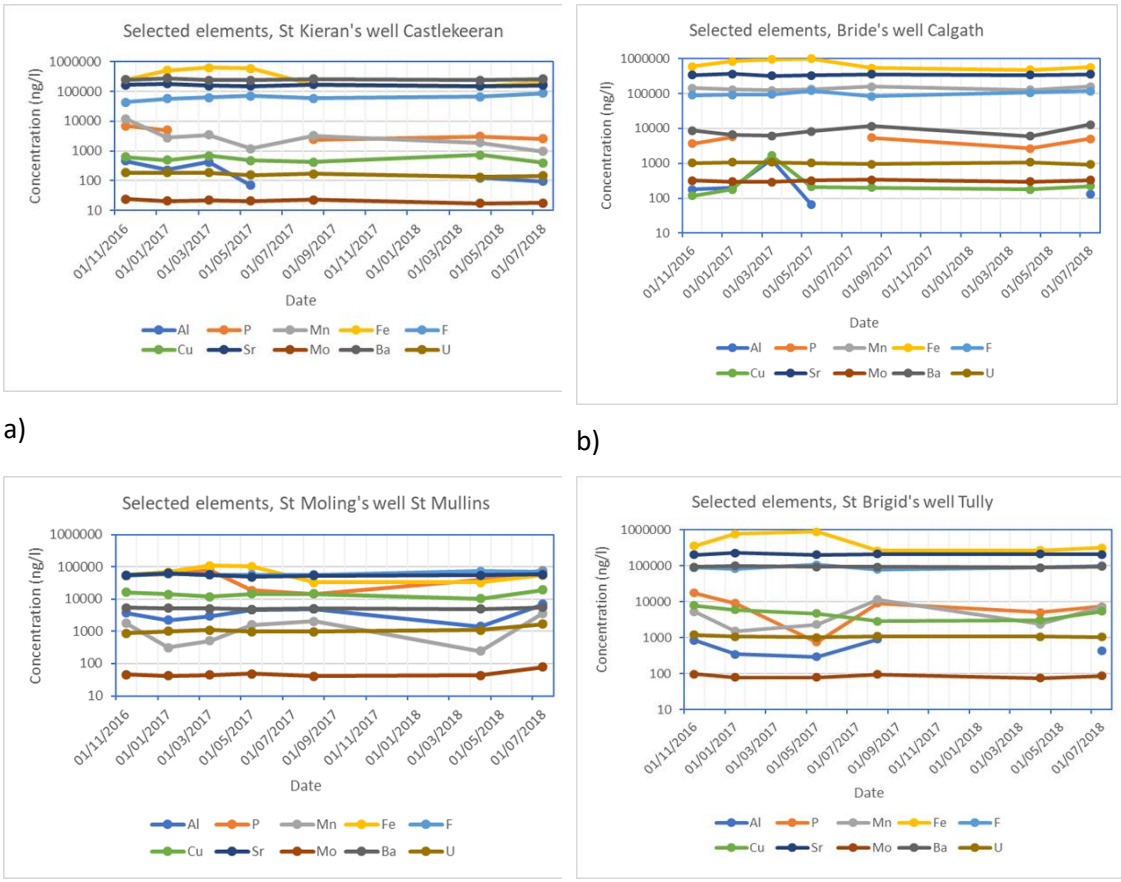



Figure 7.47 Selected minor ion and trace element concentrations (in $ngl^{-1}$) for the four monitoring wells over a 2-year sampling period: a) St Kieran's well Castlekeeran (Co Meath); b) Bride's well Calgath (Co Meath); St Moling's well St Mullins (Co Carlow); d) St Brigid's well Tully (Co Kildare)

It can be seen in Figure 7.47 that the minor ion and trace element concentrations were fairly consistent in each of the four monitoring wells throughout the monitoring period. This is especially the case for Bride's well Calgath, sourced from a confined impure limestone aquifer. There are rises in the Al and Cu concentrations in March 2017, but these are single elevated values. Interestingly, these two elevated Al and Cu values correspond to the time when the lowest pH value was measured (Figure 7.43), consistent with the increased solubility of trace metals with increased water acidity.

Bride's well is known as a chalybeate well and iron staining is visible on the well lining (Section 5.9.1). This is borne out by the relatively high mean Fe values over the monitoring period: 707 µg $l^{-1}$ in Bride's well compared to 359, 476 and 65 µg $l^{-1}$ in St Kieran's well, St Brigid's well and St Moling's well respectively. Bride's well also had the highest mean concentrations of Mn and F (and e.g. As, Sb and Pb – see Figures D.8 and D.11), but all below levels of potential concern in drinking water quality except for Mn, where the mean concentration was 138 µg $l^{-1}$ compared to an EU guide level of 50 µg $l^{-1}$ (see Tables 6.2 and 6.3). St Moling's well, which had the lowest mean pH value of the four wells (see Section 7.7.1), produced the highest mean levels of Al, Cu and U (albeit all within relevant drinking water guideline values).

Sr was one of the most abundant elements in all four wells, and its concentrations remained relatively constant throughout the monitoring period. The highest concentrations occurred in Bride's well (mean = 342 µg $l^{-1}$), and the lowest in St Moling's well (mean = 56 µg $l^{-1}$). As noted earlier (Section 7.6.3.1) the solubility limits of Sr are seldom reached in fresh waters, making Sr concentrations a good indicator of groundwater residence times. Therefore, it is unsurprising that Bride's well, with its deep confined aquifer source, should show the highest values and that St Moling's well, which taps a non-carbonate (i.e. igneous) lithology, should have the lowest concentrations.

A noticeable feature of the results for St Kieran's well was the consistently high Ba concentrations – a mean of 251 µg $l^{-1}$ compared to 93.4, 8.6 and 5.1 µg $l^{-1}$ in St Brigid's well, Bride's well and St Moling's well, respectively. It was also above the NBL of 179 µg $l^{-1}$ for the pure limestone lithological group. As mentioned in Section 7.6.3.1, the solubility of Ba is mainly controlled by its saturation in relation to the mineral barite, with high Ba concentrations generally found where $SO_4$ values are low. Here, the mean $SO_4$ concentration in St Kieran's well during the monitoring period (11.7 mg $l^{-1}$) was appreciably lower than those in St Brigid's well and Bride's well (24.5 and 21.5 mg $l^{-1}$, respectively), but slightly above that in St Moling's well (9 mg $l^{-1}$).

Phosphorus levels were elevated in St Moling's well (mean = 48.8 µg $l^{-1}$) compared to the other three monitoring wells (with means ranging from 4.0 to 8.2 µg $l^{-1}$). The NBL for total phosphorus (as P) for a poorly productive aquifer is 16 µg $l^{-1}$, and 26 µg $l^{-1}$ for a karstified aquifer (see Section 6.3.2). Phosphorus can be sourced naturally from dissolution of minerals such as apatite, but its presence in groundwater may also result from activities such as agriculture and waste disposal.

Nitrate levels were elevated in St Moling's well (Section 7.7.2), consistent with anthropogenic influences. However, St Kieran's well and St Brigid's well also had elevated nitrate levels, but their P concentrations were of the same order as that in Bride's well, where nitrate levels were low. In St Brigid's well there was a noticeable drop in P concentration in the May 2017 sample. However, there was no appreciable change in the EC or the $NO_3$ values that month, nor in the rainfall (which was slightly above average, following a dry April – see Figures 7.42 and 7.46).

Bride's well showed the highest mean concentrations of Mo, Li, Co, Zn, In and Tl, as well as Sr (see Tables D.7, D.9 and D.11). However, the levels of Mo, Co, Zn and Sr were all less than the relevant NBLs (either national or for the impure limestone lithology – including indicative values). There are no NBLs for Li, In or Tl. In their study of lithium in Carlow groundwaters (mainly from granitic bedrock), Kavanagh *et al*. (2017) recorded temporal variations in Li (with lower mean values in March and July compared to their May and September results), but were unable to propose a mechanism to explain these variations. The Li results for three of the four monitoring wells sampled during the present research were consistent for the various sampling rounds, except at Bride's well, where some variations were observed (the highest values were found in August 2017 and July 2018 samples – 6.6 and 7.0 µg $l^{-1}$, respectively - and the lowest in January and March 2017 and April 2018 – 3.8, 3.4 and 3.4 µg $l^{-1}$, respectively; see Figure D.7). It is not clear why the summer levels should be higher; there is no clear relation to pH, for example (Figure 7.43).

Despite the very low concentrations of rare earth elements (less than 1 ng $l^{-1}$ in some instances), the consistency of results (in the six or seven sampling rounds) over the 2-year period gives some confidence in the accuracy of the analyses (see Figures D.6, D.12, D18 and D.24). The samples from St Moling's well (igneous lithology) gave the highest mean values for 13 out of the 14 REEs, the exception being La (where the mean concentration in St Moling's well was second highest after that in St Kieran's well). Minerals rich in REEs such as La, Ce, Pr, Nd, Gd, Dy and Yb commonly occur in alkaline and granitic rocks and pegmatites (Reimann and Birke, 2010), so the higher groundwater concentrations encountered at St Moling's well would be expected. In addition, this site has the lowest groundwater pH (Figure 7.43), and the mobility of most REEs is enhanced under acidic conditions (MacDonald *et al*., 2017). The lowest mean concentrations for 13 out of the 14 REEs (Ce was the exception) were found in the samples from St Brigid's well (sand and gravel lithology).

The mean REE concentrations for the four monitoring wells normalised to average Mud of Queensland (MuQ) sediment values (see Section 7.6.3) is shown in Figure 7.48. The higher abundance of REEs in St Moling's well is evident. A negative Ce anomaly can also be seen in the figure, especially for St Moling's well and St Kieran's well in Castlekeeran. As explained earlier, this may be associated with loss of Ce in oxic groundwaters due to precipitation. In this respect, it is interesting that the samples from the confined aquifer, Bride's well, where anoxic conditions might be expected, did not exhibit a notable negative Ce anomaly.

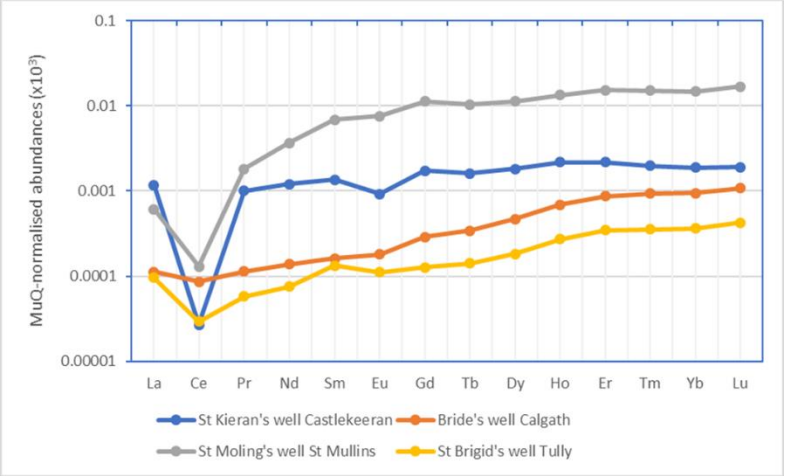



Figure 7.48 REE abundances of mean monitoring well concentrations relative to Mud of Queensland (MuQ)

## 7.8 Water chemistry results for the Spa wells

The physico-chemical parameters and major ion results for the five spa wells sampled during the research project are summarised in Table 7.30. The lithological group to which the groundwater source at each well belongs is also shown in the table. Unlike the majority of holy wells, which tap shallow unconfined aquifers, the aquifers at three of the spa wells are confined: Lady's well Mallow in Co Cork, Louisa Bridge spa well Leixlip in Co Kildare and Drumod spa well Swanlinbar in Co Cavan.

Lady's well Mallow and Louisa Bridge spa well in Leixlip both have reputations as warm water wells (Section 5.11) and this is borne out by the elevated temperatures in Table 7.30. The highest water temperature was measured in Lady's well: the source of the artesian groundwater flow here may be Dinantian limestones from a depth of more than 1000 m (see Section 5.11.4 and

Brück *et al*., 1986). The Louisa Bridge and Drumod spa wells were the most mineralised of the five samples, with EC values above 1000 µS $cm^{-1}$.

Table 7.30 Physico-chemical parameters and major ions for the spa wells

| | Lady's well, Mallow | Louisa Bridge, Leixlip | Drumod, Swanlinbar | Lisdoon, Sulphur well | Lisdoon, Twin wells | Holy wells: Med | Holy wells: Mean | NBL |
|---|---|---|---|---|---|---|---|---|
| *Lithology* | *Pure lst* | *Impure lst*[a] | *Pure lst* | *Non-calc sed* | *Non-calc sed* | | | |
| Sample date | 11/1/2017 | 31/1/2018 | 31/1/2018 | 1/8/2018 | 1/8/2018 | | | |
| pH | 7.16 | 6.75 | 6.70 | 6.54 | 6.20 | 6.50 | 6.44 | |
| EC (µS $cm^{-1}$) | 478 | 1865 | 1288 | 527 | 718 | 516 | 876 | |
| Temperature (°C) | 18.1 | 15.7 | 7.5 | 12.4 | 12.3 | 10.6 | 10.8 | |
| Ca (mg $l^{-1}$) | 77.3 | 131.9 | 149.0 | 41.6 | 66.8 | 71.0 | 78.7 | |
| Mg (mg $l^{-1}$) | 10.5 | 35.8 | 74.9 | 25.3 | 38.9 | 6.2 | 18.3 | 17[b] |
| Na (mg $l^{-1}$) | 12.3 | 161.0 | 37.0 | 55.2 | 54.1 | 10.9 | 28.8 | 13[b] |
| K (mg $l^{-1}$) | 1.11 | 9.06 | 2.90 | 1.68 | 1.86 | 1.94 | 5.45 | 2.1[b] |
| $HCO_3$ (mg $l^{-1}$) | 242 | 478 | 447 | 281 | 410 | 207.4 | 233.3 | |
| $SO_4$ (mg $l^{-1}$) | 23.8 | 54.1 | 383 | 31.9 | 13.9 | 10.5 | 30.7 | 13[b] |
| Cl (mg $l^{-1}$) | 47.8 | 321 | 12.0 | 31.8 | 34.0 | 22.7 | 147.3 | 21[c] |
| $NO_3$ (mg $l^{-1}$ as N) | 1.6 | 0.1 | 0.1 | 0.2 | 0.1 | 2.3 | 3.5 | 2.0[b] |
| Si (mg $l^{-1}$) | - | 5.3 | 10.2 | 4.8 | 6.0 | 2.6 | 3.1 | |
| IBE (%)[d] | -6 | -4 | -1 | 3 | 6 | | | |

Note: [a] Groundwater source may be from below the carbonate strata (Blake, 2016)

[b] National NBL values for unconfined aquifers

[c] National NBL value

[d] IBE = ion balance error

Nitrate concentrations were low in all five wells, below the national NBL for unconfined aquifers (and only one sample [from Lady's well] above the provisional value of 0.3 mg $l^{-1}$ [as N] for a confined aquifer). Several of the other national NBLs (for unconfined aquifers) were exceeded in one or more of the well samples: Na in four of the five samples (the exception was Lady's well); K at Louisa Bridge and Drumod spa; $SO_4$ at all wells; and Cl at four of the five wells (the exception was Drumod spa). In relation to NBLs defined by lithology, exceedances (for the relevant lithology) included Ca at Drumod spa well and $HCO_3$ at Drumod spa and Lisdoonvarna Twin wells. The Si value in Drumod spa (10.2 mg $l^{-1}$ Si = 21.8 mg $l^{-1}$ as $SiO_2$) was about twice the NBL for pure limestones of 10 mg $l^{-1}$ as $SiO_2$, and consistent with a long groundwater residence time.

The major ion chemistries are illustrated on the Durov diagram in Figure 7.49. The elevated Mg in the two Lisdoonvarna and Drumod spa wells are apparent when compared with the holy wells dataset (Figure 7.21 and Figure 7.22), whilst the Drumod spa well also has a higher proportion of $SO_4$ than the other spa wells or any of the holy wells. The Drumod spa well is a contact spring where groundwater in the Dinantian limestone aquifer is brought to the surface by contact with underlying low permeability shales (Section 5.11.2). It has a reputation for its sulphur-rich water. The Louisa Bridge spa well, which is the most mineralised well, tends most towards an Na-Cl major ion chemistry. The Louisa Bridge spa well is sourced from a deep confined aquifer. The limestone formation is Lucan Formation, although studies by Blake (2016) suggest that the groundwater source may be from below the Dublin carbonate basin (Section 5.11.3).

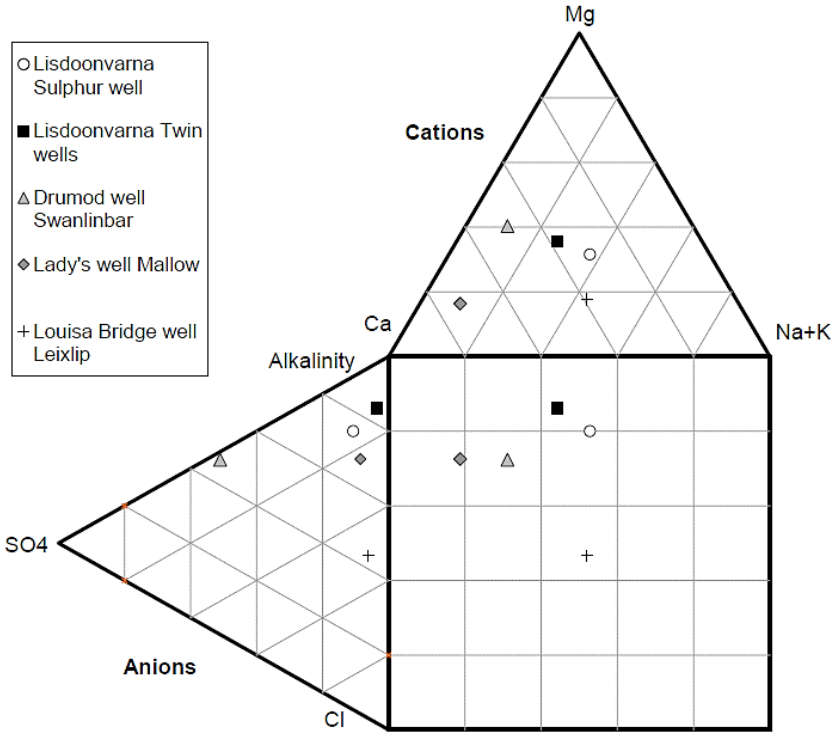



Figure 7.49 Durov plot for the Spa wells

Minor ion and trace element results for the five spa wells are summarised in Table 7.31. The REEs are included separately in Table 7.32. Median and mean values from the holy wells datasets (Tables 7.24 and 7.25) are shown in Table 7.31 for comparison, along with the NBLs (national or national unconfined aquifer) where available.

Table 7.31 Minor ions and trace element results for the spa wells (excluding the REEs, which are shown in Table 7.32)

| | Unit | Lady's well, Mallow | Louisa Bridge, Leixlip | Drumod, Swanlinbar | Lisdoon, Sulphur wells | Lisdoon, Twin wells | Holy wells: Med | Holy wells: Mean | NBL |
|---|---|---|---|---|---|---|---|---|---|
| *Samples date* | | *11/1/17* | *31/1/18* | *31/1/18* | *1/8/18* | *1/8/18* | | | |
| Aluminium (Al) | µg $l^{-1}$ | 0.33 | | | 2.12 | 1.18 | 1.62 | 21.4 | |
| Antimony (Sb) | ng $l^{-1}$ | 53.5 | 102.8 | 0.17 | 8.93 | 0.25 | 46.9 | 110.2 | 500 |
| Arsenic (As)[a] | µg $l^{-1}$ | 1.12 | 4.39 | 0.04 | 0.16 | 0.05 | 0.30 | 0.75 | 2.0 |
| Barium (Ba) | µg $l^{-1}$ | 4.06 | 88.37 | 17.16 | 1724 | 2110 | 19.6 | 42.4 | |
| Beryllium (Be) | ng $l^{-1}$ | 1.78 | 50.5 | 19.4 | 10.6 | 21.3 | 2.53 | 11.8 | <1000 |
| Cadmium (Cd) | ng $l^{-1}$ | 17.9 | 2.83 | 0.24 | 0.18 | | 10.2 | 39.5 | <400 |
| Caesium (Cs) | ng $l^{-1}$ | 23.7 | 4262 | 48.2 | 895 | 1059 | 6.41 | 32.1 | |
| Chromium (Cr)[a] | µg $l^{-1}$ | | 3.41 | 0.15 | 0.33 | 0.19 | 0.46 | 1.25 | |
| Cobalt (Co)[a] | µg $l^{-1}$ | 0.10 | 0.13 | 0.09 | 0.04 | 0.06 | 0.13 | 0.20 | <1 |
| Copper (Cu) | µg $l^{-1}$ | 0.15 | 0.32 | 0.35 | 0.41 | 0.52 | 0.94 | 3.24 | 16 |
| Fluoride (F) | µg $l^{-1}$ | 150 | 470 | 1100 | 190 | 140 | 58.8 | 75.4 | 200[b] |
| Gallium (Ga) | ng $l^{-1}$ | 2.14 | 3.95 | 0.55 | 4.91 | 2.40 | 1.15 | 4.42 | |
| Hafnium (Hf) | ng $l^{-1}$ | | 0.13 | 0.22 | 0.50 | 0.58 | 0.24 | 0.80 | |
| Indium (In) | ng $l^{-1}$ | | 0.03 | 0.01 | | | 0.04 | 0.67 | |
| Iron (Fe) | µg $l^{-1}$ | 378 | 690 | 256 | 106 | 198 | 251.7 | 380.3 | 268[b] |
| Lead (Pb) | ng $l^{-1}$ | 0.65 | 39.9 | 8.50 | 6.9 | | 14.2 | 82.7 | 2900 |
| Lithium (Li) | µg $l^{-1}$ | 5.65 | 248.1 | 34.5 | 54.0 | 63.9 | 0.95 | 4.05 | |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 0.16 | 68.0 | 37.5 | 5.0 | 28.3 | 2.09 | 27.9 | 23[b] |
| Molyb'num (Mo) | ng $l^{-1}$ | 699.7 | 1936 | 10.3 | 51.0 | 11.9 | 96.1 | 589.3 | <1000 |
| Nickel (Ni) | µg $l^{-1}$ | 0.83 | 0.79 | 0.68 | 0.28 | 0.39 | 1.24 | 1.69 | 2.1[b] |
| Niobium (Nb) | ng $l^{-1}$ | 0.09 | | | 0.82 | 0.22 | 0.37 | 1.30 | |
| Phosphorus (P) | µg $l^{-1}$ | 4.68 | 0.81 | 12.0 | 9.9 | 4.1 | 17.2 | 85.5 | 17 |
| Rubidium (Rb) | µg $l^{-1}$ | 0.60 | 30.6 | 2.3 | 3.9 | 4.4 | 0.86 | 2.27 | |
| Scandium (Sc) | µg $l^{-1}$ | 1.17 | 1.0 | 1.47 | 0.75 | 0.99 | 0.58 | 0.63 | |
| Selenium (Se) | ng $l^{-1}$ | | 273.4 | 12.3 | | | 36.1 | 63.5 | |
| Strontium (Sr) | µg $l^{-1}$ | 140.8 | 1961 | 22220 | 2415 | 2881 | 169.9 | 262.3 | |
| Tantalum (Ta) | ng $l^{-1}$ | 0.009 | | | 0.012 | | 0.02 | 0.04 | |
| Thallium (Tl) | ng $l^{-1}$ | 57.5 | 16.8 | 0.49 | 0.39 | 0.39 | 2.50 | 11.07 | |
| Thorium (Th) | ng $l^{-1}$ | 0.02 | 0.15 | 0.11 | 0.15 | 0.13 | 0.21 | 2.35 | |
| Tin (Sn) | ng $l^{-1}$ | 1.85 | 2.71 | 0.32 | 1.38 | 1.43 | 2.36 | 7.07 | |
| Titanium (Ti)[a] | µg $l^{-1}$ | 0.38 | 0.67 | 1.98 | 0.22 | 0.10 | 0.25 | 0.68 | |
| Tungsten (W) | ng $l^{-1}$ | 15.7 | 23.7 | 2.7 | 26.4 | 7.4 | 0.58 | 9.45 | |
| Uranium (U) | ng $l^{-1}$ | 4658 | 448 | 1.65 | 64.7 | 30.1 | 445.3 | 786.4 | |
| Vanadium (V)[a] | µg $l^{-1}$ | | 1.16 | 0.0008 | 0.67 | | 0.25 | 0.62 | |
| Yttrium (Y) | ng $l^{-1}$ | 48.4 | 27.5 | 77.6 | 25.7 | 39.4 | 68.1 | 210.1 | |
| Zircon (Zr) | ng $l^{-1}$ | 0.31 | 9.0 | 26.5 | 16.1 | 43.2 | 11.3 | 31.1 | |
| Zinc (Zn)[a] | µg $l^{-1}$ | | 4.4 | | | | 2.67 | 15.3 | |

Notes: [a] Results prone to chloride interferences

[b] NBL for unconfined aquifer

A few observations in relation to the minor ions and trace elements in Table 7.31 are given below:

a) Strontium concentrations in four of the five spa wells exceeded the mean values for the holy wells, with the concentration at Drumod spa well being especially elevated (22.2 mg $l^{-1}$). The values for Drumod and Lisdoonvarna spa wells also exceeded the NBL for the pure limestone and non-calcareous sedimentary lithologies, respectively. As noted previously, Sr is a useful indicator of groundwater residence times, and the elevated values suggest longer residence times for the more mineralised spa waters than is typically the case for the shallow holy wells.

b) Barium concentrations in the two Lisdoonvarna well samples were much higher than in the other three spa wells, and higher than the maximum value recorded in any holy well (538 µg $l^{-1}$ in St Colmcille's well in Kells, Co Meath, which taps a metamorphic rock aquifer). As mentioned earlier Ba solubility is mainly controlled by saturation with respect to barite, and so Ba values are usually low where sulphate is elevated. At first sight, then, the high Ba concentration is surprising as the two wells sampled at Lisdoonvarna have reputations for their sulphur (indeed, the main well is referred to as the Sulphur well, and the Twin wells are known for sulphur and iron – see Section 5.11.1). However, it can be seen from Table 7.30 that the sulphate concentration in neither well sample was particularly elevated – the higher value, in the main Sulphur well, being similar to the mean value for the holy wells, although it was above the NBL. The spa well with the highest $SO_4$ concentration, Drumod spa, had a relatively low Ba concentration.

c) Lithium concentrations are higher than the mean holy well concentrations in all the spa wells, although only by a small amount in Lady's well Mallow (there is no NBL for lithium). The concentration in the sample from Louisa Bridge was especially high (see Section 8.2.3 for discussion of Li results in relation to health).

d) In addition to elevated Li, the Louisa Bridge spa well gave the highest concentrations of several elements, including: Fe, Mn, Pb, Sb, As, Be, Cs, Cr, Co, Mo, Rb and Se. Several of these were at concentrations above the NBL - As, Fe, Mn, Mo. However, the NBL values in Table 7.31 are for unconfined aquifers, whereas the aquifer at Louisa Bridge is confined. Whilst there were insufficient data available to define NBLs for confined aquifer conditions (Tedd et al., 2017), indicative values were provided for information

(Table 6.4). The Fe and Mn values at Louisa Bridge were below these indicative NBL values.

e) The highest fluoride value was encountered at Drumod spa well but, at 1.1 mg $l^{-1}$, was still within drinking water limits (Table 6.3).

f) The highest uranium concentration was in the sample from Lady's well Mallow. Although this value of 4.7 µg $l^{-1}$ was above the NBL of 2.8 µg $l^{-1}$ for pure limestones, it was well below the WHO drinking water guideline value of 30 µg $l^{-1}$ (Table 6.2).

Lady's well Mallow had the highest concentrations of 10 of the 14 lanthanide REEs in Table 7.32, with Lisdoonvarna Twin wells having the highest concentration of three REEs (La, Sm and Eu) and Louisa Bridge the highest value of Ce. However, none of the values exceeded the mean for the holy wells dataset, and most were below the median value for that dataset.

Table 7.32 Lanthanide rare earth element results for the spa wells. All values are in ng $l^{-1}$

| | Lady's well, Mallow | Louisa Bridge, Leixlip | Drumod, Swanlinbar | Lisdoon, Sulphur wells | Lisdoon, Twin wells | Holy wells: Med | Holy wells: Mean |
|---|---|---|---|---|---|---|---|
| *Sample date* | *11/1/17* | *31/1/18* | *31/1/18* | *1/8/18* | *1/8/18* | | |
| Lanthanum (La) | 4.2 | 4.1 | 1.0 | 15.5 | 19.5 | 12.45 | 108.2 |
| Cerium (Ce) | 0.22 | 6.1 | 0.9 | 1.8 | 4.4 | 4.11 | 108.2 |
| Praseodymium (Pr) | 1.3 | 0.8 | 0.14 | 0.30 | 0.70 | 3.39 | 32.2 |
| Neodymium (Nd) | 6.2 | 3.8 | 0.67 | 3.4 | 5.9 | 15.89 | 151.5 |
| Samarium (Sm) | 1.6 | 1.1 | 0.18 | 7.5 | 10.1 | 4.25 | 40.5 |
| Europium (Eu) | 0.40 | | 0.005 | 0.27 | 2.8 | 1.23 | 11.0 |
| Gadolinium (Gd) | 2.8 | 1.2 | 0.20 | 0.52 | 1.9 | 5.49 | 45.4 |
| Terbium (Tb) | 0.38 | 0.18 | 0.03 | 0.06 | 0.26 | 0.77 | 5.59 |
| Dysprosium (Dy) | 2.6 | 1.3 | 0.22 | 0.46 | 1.4 | 4.98 | 29.6 |
| Holmium (Ho) | 0.77 | 0.36 | 0.04 | 0.10 | 0.37 | 1.24 | 6.24 |
| Erbium (Er) | 2.4 | 0.99 | 0.13 | 0.29 | 1.14 | 4.05 | 17.06 |
| Thulium (Tm) | 0.31 | 0.16 | 0.02 | 0.04 | 0.19 | 0.64 | 2.41 |
| Ytterbium (Yb) | 2.1 | 0.78 | 0.12 | 0.24 | 1.1 | 4.22 | 14.98 |
| Lutetium (Lu) | 0.36 | 0.16 | 0.02 | 0.06 | 0.21 | 0.71 | 2.45 |

## 7.9 Comparisons with data from previous studies of holy wells and spa wells

Comparisons between the holy well and spa well results with natural background levels have already been described. This section will discuss the study findings in relation to the previous Irish studies of holy wells and spa wells (see Section 6.4). The main physico-chemical parameters

and major ion results for selected holy wells and spa wells from previous studies are compared with the results from this research in Table 7.33.

Table 7.33 Physico-chemical parameters and major ion results compared to analyses from previous studies of holy wells and spa wells. Values in mg $l^{-1}$ except for EC and pH

| Well name | Date(s) | EC (µS $cm^{-1}$) | pH | T (°C) | Ca | Mg | Na | K | $HCO_3$ | $SO_4$ | Cl | $NO_3$ (as N) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| St Brigid's well Tully (Kildare) | 2012 | 365 | 7.43 | 10 | 150 | 19.3 | 10.9 | 5.2 | 554 | <25 | 19.3 | 4.5 | Buckley (2012) |
| | 2016-18[a] | 775 | 6.67 | 10.4 | 137 | 17.0 | 11.2 | 5.8 | 441 | 24.5 | 24.1 | 4.6 | Misstear (2020) |
| St Kieran's well Castlekeeran (Meath) | 2012 | 356 | 7.35 | - | 141 | 13.1 | 8.5 | 1.9 | 362 | 15.3 | 10.9 | 7.1 | Buckley (2012) |
| | 2016-18[a] | 571 | 6.58 | 10.4 | 92 | 12.6 | 10.3 | 1.9 | 281 | 11.7 | 23.3 | 6.7 | Misstear (2020) |
| Bride's well Calgath (Meath)[b] | 7/12/79 | - | 7.24 | 13.2 | 92 | 24.9 | 10 | 1 | 393 | - | 17 | 3.4 | Aldwell & Burdon (1980) |
| | 2012 | 284 | 7.45 | 14 | 150 | 25.7 | 10.9 | 1 | 525 | 15.8 | 17.2 | 0.7 | Buckley (2012) |
| | 2016-18[a] | 631 | 6.84 | 12.7 | 94 | 24.2 | 9.9 | 1 | 377 | 21.5 | 18.2 | 0.1 | Misstear (2020) |
| St Gorman's well (Meath) | 7/12/79 | - | 7.26 | 20.2 | 96 | 14.6 | 9 | 1 | 354 | 7 | 18 | 0.8 | Aldwell & Burdon (1980) |
| | 2012 | 450 | 7.52 | 15 | 132 | 12.7 | 9.1 | 2.8 | 466 | 9 | 15.2 | 1.4 | Buckley (2012) |
| | 31/1/18 | 718 | 6.86 | 10.3 | 144 | 9.3 | 7.4 | 4.8 | 425 | 16.3 | 16.8 | 4 | Misstear (2020) |
| Tobar na nGealt (Kerry) | 2012 | 195 | 6.8 | - | 16.3 | 3.6 | 12.4 | 0.5 | 70 | 5.7 | 20.7 | 10.9 | Buckley (2012) |
| | 13/11/18 | 175 | 5.57 | 11.4 | 16.2 | 3.5 | 13.8 | 0.6 | 53.7 | 4.9 | 25.5 | 1.1 | Misstear (2020) |
| St Brigid's well Newcastle West (Limerick) | 4/12/79 | - | 7.84 | 13.8 | 68 | 16.1 | 14 | 1 | 282 | - | 21 | 3.4 | Aldwell & Burdon (1980) |
| | 11/79 – 12/83[c] | 414 | 7.29 | 13.1 | 68 | 13.2 | 16.3 | 1.1 | 257 | 13.0 | 24.4 | 0.3 | Brück *et al.* (1986) |
| | 3/8/17 | 483 | 6.72 | 13.8 | 70 | 12.9 | 14.3 | 0.9 | 273 | 9.4 | 20.4 | 0.6 | Misstear (2020) |
| Louisa Bridge spa well (Kildare) | 7/12/79 | - | 7.28 | 16.2 | 118 | 33.2 | 209 | 9 | 329 | - | 446 | 1.4 | Aldwell & Burdon (1980) |
| | 31/1/18 | 1865 | 6.75 | 15.7 | 132 | 35.8 | 161 | 9.1 | 478 | 54.1 | 321 | 0.1 | Misstear (2020) |
| Spa well Swanlinbar (Cavan) | 2012 | 558 | 7.21 | 8 | 188 | 77.2 | 40.9 | 3.6 | 902 | 349 | 15.2 | 0.5 | Buckley (2012) |
| | 31/1/18 | 1288 | 6.70 | 7.5 | 149 | 74.9 | 37.0 | 2.9 | 446 | 383 | 12.0 | 0.1 | Misstear (2020) |
| Spa well Lisdoonvarna (Clare) | 2012 | 554 | 7.31 | 9 | 74 | 23.9 | 45.6 | 1.7 | 226 | 9.2 | 32.9 | 0.05 | Buckley (2012) |
| | 1/8/18 | 527 | 6.54 | 12.4 | 41.6 | 25.3 | 55.2 | 1.7 | 281 | 31.9 | 31.8 | 0.2 | Misstear (2020) |
| Spa well Mallow (Cork) | 15/11/79[d] | - | 7.52 | 20.7 | 72 | 15.6 | 12 | 1 | 254 | 22 | 22 | 2.4 | Aldwell & Burdon (1980) |
| | 11/79 – 12/83[e] | 466 | 7.34 | 19.5 | 73 | 10.5 | 15.3 | 1.5 | 234 | 17.4 | 27.3 | 0.7 | Brück *et al.* (1986) |
| | 2012 | 290 | 6.79 | 14 | 85.8 | 10.3 | 13.4 | 1.4 | 276 | 20.4 | 21.7 | 12.1 | Buckley (2012) |
| | 11/1/17 | 478 | 7.16 | 18.1 | 77.3 | 10.5 | 12.3 | 1.1 | 242 | 23.8 | 47.8 | 1.6 | Misstear (2020) |

Notes:
[a] Mean values of between 7 and 9 samples
[b] Also referred to as "Bride's River", Breda's well, Kilcock and St Brigid's well Mulhussay.
[c] Mean values from 10 analyses.
[d] Two analyses are given for this spa well site on this date, one having normal groundwater temperature (11.3°C) and the other with warm water (20.7°C). The warm water analysis is included here.
[e] Mean values from 14 analyses.

In reviewing the data in the table, it should be borne in mind that the analytical procedures will have differed between different studies and this will affect the results. For example, as noted in Section 6.4.1, the EC values recorded by Buckley in 2012 are low when compared with the sum of the total ions in his data, and this is confirmed by higher EC measurements in the current research. Again, Buckley's bicarbonate values are consistently higher than those measured in the current study, and higher than measurements made by other researchers. The remaining major ion results reported by Buckley are generally consistent with those reported here, although there are some exceptions, e.g. Buckley reported higher Ca and lower Cl concentrations in St Kieran's well Castlekeeran; higher Ca in Bride's well Calgath; elevated nitrate in Tobar na nGealt (two sets of duplicate samples in the current research all gave low $NO_3$ concentrations); and lower $SO_4$ in the spa well (Sulphur well) in Lisdoonvarna. For the Aldwell and Burdon data from 1980, the Ca and Mg results were apparently reported as mg $l^{-1}$ $CaCO_3$ (this is not stated, but can be inferred from the values given as meq $l^{-1}$), and have been adjusted accordingly for Table 7.33. For the Brück *et al*. (1986) data, it has been assumed here that the nitrate results were given as mg $l^{-1}$ $NO_3$, and have been converted in the table to mg $l^{-1}$ as N.

Of the wells for which there are analyses dating back 40 years, to the late 1970s and the 1980s:

a) The major ion water chemistry at Bride's well Calgath in the recent monitoring samples is similar to that reported by Aldwell and Burdon (1980) for the sample collected in December 1979. As noted in Section 5.9.1 and Section 7.7, this well taps a confined impure limestone (Calp) aquifer. Although it has a reputation as a warm water well, it is interesting that the temperature recorded by Aldwell and Burdon of 13.2 $^{o}$C was not particularly elevated, and was in line with the range of temperatures measured in the current research (12.4-14.6 $^{o}$C), and nothing like the maximum temperature of 70 $^{o}$F (21 $^{o}$C) reported on the local signboard.
b) The recent sample from St Gorman's well gave a lower water temperature than that reported by Aldwell and Burdon in 1979. Both samples, and the one collected by Buckley in 2012, all show a Ca-$HCO_3$ water chemistry. The hydrogeology of this site was studied in detail by Blake (2016), as described in Section 6.4.2. Blake sampled artesian boreholes close to the holy well (which often dries up). Her study confirmed the Ca-$HCO_3$ major ion chemistry for this confined pure limestone (Waulsortian) aquifer, which is enriched

in bicarbonate and silica compared to other calcium-bicarbonate type groundwaters. Blake noted – using trace element as well as major ion data, which were subjected to principal component analyses and multivariate statistics - that the hydrochemistry was less evolved in winter than in summer and concluded that cool recharge water infiltrates in winter to depths of at least 500 m, is heated up, and then rises rapidly in a karst conduit flow system to the surface (Blake *et al*., 2016). (The raw chemical data are not included in Blake's published thesis, so are not included in Table 7.33; in any case, her data were from the nearby boreholes rather than the holy well itself).

c) St Brigid's well at Shangarry in Newcastle West Co Limerick was sampled previously by both Aldwell and Burdon (1980) and Brück *et al*. (1986). Their results agree well with each other, and with the sample results from the current research. The well water has a Ca-$HCO_3$ type chemistry and the groundwater source is probably pure limestone (Waulsortian) below an impure (Visean) limestone (see Section 5.9.2). Brück *et al*. (1986) noted that the $HCO_3$ concentration was less than that in a local well chosen as a control for comparison, and also that the Mg concentration was somewhat elevated. These observations were attributed, respectively, to the lower solubility of bicarbonate in warm water and the presence of some dolomite in the aquifer source.

d) The spa water at Louisa Bridge in Co Kildare has a water chemistry enriched in Na and Cl, indicative of a long aquifer residence time, with broadly similar results for the samples collected in the present study and in the study by Aldwell and Burdon (1980) nearly 40 years earlier. This well was also studied by Blake (2016) as part of her research on thermal groundwaters in Leinster. She also observed the Na-Cl water chemistry and, based on detailed analysis of major ion and trace element chemistry – including evidence for dissolution of evaporitic minerals – she concluded that there was a deep groundwater source, possibly from below the Dublin carbonate basin.

e) The sample results in Table 7.33 for the Spa well at Mallow (Lady's well) are broadly consistent, except for a lower EC and higher $NO_3$ reported by Buckley (2012) and a higher chloride determined in the present study. As noted in Section 5.11.4, the warm water in this well issues from a pure limestone aquifer from a probable depth of more than 1000 m (Brück *et al*., 1986).

For those wells in Table 7.33 for which the only datasets are from the more recent study by Buckley in 2012 and the current research, the two sets of results are broadly consistent, apart from those anomalies already referred to above (notably the generally lower EC and higher

$HCO_3$ values in the Buckley data). The samples from St Brigid's well at Tully (sand and gravel aquifer) and St Kieran's well Castlekeeran (karst limestone) show a Ca-$HCO_3$ type chemistry, whilst the sandstone well (really a spring) at Tobar na nGealt is less mineralised. The samples from the Spa well at Swanlinbar (Drumod spa well) both show high $SO_4$ concentrations, consistent with its reputation as a sulphur well. Buckley also measured a number of minor ions and trace elements in his study, and those results are compared with the present findings in Table 7.34.

Table 7.34 Comparison of minor ion and trace element concentrations in the water samples analysed by Buckley (2012) with those determined in the present study (in blue). All values are in µg $l^{-1}$

| Well name | Date | Al | As | Be | Cu | F | Fe | Li | Mn | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| St Brigid's well Tully (Kildare) | 2012 | 47 | <0.37 | <0.3 | 16 | 100 | 143 | 1.4 | 28 | <1.9 |
| | 7/8/17 | 0.9 | 0.18 | 0.002 | 2.9 | 79 | 259 | 1.3 | 11.5 | 2.8 |
| St Kieran's well Castlekeeran (Meath) | 2012 | 15 | <0.37 | <0.3 | 9 | 100 | 41 | 1.5 | 10 | <1.9 |
| | 18/7/18 | 0.1 | 0.10 | 0.002 | 0.4 | 87 | 203 | 1.6 | 1.0 | 1.8 |
| Bride's well Calgath (Meath) | 2012 | <5 | 1.4 | <0.3 | 5 | 100 | 245 | 5.2 | 142 | 23 |
| | 19/5/17 | 0.07 | 1.9 | 0.03 | 0.2 | 120 | 983 | 4.9 | 133 | 26.9 |
| St Gorman's well (Meath) | 2012 | <5 | 0.4 | <0.3 | 10 | 100 | 218 | 5.1 | 19 | <1.9 |
| | 31/1/18 | 0.02 | 0.37 | 0.002 | 0.6 | 128 | 271 | 3.2 | 4.4 | 3.8 |
| Tobar na nGealt (Kerry) | 2012 | 6 | 0.43 | <0.3 | 8 | <100 | 9 | 55.6* | 2 | <1.9 |
| | 13/11/18 | 2.2 | 0.23 | 0.015 | 0.1 | - | 48.0 | 0.57 | 0.8 | |
| Spa well Swanlinbar (Cavan) | 2012 | <5 | <0.37 | 0.3 | 4 | 1000 | 10 | 34 | 32 | <1.9 |
| | 31/1/18 | - | 0.04 | 0.02 | 0.3 | 1100 | 256 | 34.5 | 38 | - |
| Spa well Lisdoonvarna (Clare) | 2012 | 6 | 0.37 | 0.3 | 31 | 2100 | 1221 | 51 | 15 | 8 |
| | 1/8/18 | 2.1 | 0.16 | 0.01 | 0.4 | 190 | 106 | 54 | 5.0 | - |
| Spa well Mallow (Cork) | 2012 | 5 | 0.86 | <0.3 | 9 | <100 | <7.2 | 5.1 | 4 | <1.9 |
| | 11/1/17 | 0.33 | 1.12 | 0.002 | 0.15 | 150 | 378 | 5.6 | 0.2 | - |

*Li result from Southern Scientific

The two sets of results confirm low concentrations of trace elements such as As, Be and Cu in most samples. Elevated Zn was shown by both the 2012 and more recent samples from Bride's well Calgath, but these are within the provisional NBL of 30 µg $l^{-1}$ for impure limestone groundwaters. Fluoride values are low across most samples, although Buckley recorded a high value at the Spa well in Lisdoonvarna (the Sulphur well). Iron values show some variations between the two datasets, as might be expected for a parameter that is sensitive to redox

conditions (and Buckley's samples for trace elements do not appear to have been filtered, at least in the field).

Perhaps of most interest in Table 7.34 are the results for lithium. The data from the two studies agree well, with generally low Li concentrations recorded for the holy wells and high values in two of the spa wells, at Swanlinbar and Lisdoonvarna. However, there is a major difference between the high value reported by Buckley for Tobar na nGealt and the low concentration measured in the current research. In his (unpublished) dissertation Buckley quoted a value of 55.6 µg $l^{-1}$ determined by Southern Scientific lab in May 2012 prior to a TG4 television programme about this well, and did not include his own value (see Section 8.2.3 for further discussion about lithium results and their potential association with mental health cures).

## 7.10 Concluding remarks

Detailed conclusions about hydrochemistry are included in Chapter 9, and only a few remarks will be given here. The comprehensive sampling and analysis programme (involving 167 holy wells) showed that the wells had a wide range of water chemistries, from low EC groundwater in mountain settings (minimum EC = 38 µS $cm^{-1}$) to more highly mineralised waters near the coast (maximum EC = 61,150 µS $cm^{-1}$, in a well containing seawater). The dominant water type was Ca-$HCO_3$, typical of Irish groundwaters, especially those groundwaters where flow paths are relatively short. However, differences in water chemistry were observed between wells in different lithological groups: wells in the non-carbonate lithologies tended to have softer, less mineralised water, with lower EC, Ca and $HCO_3$ concentrations. ANOVA tests showed that the mean concentrations of these parameters were significantly different between the non-carbonate and carbonate lithological groups (the latter comprising the impure and impure limestones, plus the sand and gravel and mixed bedrock and gravel groups).

Lithology was also shown to be an important influence on trace element distributions. For example, higher concentrations of Fe, Sr, Co and Mo were found in the impure and pure limestones (and in the sand and gravel and mixed group) compared to the non-carbonate lithologies, whereas elevated concentrations of some other elements such as Cr, Li, As and Rb were found in the igneous group. As and Li levels were lower than those reported at some sites in previous Irish studies (McGrory *et al*., 2017; Kavanagh *et al*., 2017). Strontium levels were higher in the limestone lithologies, possibly reflecting longer flow paths in these aquifers.

ANOVA tests on trace element results for the seven lithological groups showed a complex set of relationships. For most elements, significant differences in means were shown between one or more groups, and especially between one or more of the non-carbonate lithologies with elements in the impure limestone and pure limestone groups. A plot of mean REE values normalised to Mud of Queensland sediment values (a proxy for weathered continental crust) illustrated the greater abundance of REEs in the non-calcareous sedimentary, igneous and metamorphic lithologies compared to the limestones, sands and gravels and mixed bedrock and gravel groups.

In addition to lithology, coastal setting was also found to be a major influence on well hydrochemistry. The wells in coastal settings (n = 31) had elevated concentrations of EC and several major ions (notably Na and Cl) compared to the inland wells. Mann-Whitney U tests showed that the median values of EC, Mg, Na, K, $SO_4$, Cl and Si were statistically different between the coastal and non-coastal well samples. Regarding minor ions and trace elements, Mann-Whitney U tests indicated significant differences in median values for 26 of the 51 parameters, with the concentrations being higher in the coastal setting for 25 of these, including 11 out of the 14 REEs.

Nitrate concentrations exceeded the natural background level (NBL) of 2 mg $l^{-1}$ (as N) in just over half the wells sampled, suggesting significant anthropogenic influences. However, there was very little association between the nitrate values and the groundwater vulnerability class: the mean $NO_3$ concentration exceeded the natural background level (NBL) across the five vulnerability classes (ranging from X Extreme to Low – see Section 3.2 and Section 4.2.7), and an ANOVA test showed that the means were only significantly different between two of the vulnerability classes (High and Low). This finding suggests that these shallow spring wells are susceptible to contamination even where the geological rating of groundwater vulnerability is Moderate or Low, a finding in line with an earlier study of private well water quality in Ireland (Hynds et al., 2012).

The chemical analysis results were compared to the NBLs established by Tedd *et al*. (2017), using both the full holy wells dataset and the wells with low nitrate values. Many of the samples exceeded the NBLs for major (e.g. 54.5% of samples for Cl) and minor (e.g. 44% for Fe) ions and trace elements, but the interpretation of these comparisons is constrained by several differences in the datasets: the data used for establishing NBLs for many of the parameters were

monitoring records collected from a small number of borehole sites (typically 21), mainly in productive aquifers, and after a screening process to remove boreholes liable to anthropogenic influences, whereas the holy wells dataset comprised one-off samples from 167 shallow spring wells, many of which would be susceptible to contamination.

The chemical analysis results from the four monitoring wells were also presented in this chapter. Physico-chemical parameters, major ions, minor ions and trace elements were measured over a two-year period. The results are important in that they indicate how water chemistry may vary with the seasons, either due to variations in recharge or because of anthropogenic influences which may vary seasonally (e.g. fertiliser application to land). The majority of holy wells were sampled only once during the research and hence the results represent the water quality only at the time of sampling.

The well that exhibited the greatest seasonal variations was St Kieran's well at Castlekeeran in Co Meath. This is a spring well that issues from karstified limestone, and the water chemistry variations showed some links to rainfall, with the sample having the lowest ionic concentration corresponding to a wet period in the Spring of 2018. In contrast, Bride's well at Calgath in Co Meath showed the least variation in pH, EC, water temperature and chemistry over the monitoring period. This was to be expected, because the well taps a confined aquifer with a relatively deep groundwater source and hence long flow path. St Brigid's well at Tully in Co Kildare also showed a fairly consistent major ion water chemistry, dominated by Ca and $HCO_3$, suggesting that the groundwater feeding this sand and gravel well also has a relatively long flow path. Concerning trace elements, generally only relatively small variations in concentrations were observed throughout the monitoring period. Bride's well, which is known as a chalybeate well, had elevated levels of Fe and, of the four monitoring wells, also gave the highest mean concentrations of several elements including Mn, As, Sb, Li, Co, Zn and Sr. St Moling's well showed the highest concentrations of REEs, consistent with this well having the lowest pH water and the fact that minerals rich in REEs are commonly found in alkaline and granitic rocks.

The five spa wells sampled during this research included three wells in confined aquifers. The spa reputations for two of these wells were associated with their warm waters: Louisa Bridge at Leixlip in Co Kildare and Lady's well at Mallow in Co Cork, where temperatures of 15.7 and 18.1 $^{o}$C, respectively, were recorded in this study. The Louisa Bridge well had the most mineralised water (EC = 1865 µS $cm^{-1}$), including high Na and Cl levels, followed by the Drumod Sulphur well

at Swanlinbar in Co Cavan (EC = 1288 µS $cm^{-1}$), with high $SO_4$. Mg and $SO_4$ concentrations in samples from all five of the spa wells were above the median value for the holy wells dataset. Elevated magnesium and sulphur values are common in spa groundwaters (Section 8.1.1). Strontium concentrations in four of the five spa wells were above the median and mean values for the holy wells, in line with generally longer residence times for the spa groundwaters. Lithium concentrations exceeded the mean holy well values in all five of the spa wells (albeit only slightly in the case of Lady's well), whilst the spa well with the most mineralised water, Louisa Bridge, gave the highest concentrations of several trace elements including Fe, Mn, Pb, Sb, As, Be, Cs, Cr, Co and Li.

The chapter ended with a short comparison between the chemical analysis results from this research with those from earlier studies of holy wells and spa wells in Ireland. In making these comparisons, it was recognised that variations in sampling and analytical techniques between the different studies would have a bearing on the results. Nevertheless, the current major ion results were found to be broadly similar to those reported 40 years ago by Aldwell and Burdon (1980) for Bride's well at Calgath, the Louisa Bridge spa well, and St Brigid's well at Shangarry in Co Limerick. This latter well, which is probably sourced from a pure limestone confined aquifer, was also monitored in the 1980s by Brück *et al*. (1986), along with Lady's well in Mallow, and their findings were also in line with the present sampling results.

This chapter has focused on the general hydrochemistry of holy well and spa well waters, including the relationships of ionic and trace element distributions to lithology and hydrogeological setting. The implications of the chemistry results for human health are considered in the next chapter.

# 8 Holy wells, health and heritage

The chapter begins with further discussion of the reputed cures associated with holy wells and the links between water chemistry and health, building on the earlier discussions in Chapters 2 and 6, respectively. The results of the well surveys (Chapter 5) and the chemical analyses (Chapter 7) are then considered in relation to their possible health implications. The chapter moves on to describe Irish holy wells more generally in terms of therapeutic landscapes, before concluding with some remarks about the importance of holy wells as part of our geological as well as our cultural heritage, and as a community resource.

## 8.1 Holy wells, spa wells and health

### 8.1.1 Reputed cures

Holy wells have long had reputations for curing medical ailments (Section 2.2). Some wells are associated with specific cures, whereas others have reputations for multiple cures or for general cures that are unspecified. The studies by Bord and Bord (1985) across Britain and Ireland revealed 75 different illnesses for which cures at holy wells were associated. The most common were eye problems, infertility, child ailments such as whooping cough and rickets, warts, scrofula, leprosy, skin complaints, mental problems, rheumatism, and toothache. The other ailments listed by the authors were: 'tumours, deafness, lameness, jaundice, fever, headache, stomach problems, ague, epilepsy, ruptures, gout, erysipelas, sprains and swellings, consumption, asthma, scurvy, broken bones, dropsy, paralysis, ulcers, sores and abscesses, gravel, hydrophobia, debility, fits, melancholia, cancer, dyspepsia and indigestion, measles, freckles, wounds, piles, coughs, alcoholism, female complaints, bowel complaints, shortness of breath, colic, lumbago, diarrhoea, nausea, dumbness, gangrene inflammation, glandular problems, numbness, itch, polypus, pox, dysentery, spasms, weak back and sinews, wens, and bladder stone.' Some of these ailments are rather vague, and others partly duplicate one another, but they form an impressive list nonetheless.

Bord and Bord (1985) went on to say that many people nowadays continue to find cures at holy wells. Although unclear as to what brings about the cure, Bord and Bord discussed two possibilities:

1. The water does contain something which acts upon the body; or
2. The patient's own intrinsic healing abilities are stimulated by visiting the well.

Whilst the latter would be assisted by the faith gained from the various religious beliefs and practices associated with holy wells, the former raises the question, in Bord and Bord's view: if the water in a holy well does have beneficial physical properties, then how would our ancestors have discovered which diseases a well would cure? Was this simply by trial and error or, as Bord and Bord seem to suggest, using herbalism as an analogy, were our predecessors closer to nature and more sensitive to the life force of plants and water?

In their study of more than 500 well sites in Ireland Brenneman and Brenneman (1995) argued that well location is important for the power of the well, including its healing properties. They suggested, for example, that the power was 'hard and cutting' in rocky or mountainous locations and wells in such places were often linked to cures for aching limbs or teeth. In contrast, wells near the sea, where fresh water and salt water may combine, were associated with fecundity, and women often sought cures for barrenness at such locations.

The most common cure associated with holy wells is for sore eyes. For example, Oestigaard (2013) reports that there are 600 wells in England with reputations for treating eye problems. Binnal (1945) offered four explanations for the prevalence of 'eye wells':

1. That bathing sore eyes in water would be good for the eyes, but, in the absence of scientific understanding, this efficacy would have been attributed by people to supernatural powers.
2. That since holy wells were associated with baptism, then through this process, pilgrims experienced 'the light of faith'.
3. That eye wells were linked to the cult of Odin and sun worship. According to myth, Odin was forced to leave his eye 'in pledge before he could drink of Mimir's well'.
4. That holy wells were in some way representative of the eye of God. This belief, whose origins go back to the time of the Pharaohs, may have been present among Celtic (Iron

> Age) peoples, as indicated by the use of the word *llygad* or eye for the source of a river in Welsh.

Binnal favoured the last explanation, suggesting that the name eye well may have been a result of its 'supposed properties and the connection between the life-giving eye of the god and its counterpart, the health-giving well'.

Varner (2009), on the other hand, speculated that the reputation for healing eye ailments might be due to the pilgrims having insufficient Vitamin A in their diet, leading to the dry eye condition xerophthalmia.

Most recently, Ray (2020c) has highlighted that eye cures were the most common healing properties associated with holy wells in Ireland, giving rise to many wells with names like *tobar na sul*. She notes that 'sore eyes are commonly dry eyes and have been treated with collyrium (mostly sodium chloride) since ancient times; major pharmaceutical companies such as Bausch and Lomb offer collyrium today as an eye wash'. Eye irritations would have been common in the past, with people often living in poorly ventilated hovels filled with smoke from turf fires, and therefore bathing eyes in clean well water would have helped relieve the irritation. Brenneman and Brenneman (1995) have confirmed that many pilgrims bathe their eyes at holy wells. Many eye wells were included among the wells surveyed as part of this research, and the possible links between these wells and eye cures are explored further in Section 8.2.

After eye cures, probably the next most common group of cures are for various ailments associated with aches and pains to joints, including rheumatism, arthritis and unspecified foot ailments. Exposure to cold water may alleviate rheumatic symptoms, especially if the sufferer immerses himself or herself in the water, as in a spa well. There are a number of holy wells in Ireland which have (or had) pools down gradient that were fed from the spring well. Whilst these may have been used for baptismal purposes, they may also have been places where people could bathe sore limbs. Examples include St Bartholomew's well at Kinsalebeg in Co Waterford, a well with a reputation for treating sore eyes (Broderick, 2016), but which may have been used for other purposes; St Kieran's well at Seir Kieran in Co Offaly, where there are steps and railings to help people down into the rectangular well, which thus has the appearance of an

immersion pool[31] ; and St John's well at Johnswell in Co Kilkenny, where there is a baptismal basin (now dry) below the well (Figure 8.1). Interestingly, this researcher met a couple of members of the Traveller community at St John's well who mentioned that the well has a reputation for curing sore backs, as well as warts. (Given that the basin was dry, the 'performance of health' [Foley, 2011] – see Section 2.2.3 - undertaken by these two pilgrims was to splash well water down their backs).



a)



b)



c)



d)

Figure 8.1 Three wells with pools or basins: a) St Bartholomew's well Kinsalebeg (Co Waterford), with its whitewashed well house and basin downstream, with steps on the left; b) St Kieran's well Seir Kieran (Co Offaly), with steps and railings down into the well; c) St John's well at Johnswell (Co Kilkenny), with the baptismal basin on the left and the well building on the right; d) another view of St John's well, looking from the (dry) basin back towards the well building. Photos by Bruce Misstear

[31] http://irelandsholywells.blogspot.com/2012/10/saint-kierans-holy-well-seir-keiran.html (accessed 11/5/2020)

Another notable cure associated with some Irish holy wells is for mental illness. Wells with reputations for treating mental health problems include Tobar na nGealt in Gleann na nGealt in Co Kerry (Section 5.4.1.3) and the two St Dympna's wells in Co Meath (at Kildalkey) and Co Monaghan (at Caldavnet). The reputed link between water chemistry and mental health at Tobar na nGealt will be discussed further in Section 8.2.3. St Dympna is the patron saint of the mentally ill and, for St Dympna's well at Kildalkey, the reputed cures also include headaches. Both of these ailments are mentioned in connection with Father Moore's well in Co Kildare (Section 5.7.1.2; Logan 1980; Foley, 2010). More generally, holy wells as therapeutic landscapes may give rise to benefits in terms of mental health and general wellbeing (Section 8.3.1).

Apart from treatments for humans, cures for sick animals (or protections against animals becoming sick) are mentioned in the literature for several holy wells (e.g. Logan, 1980), including three of the wells surveyed during this research: St Senan's well Mollugha Co Clare (treatment for the parasite bots in horses), holy well at Shrone in Co Kerry (treatment of sick cattle; Section 5.4.1.2) and St Patrick's well Tullaghan in Co Leitrim (treatment for murrain, red water and spine disease in cattle).

Whilst the water at holy wells may be perceived to possess healing properties, these are not necessarily constant throughout the year. The healing properties are often considered most efficacious around the time of the pattern day (Ray, 2020c). In the case of a sacred well in South Korea, the Seokjeong Full Moon well in Seoul (Figure 2.3), it was believed that this well gave 'clear water' for half a month and 'unclear water' for the remainder of the month. This well is not close to a shoreline, where some tidal cause for a periodicity in water quality might at least be postulated (albeit with difficulty), and this author can offer no hydrogeological explanation for the reported cyclical behaviour in its water properties.

In any review of potential treatments associated with either drinking or bathing in waters, it is important to recognise the spiritual dimension. In Section 2.2, it was noted that scholars such as Foley (2010) have stressed that faith in the healing properties of the water and its religious significance are key facets of the water cure. Whilst Varner (2009) discussed the constituents of water that have health-related attributes, he prefaced his discussion by commenting that relief at holy wells mainly arises from 'a combination of a psychic/spiritual connection with the power of place'.

Foley (2010) has also written about the associations between holy wells and spas: holy wells could be regarded as an early type of spa, and the development of spa culture was partly associated with a decline in the importance of holy wells. Spas that developed at sites of holy wells include Malvern in Shropshire (St Ann's well) and Mallow (Lady's well) in Co Cork. As reported in Section 2.3, spa culture is still very popular across the world today, with 34,000 thermal/mineral springs operating in 127 countries (2017 figures, reported by the Global Wellness Institute in October 2018). It is also worth noting that spa treatments are considered in some countries (in continental Europe especially) as *bona fide* supplements to conventional modern medical treatments (Cocherri *et al*., 2008).

Loveless *et al*. (2016) have summarised the reputations of different types of mineral and thermal springs for treating ailments (Table 8.1). The springs used in spa treatments are often highly mineralised, and cures may involve either drinking or bathing in the water. Drinking water enriched in magnesium sulphate, for example, may produce a laxative effect which some people may regard as a beneficial treatment for certain digestive disorders, whilst bathing in warm, mineralised water can bring relief to rheumatic aches and also treat skin diseases (sulphur-rich waters have antibacterial and anti-fungal properties; Hamidizadeh *et al*., 2017).

Table 8.1 Health benefits associated with different types of mineral and thermal springs (from Loveless *et al*., 2016)

| Spring type | Apparently active solutes | Ailments for which the spring has perceived benefits |
|---|---|---|
| Saline | Sodium, chloride | Gout and rheumatism |
| Radioactive | Uranium, radium, radon | Rheumatism and arthritis, heart, cancer |
| Alkaline | Bicarbonate | Rheumatism, skin diseases and digestive disorders |
| Sulphur | Sulphide | Eczema, skin diseases, respiratory, gastritis, heartburn, bladder and kidneys, rheumatism, gout, nerves |
| Soda springs | Carbon dioxide | Indigestion |
| Chalybeate | Iron | Infertility, anaemia, hangovers, obesity and general debility |
| Magnesium | Magnesium | Eczema, skin diseases, respiratory, gastritis, heartburn, bladder and kidneys, tubercular diseases |

The inclusion in the above table of springs with radioactive constituents is perhaps surprising, but not unique. Varner (2009) has written about radon gas in spa waters and sacred wells, and gave St Madron's well in Cornwall as an example of a holy well where the presence of radon causes pilgrims to become drowsy.

Not all spa waters are highly mineralised. As noted in Section 2.3, the hydropathic centres established in Scotland in the 19th century to provide clean water (and air) to clients travelling from more polluted, industrialised areas, relied on 'normal' potable groundwater sources (Spence and Robins, 2004). Of the former spa centres in Ireland that were visited in this research, the water at Lady's well in Mallow is renowned for its thermal properties but its groundwater chemistry is fairly typical of other limestone aquifers (Section 7.8). Again, the various former spa wells in Lisdoonvarna were known for particular chemical constituents (sulphur, iron, magnesium), but are not highly mineralised overall.

### 8.1.2 Nutritional benefits of drinking water

Section 6.2 provided a scientific overview of the links between the constituents in water and human health. The constituents were grouped into three categories (although it was pointed out that it was not always certain as to which category every element fell into):

1) Elements or ions in groundwater that are essential or probably essential for human health e.g. Ca, Mg, $HCO_3$, Li, Si, etc.
2) Elements or ions in groundwater that are essential or probably essential for health, but which may be toxic or undesirable if present at high concentrations, e.g. F, Zn, Cu, Se, etc.
3) Elements or ions in groundwater harmful to health, e.g. As, Ba, Cd, Pb, etc.

In broad terms, elements or ions in the first two categories are regarded as bioessential, whereas those in the third group are harmful, with little or no evidence that they are necessary for physiological development.

Although the focus of water chemistry studies of drinking water has generally been on the potential harmful effects of certain parameters when present in excess (i.e. on parameters falling within the second and third categories above), authors such as Hopps and Feder (1986),

Kozisek (2014) and Hoque and Butler (2016) have pointed out that the potential health benefits arising from certain substances have received much less attention in the literature. In this respect, the WHO, EU and other water quality standards (see Section 6.2) focus on the negative aspects of water quality and health; there are no international water quality guidelines based on the *positive* benefits of macro and micro nutrients.

The chemical constituents of water may play a positive role in human health in two ways: firstly, by supplying macro or micro elements that are essential for health i.e. that have a 'nutritional' role; and secondly, by supplying elements that may inhibit the absorption or harmful effects of toxic elements i.e. that have an 'anti-toxic' effect (Hopps and Feder, 1986). Examples of the latter effect include high Zn giving some benefit against the uptake of Pb, whilst Se reduces the toxic effects of Cd.

Hopps and Feder (1986) also reported that the main health benefits arising from macro and micro elements in drinking water relate to cardio-vascular mortality (CVM), notably the inverse relationship between water hardness and CVM. Based on studies of Ca and Mg in drinking water in two regions of the US, they concluded that it was Mg (at concentrations above 20 mg $l^{-1}$) that had the strongest influence on decreased CVM. Hoque and Butler (2016), on the other hand, report that a Ca:Mg mass ratio above 2 is good for cardio-vascular health, implying that the relative amount of Ca is more important than Mg. Aside from their contribution to cardiovascular health, Ca and Mg have other health benefits e.g. Ca in bone health; and Mg in birth weight (Mg deficiency has been correlated with low birth weight; Takaya *et al*., 2006).

Whilst most of the daily intake of nutrients is from food, the nutrients for which the largest proportions are obtained from drinking water are Ca and Mg. WHO (2005) indicate that up to 20% of the daily intake may come from the drinking water, although the study by Hoque and Butler (2016) described below concluded that the percentage may be higher in certain environments. Wojtaszek and Pienak (2014) have reported that food diets in Poland supply only 40-80% of the required calcium, and hence that this deficit (and a deficiency in Mg) can be made up by drinking mineral water. WHO also note that water may provide an important contribution of nutrients such as Fe, Zn, Cu and Se, especially where there are poor diets.

Kozisek (2014) has suggested that the minimum desirable levels of Ca and Mg in drinking water are 20-30 mg $l^{-1}$ and 10 $mg^{-1}$, respectively, whilst the optimum levels are in the ranges 40-80 mg

$l^{-1}$ and 20-30 mg $l^{-1}$, respectively. He also noted that because Ca and Mg are 'metabolic antagonists' (i.e. one can interfere with the other in their biological uptake), their relative levels are important in addition to their absolute concentrations. For the optimum absorption of both elements, Kozisek (2014) suggests that the ratio of Ca:Mg in drinking water should be between 2 and 3 (although he does not indicate the units on which the ratios are based). Razowska-Jaworek (2014) indicates that the optimum Ca:Mg ratio for human health is 2:1, and expresses this as a molar ratio.

The FAO and WHO (2001) and WHO (2005) have provided information on recommended daily intakes (RDIs) for macro and micro nutrients, which is summarised in Table 8.2. The RDI for an individual depends on a large variety of factors, including body weight, age, development stage, gender, pregnancy, diet and bioavailability (the latter is especially relevant for Fe and Zn). Therefore, Table 8.2 includes ranges of values from the literature, together with an adopted, conservative value used for the calculations that follow in Section 8.2.4.

Table 8.2 Recommended daily intakes (RDI) for selected macro and micro nutrients (based on FAO and WHO, 2001; WHO, 2005)

| Nutrient | Recommended daily intake (mg) | | | |
|---|---|---|---|---|
| | Infants, children & adolescents[1] | Adult males | Adult females | Value used in this research |
| Ca | 300-1300 | 1000-1300 | 1000-1300 | 1000 |
| Mg | 26-250 | 230-400 | 190-310 | 300 |
| Fe | 0.3-65 | 9-27 | 8-59 | 25 |
| Zn | 0.8-19.2 | 4.2-14 | 3-20 | 10 |
| Cu | 0.2-0.75 | 0.9-1.35 | 0.9-1.4 | 1 |
| Se | 0.006-0.034 | 0.034 | 0.026-0.042 | 0.03 |

Note [1] The infants, children and adolescents category covers babies, children and adolescents up to the age of 18. The Adult categories are men and women from 19 and older.

Iron is a bioessential element, but its low bioavailability in diets means that about 40% of the world's women are estimated to be anaemic (WHO, 2005). The main effects of Zn deficiency are impaired growth, skin problems and lower resistance to infections (FAO and WHO, 2001). Copper deficiency can lead to osteoporosis and other bone abnormalities, and anaemia (WHO, 2005). Health problems associated with Se deficiency include anaemia and impeded growth (Edmunds and Smedley, 1996). As noted in Section 6.2, Reimann and Birke (2010) observed that

'In large parts of the world, Se deficiency is probably a greater threat to the health of the general population than Se toxicity'.

Hoque and Butler (2016), in a study of medical hydrogeology in the deltas of south and east Asia, reviewed the recommended daily intake (RDI) of certain macro and micro parameters that may be available from groundwater supplies. They used data on RDIs from the 2001 FAO and WHO report. Assuming a daily water consumption of 2 litres per person, from the same well, and that the elements in the drinking water can be easily taken up by the body, they calculated that up to 50% of the RDI of Ca, Mg and Fe are available from the groundwater sources in some deltaic areas. The well water therefore can make an important contribution to nutrition, especially given the poor food diets experienced by many people in such regions (e.g. where cereal-based diets are dominant). For Mn, up to 20% of the wells can provide all of the RDI in certain aquifers, but the authors noted that Mn could have negative health impacts at high concentrations (see Section 6.2).

### 8.1.3 Potential negative aspects of drinking water from holy wells

It must be recognised that consuming water from holy wells – as from any other types of well – could potentially have some negative effects, although few studies have been carried out on the quality of water from sacred wells or springs. One important study referred to briefly in Section 2.2.2 was by Kirschner *et al*. (2012) in Austria. They collected 50 samples from 21 holy springs (and 53 samples of holy water from fonts in 16 churches and 2 hospital chapels). Perhaps unsurprisingly, a high percentage of the spring samples had faecal indicator bacteria, including 76% with coliforms, 38% with *E. coli* and 32% with enterococci. The chemical analyses included physico-chemical parameters such as pH and total organic carbon (TOC), plus major ions, but did not include trace elements. These analyses also showed strong evidence of anthropogenic contamination, with 9 out of 41 samples exceeding the 50 mg $l^{-1}$ drinking water standard for nitrate, and high TOC values being correlated with high bacteriological heterotrophic plate counts. Only 14% of the holy springs met the drinking water regulations in terms of nitrate and/or microbiological water quality. Kirschner *et al*. (2012) recommended that it is necessary to raise public awareness that holy springs can be a source of illness. Interestingly, during their sample collection programme they observed parents telling their children about the good quality of the holy spring water.

Concerns have also been raised about the water quality in one of the most famous sacred wells, the Zamzam well in Mecca in Saudi Arabia (indeed, this is reported to be the only well in Islam where the water is sanctified; Ghabin, 2020). This well is located close to the Ka'ba and pilgrims drink water from the well during their pilgrimage and also collect bottles for bringing back to their home country. It is believed the water is divinely blessed, and that it has medicinal qualities. The well is 30 m deep and is constructed in wadi alluvium and diorite bedrock. The main groundwater inflow occurs in the weathered zone at the base of the alluvium and top of fractured bedrock. (The present writer has observed that the weathered zone at the base of wadi alluvium is commonly the main aquifer horizon in similar hydrogeological environments in neighbouring Oman).

The hydrochemistry of the Zamzam well has been studied by Shomar (2012). This publication followed a 2011 BBC report 'Contaminated Zam Zam holy water from Mecca sold in UK'[32]. Shomar's study showed alkaline groundwater (pH = 8) with elevated levels of some parameters including arsenic (mean concentration of 30 samples = 27 µg $l^{-1}$) and nitrate (mean = 120 mg $l^{-1}$). Shomar argues that the alkaline water with elevated values of As (as well as other parameters such as Li – mean = 15 µg $l^{-1}$) may have some health benefits. As noted in Sections 6.2.2 and 8.1.2), alkalinity (normally present in groundwater as bicarbonate) is considered to be bioessential. Regarding the elevated Li, the reader is referred to the discussion in Section 8.2.3 below concerning Tobar na nGealt in Co Kerry and the potential Li dosage from trace levels in groundwater. Regarding the elevated arsenic, Shomar refers to a number of papers that discuss arsenic in terms of cancer treatment, including Antman (2001). Whilst some publications do include arsenic as one of the elements essential for biological functions in humans (e.g. Koller and Saleh, 2018), the WHO reports that there is no evidence to indicate that arsenic is bioessential to humans, and indeed states that 'every effort should be made to keep concentrations as low as reasonably possible'. Moreover, Shomar puts no arguments forward for any health benefits arising from the high nitrate concentrations. (As an aside, Shomar reports that the Zamzam well was pump tested at a discharge of 8000 l $s^{-1}$ for a drawdown of 10.16 m which, if correct, would imply a specific capacity of 68,000 $m^3$ $d^{-1}$ $m^{-1}$ – an extraordinarily high value).

It is also worth adding a few words of caution here concerning bottled waters. These are increasingly popular across the globe, and in Europe alone the average bottled water

[32] https://www.bbc.com/news/uk-england-london-13267205; accessed 4/12/2019

consumption is more than 50,000 $m^3$ per annum, equivalent to about 60 litres per person (Loveless *et al*., 2016). Nevertheless, in their exhaustive survey of the geochemistry of European bottled waters, Reimann and Birke (2010) speculate as to whether drinking some bottled waters *may* be harmful to health. For example, consumers who require a low-sodium diet may be consuming sodium-rich bottled water. Again, some bottled waters have high fluoride or even significant levels of uranium, and Reimann and Birke ask 'is there a cause for concern?'

### 8.1.4 Water chemistry and homeopathy

The review of groundwater chemistry in relation to health in Chapter 6 drew on authoritative science-based sources including the World Health Organization, the US EPA and various peer-reviewed articles in scientific and medical journals. The discussion of the nutritional benefits that can be gained from potable water was also based on these scientific publications. In contrast, the sources of information for cures associated with holy wells and spas (in Section 8.1.1) included perspectives from folklore, religious studies, history and anthropology.

There is also an extensive body of literature surrounding 'alternative medicine', including homeopathic remedies linked to particular elements. Homeopathy can be defined as 'a method of treating disease by the use of small amounts of a drug that, in healthy persons, produces symptoms similar to those of the disease being treated' (Collins, 2003). With homeopathic treatments a substance such as a chemical or plant is diluted in water (or sometimes alcohol) and is 'potentised' by shaking or banging the container against a surface. Homeopaths believe that the potentised dilution retains a 'memory' of the original substance that contributes to healing.

One of the most exhaustive treatises on the supposed homeopathic attributes of the different elements was written by the Dutch homeopath Jan Scholten (2010). In this tome, each of the seven rows in the periodic table is assigned characteristics associated with different developmental levels and themes, and is given the name of 'its most characteristic element'. For example, the first series (Hydrogen) represents the foetus coming into existence (where the theme is 'being'), the fourth series (Ferrum) represents the young adult focused on the theme of work and duty, and the sixth series (Gold) represents 'ripe age', with leadership as its main theme. The 18 vertical columns of the periodic table represent different stages of progress, beginning with a rise, reaching a peak, and followed by a decline and loss.

According to Scholten's thesis, the homeopathic properties of each of the elements in the periodic table can be described according to the concepts associated with the seven series (rows) and 18 stages (columns). By joining the end of one series (row) to the start of another, he extends the format of the periodic table into a spiral, with the stages (columns) forming spokes leading out from the origin to the outermost spiral, which is the Uranium series representing old age. For followers of homeopathy, the book represents a 'Materia Medica of the periodic system' (to quote from its Foreword). There are many individual case histories presented in the book – these describe many aspects of the individual's life and environment, including their emotional and physical wellbeing, analysing this information in the context of the concepts developed in the book. The case histories conclude with an account of the person's reaction to the homeopathic remedy, which often seems to be a reduction or complete removal of the negative symptoms.

It will be clear from the definition of homeopathy given earlier that even toxic substances such as arsenic may be employed in homeopathic treatments, albeit in very low doses, and indeed Scholten (2010) does include a case study of a woman who, suffering from anxiety and depression, is treated with Arsenicum album (i.e. $As_2O_3$), and is cured completely of these symptoms. Again in relation to arsenic, Belon *et al*. (2007) conducted trials in a village of West Bengal with arsenic contaminated water supplies and reported some positive outcomes from homeopathic treatments (but see below).

A comprehensive review of the medical effectiveness of homeopathy was undertaken by the National Health and Medical Research Council in Australia (NHMRC, 2015). As part of the review, the NHMRC considered studies that compared the effects of homeopathic treatments with placebos or other treatments. In their literature review, the NHMRC excluded studies that were not controlled, and also excluded non-peer review publications such as newspaper articles or book chapters. In this regard, the book referred to above by Scholten - and other books by the same author - were excluded, as a 'level of evidence' could not be assigned. The NHMRC review concluded that 'there are no health conditions for which there is reliable evidence that homeopathy is effective'. In relation to arsenic, the study by Belon *et al*. (2007) referred to above was reviewed and was judged to be at high risk of bias.

## 8.2 The well survey and water chemistry results in relation to their potential health implications

When considering possible associations between holy wells and health, it is relevant to take account of the extent to which the water at a holy well is drunk, either as part of a ritual, or more generally, including water collected from wells and brought to people's houses, or given to emigrants on their departure as part of the Irish diaspora (Ray, 2014). In this respect, some evidence of water being consumed from holy wells was found for 59 wells, or just over a quarter of the 215 holy wells surveyed (27%) in this research study. This 'evidence' took several forms: the presence of drinking water cups or ladles, signage at the well, reports of people drinking water from the well (either now or in the past) and the researcher's own observations of people drinking at the well (Figure 8.2). Of course, the volume consumed as part of the rituals at a holy well, or from a bottle filled from the well, would often be small, especially when considered against the consumption rates generally assumed when health risks are calculated in relation to particular chemical parameters e.g. 2 litres per person per day for an extended period (WHO, 2011).

The use of holy well water for domestic purposes is often considered unlucky, a reason given in folklore for a well to move in offence at such practice (Ray, 2013), although there are reports of people resorting to a holy well when their main water supply has been impacted by pollution (Ray, 2020a). This researcher has observed people taking water away from a holy well in large containers (circa 5 litres), suggesting a significant level of consumption; moreover, at a few sites there is a separate side well which is used for domestic purposes (Figure 8.2d). In addition to potable water, holy wells may also be used for washing or bathing an affected part of the body with the water (such as for treating eye ailments and possibly various rheumatic and other joint pains), as discussed in Section 8.1.1.



a)



b)



c)



d)




e)




f)

Figure 8.2 Evidence of water consumption at holy wells: a) Tubrid Millstreet, Co Cork, where a line of cups is visible on a rail beside this spring; b) cups on top of the stone lintel covering St Ciaran's well at Kilcar, Co Donegal; c) ladle on a post beside St Kieran's well at Seir Kieran, Co Kilkenny; d) St Flannan's well Drumanure, Co Clare, where the side well on the right is used for domestic purposes; e) County Council sign about drinking water, inside Tobercornan in Co Clare; f) Co Co sign at St Cuan's well in Mothel, Co Wexford, advising consumers to boil the water before using it for domestic purposes. Photos by Bruce Misstear

### 8.2.1 Number of surveyed wells with reputed cures

In the current research some information was found for reputed cures being associated with 123 of the 215 surveyed holy wells, i.e. 57% of the total, and 96 of the 167 wells that were sampled (also 57%). The main cures and associated numbers of wells are listed in Table 8.3 and illustrated by the bar graph in Figure 8.3. It must be stressed that this table and figure are based on a variety of sources, ranging from peer-reviewed publications to web sources, to oral accounts told to the researcher when visiting a well. Of course, there may be cases of other wells where local knowledge of a reputed cure was not revealed by the author's researches. Therefore, the numbers of reputed cures are probably underestimates. It should also be noted that more than one a cure is sometimes associated with a well (hence the number of wells surveyed with particular reputed cures listed in the Table 8.3 is 185, i.e. more than the total of 123 wells with reported associated cures). It should also be stressed that in every case we are referring to *reputed* cures.

Table 8.3 Reputed cures associated with the 215 surveyed and 167 sampled holy wells

| Reputed cure | Wells surveyed | Wells sampled |
|---|---|---|
| Eyes, blindness | 58 | 47 |
| General or unspecified cure | 31 | 15 |
| Rheumatism, arthritis, general aches and pains, neuralgia | 23 | 19 |
| Toothache | 17 | 10 |
| Headaches | 14 | 9 |
| Lameness, foot ailments | 13 | 8 |
| Warts | 11 | 9 |
| Earache, deafness | 5 | 5 |
| Mental health | 5 | 4 |
| Colds, sore throats | 4 | 4 |
| Cancer | 4 | 3 |

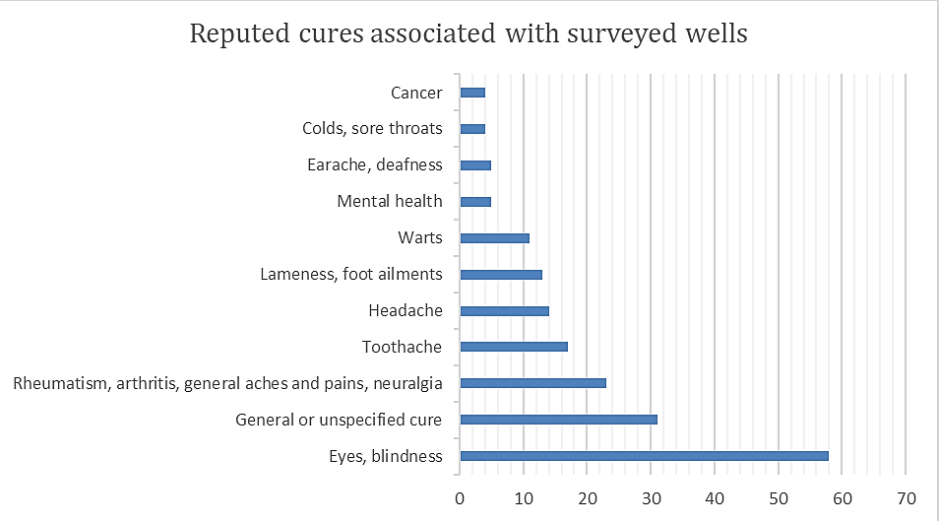



Figure 8.3 Reputed cures associated with the surveyed holy wells

In addition to those reputed cures listed in Table 8.3 and illustrated in Figure 8.3, cures for the following other ailments are associated with at least one of the surveyed wells: ringworm, skin complaints, plague, fertility problems, influenza, jaundice, bad veins, ulcers, stomach sickness, vomiting, kidney complaints, thrush, rickets, lungs, sore lips, speech impediments, leprosy, whooping cough and scurvy - the latter in connection with sailors drinking water from St Begnet's well on Dalkey Island (Section 5.10.4).

It can be seen in the Table 8.3 and Figure 8.3 that the most common cure is for eye ailments, reported at 27% (58) of the wells. This finding is very much in agreement with previous studies suggesting that eye cures are the most common (e.g. Varner, 2009; Oestigaard, 2013; Ray, 2020). As noted in Section 8.1.1, it seems reasonable to assume that people living in poorly ventilated homes in the past, and who cooked using turf or wood fires, would often have suffered from eye complaints, so it is not surprising that bathing eyes in well water would have yielded some benefit. Figure 8.4 is a photo of a statue at a holy well in Co Roscommon which has a reputation for eye cures; the statue is adorned with pairs of spectacles.



Figure 8.4 Pairs of spectacles placed on an engraving of the passion of Christ at St Ronan's well Taughmaconnell (Co Roscommon); this well has a reputation for curing eye ailments. Photo by Bruce Misstear

For 14% (31) of the wells, the cures associated with the well are general or unspecified. At 23 wells (11%) there are reputedly treatments for various rheumatic, arthritic aches and pains, including sprains and backache. Whatever the effects of drinking water from a well, bathing an aching joint in well water may be perceived to have some efficacy (see Figure 8.1). The same might apply to toothache, a cure reported at 17 (8%) of the wells.

### 8.2.2 Statistical analysis of results in relation to specific reputed cures

The first statistical test carried out was to see if there were differences between wells with reputations for any or several cures (n = 96) and the remainder of the wells sampled (n = 71). As the data were generally not normally distributed, the non-parametric Mann-Whitney U test was applied (see Section 7.4). There were no significant differences found for the median values for pH, EC and eight of the nine major ions. The exception was Na, where the test was significant, i.e. the null hypothesis that the median values were the same was rejected ($W = 8742$, $p < 0.05$). The likely reason for this is the large number of wells with reputations for eye cures, as discussed below. When the distribution of wells with reputations for cures is examined by lithological grouping, it can be seen that these wells occur in all seven of the groups, generally in similar proportion to the total wells sampled in each group (Figure 8.5). The Mann-Whitney U test was also applied to the minor ion and trace element results for those wells associated with cures (n

= 92 i.e. four fewer wells than for the major ions since fewer well samples were subjected to trace element analyses; Section 7.6) and the other wells (n = 64). Cr was the only parameter where the median value was significantly different between the two groups of wells (W = 5906, P < 0.05), although the probability of the medians being significantly different was close to the threshold for Li (W = 7748, p = 0.058).

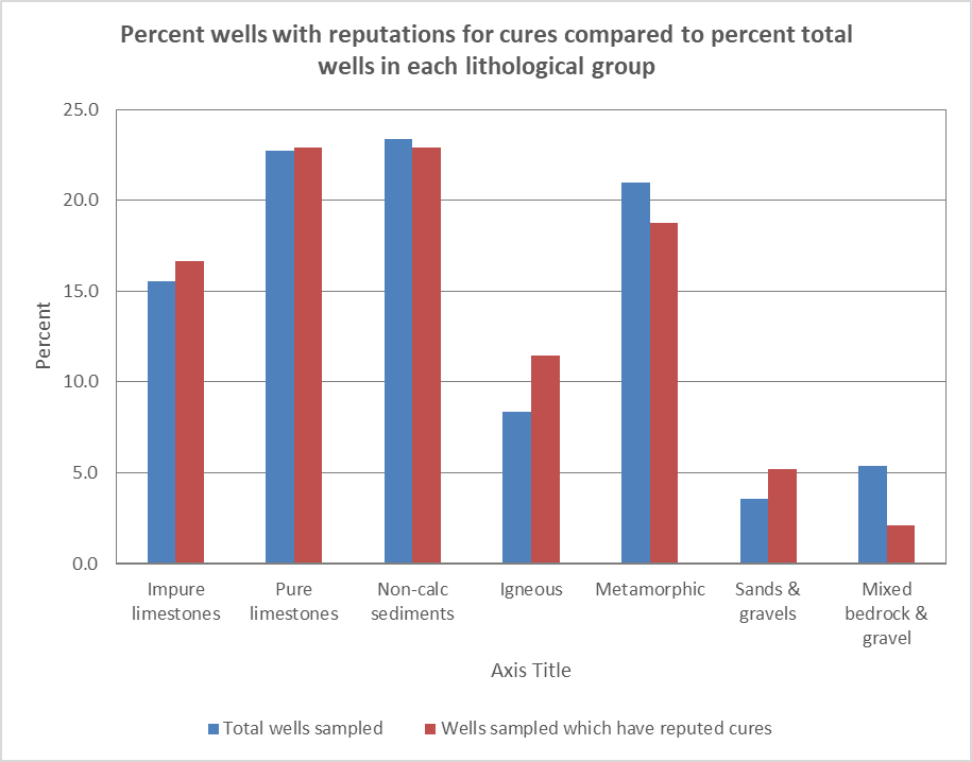



Figure 8.5 Comparison of percent wells sampled which have reputations for cures (n = 96) with percent total wells sampled (n = 167) in each lithological group

As indicated in Table 8.3, 47 wells with reputations for treating eye ailments were amongst the wells sampled. Mann-Whitney U tests were carried out to compare pH, EC and major ion concentrations between the eye wells and the remaining wells. For Na and Cl, the tests showed that the median values were significantly different between these two groups (W = 4896, p < 0.01 for Na, and W = 4835, p < 0.01 for Cl). The tests for the other parameters did not reject the null hypothesis of the medians being the same, although the p values for EC (p = 0.055) and $SO_4$ (p = 0.061) were close to the 0.05 threshold.

The finding of significant differences in Na and Cl between eye wells and others is interesting, in view of the fact that bathing eyes in sodium chloride would be regarded as a common treatment for eye irritations, as noted by Ray (2020c) in Section 8.1.1 above.

Figure 8.6 shows the percent eye wells sampled in different lithologies compared to the percent total wells sampled. It can be seen that eye wells occur, and were sampled, in all the groups, albeit only one well was sampled in each of the sand and gravel and mixed bedrock and gravel groups. Perhaps of most relevance is that of the 47 eye wells sampled, 15 (32%) were wells within 500 m of the coast, whereas of the remaining 120 wells, only 16 (13%) were coastal. This is consistent with the elevated Na and Cl median values found in the eye wells (14.3 mg $l^{-1}$ Na in eye wells compared to 10.3 mg $l^{-1}$ in other wells; 27.0 mg $l^{-1}$ Cl in eye wells compared to 20.8 mg $l^{-1}$ in other wells). The eye wells close to the coast include St Kee's well at Foohagh (Co Clare), St Colmcille's well at Glencolmcille (Co Donegal), St Augustine's well in Galway city, St Finian's well in Kenmare (Co Kerry), St Colman's well at Salterstown (Co Louth), St Deirbhle's well in Belmullet (Co Mayo) and St Declan's well in Ardmore (Co Waterford).

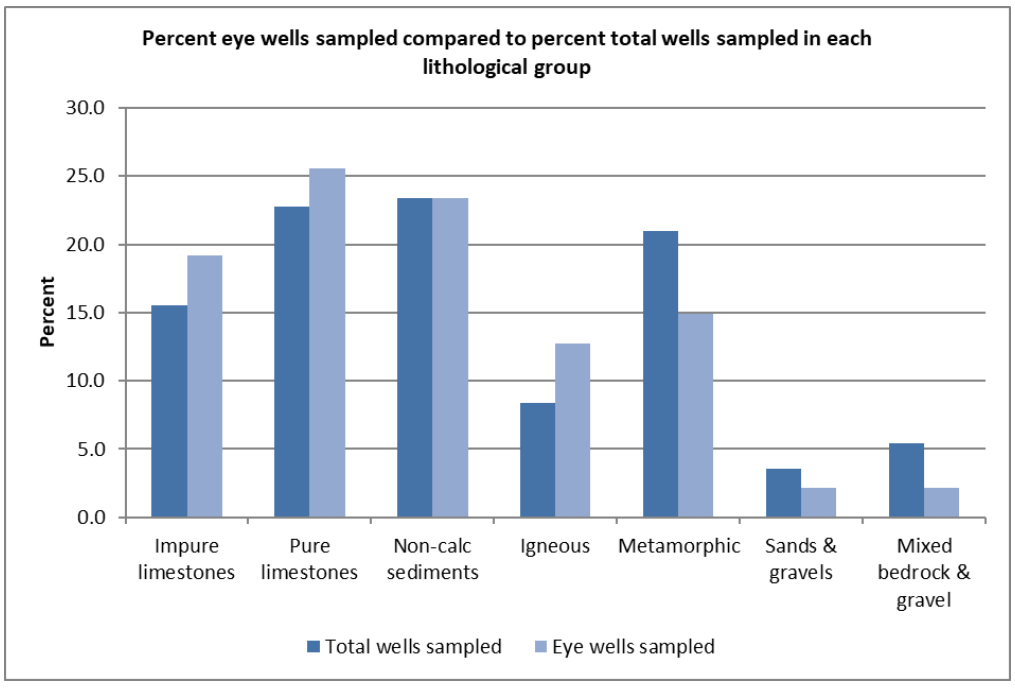



Figure 8.6 Comparison of percent eye wells sampled (n = 47) with percent total wells sampled (n = 167) by lithological group

Mann-Whitney U tests were also performed on minor ions and trace elements to compare values in eye wells with the other wells (note that analyses for these parameters were carried out for a maximum of 156 wells, not the full 167 wells as in the major ion analyses; see Section 7.6). The only elements to show a significant difference in median values between eye wells and other wells were V ($W = 3119.5$, $p < 0.01$), Cr ($W = 3327.5$, $p < 0.01$), Se ($W = 2101$, $p < 0.01$) and Ba ($W = 2798$, $p < 0.01$). V, Cr and Se were also found to be significantly different in their median

values between the coastal and non-coastal wells (see Section 7.6.4), with the values in coastal environments elevated in all three cases. No significant difference was found in Ba median values between coastal and non-coastal environments.

A total of 19 wells were sampled with reputations for treating aches and pains, including rheumatism and arthritis. Note that nine of these wells (i.e. nearly half) also have reputations for treating sore eyes, so there is an overlap with the eye wells in the above analysis. Applying the Mann-Whitney U test, no significant differences were shown for the median values of pH, EC or major ions between those wells with reputations for curing aches and pains, and the remaining wells. With the minor ions and trace elements (18 wells sampled with reputations for aches and pains), the Mann-Whitney tests showed significant differences in the median values between the two groups of wells for the following three elements: Li ($W = 1979$, $p < 0.01$), Co ($W = 1783$, $P < 0.05$) and U ($W = 1811$, $P < 0.05$). In addition, four parameters "failed" the alternate to the null hypothesis (of equal medians) by small amounts, with p values between 0.06 and 0.07: Ti, Cr, As and Mo. For all seven elements, the median concentrations were higher in the wells associated with cures for aches and pains. Whilst bathing an affected joint in mineralised water is a common spa treatment (Section 8.1.1), it should be borne in mind that the concentrations of these trace elements are very low overall, and that the major ion chemistry of almost all holy wells would not be regarded as highly mineralised.

For wells with a reputation for curing toothaches (n = 10), the Mann-Whitney U tests did not show any significant difference in median values between these wells and the other wells for any parameters save Ba ($W = 1068$, $p < 0.05$). The median Ba concentration in the toothache well samples of 42.6 µg $l^{-1}$ was more than twice that for the other wells (18.1 µg $l^{-1}$). Barium is normally included amongst those elements harmful to health (see Section 6.2.4), as it is linked to high blood pressure and cardiovascular disease (WHO, 2011). The WHO guideline level for Ba in drinking water is 0.7 mg $l^{-1}$ (Table 6.2), i.e. 700 µg $l^{-1}$, which is well above the median value for the toothache wells. (Indeed, the maximum observed Ba concentration of 538 µg $l^{-1}$ was within the WHO guideline).

Four wells with reputations for curing mental illness were sampled: Father Moore's well in Co Kildare, St Dympna's wells at Caldavnet in Co Monaghan and Kildalkey in Co Meath (St Dympna is patron saint of mental illness – see Section 8.1.1) and Tobar na nGealt in Co Kerry. Mann-Whitney tests on pH, EC, major and minor ions and trace elements showed that the median

values for all parameters bar one were not significantly different: the exception was $SO_4$, where the median of the wells with reputations for curing mental health problems was significantly different to the median for the other wells ($W = 91$, $p < 0.05$). Interestingly, in the test for Li (a parameter considered beneficial for mental health – see Section 6.2.2), the median value of those wells associated with mental health cures was *lower* than that for the other wells (520 ng $l^{-1}$ compared to 956 ng $l^{-1}$). The mean values are even further apart (565 and 4144 ng $l^{-1}$, respectively), which partly reflects a very high Li value (293 µg $l^{-1}$ in the seawater St Brendan's well at Roskeen in Co Mayo). However, it must be emphasised that four wells represent a very small sample for meaningful statistical analysis, and over-interpretation of the results should be avoided. The information concerning Li at Tobar na nGealt is discussed in a separate subsection below, in view of its high profile.

Nine wells were sampled that are associated with cures for headaches: two of these also have reputations for curing mental health (Father Moore's well in Co Kildare and St Dympna's well in Co Meath); two have reputations for curing aches and pains (Father Moore's well again and St Flannan's well at Drumanure in Co Clare); three are also toothache wells (St Kieran's well at Castlekeeran in Co Meath, Planxty well in Smithborough in Co Monaghan and St Dympna's well Kildalkey in Co Meath); whilst two are also eye wells (St Colmcille's well near Glencolmcille in Co Donegal and St Moling's well at St Mullins in Co Carlow). Mann-Whitney U tests did not show any significant differences in the median values for pH, EC or major ions between the wells with reputations for treating headaches and the other wells. However, the parameter closest to the significance threshold of $p < 0.05$ was $SO_4$ ($W = 516.5$, $p = 0.09$), which is broadly consistent with the test applied to the wells with reputed cures for mental health. With the statistical tests on minor ions and trace elements, the median values for V ($W = 373$, $p < 0.05$) and As ($W = 391$, $p < 0.05$) were significantly different from the median values of the remaining wells. The median concentrations of V and As were similar to each other in the two groups of samples, at 0.1 µg $l^{-1}$ for the headache wells compared to 0.3 µg $l^{-1}$ for the remaining wells.

### 8.2.3 Tobar na nGealt and mental health

This site near Camp in Co Kerry has received a lot of media attention in recent years, justifying some further discussion here. The hydrogeological setting for Tobar na nGealt has already been described in Section 5.4.1.3. The current 'well' is in fact part of a small stream (the original spring well feeding the stream is inaccessible).

The well has a reputation for curing madness, and so an elevated value of lithium reported previously received a lot of publicity, and was highlighted in a TG4 programme in 2012. The Li value quoted in media reports is 55.6 µg $l^{-1}$. The analysis was performed by the Southern Science Laboratory in Tralee. This researcher has been unable to find any document that describes the sampling and analysis procedures. However, an email (19th June 2019) from Dr Henry Lyons, formerly of IT Tralee, who was filmed in the TG4 programme, provided the following information: a) the samples were collected before he observed the lab analyses (which were carried out using ICP spectrometry), and b) 'it was not a rigorous experiment based on standard sampling procedures ….. but the analysis was carried out using the correct lithium standards and properly calibrated instruments. The only conclusion that could be drawn was that the levels of lithium in the Gleann na nGealt water was significantly higher than in local tap water supplied by Kerry Co Council i.e. a qualitative rather a quantitative one'. So, the details of the sampling are not known, including the types of bottles, whether the samples were filtered or acidified, etc.

The well was subsequently sampled and analysed by Brendan Kelly, Professor of Psychiatry at Trinity College Dublin, as part of the research for his book '*Hearing Voices: History of Psychiatry in Ireland*' (Kelly, 2016). Again no details of the sampling or analysis procedures are given (other than that the samples were collected by Kelly in August 2015), but he found that the lithium concentration was less than 5 µg $l^{-1}$, and that this was similar to levels in Dublin tap water and in a Kerry stream (near Inch) and another holy well (Our Lady's well at Dromore near Kenmare), which were sampled at the same time. Kelly also noted that the concentration of Li at Tobar na nGealt was 'too low to have any detectable therapeutic benefits at the individual level'. He expanded on the last point by saying that even if the Li concentration was 1 mg $l^{-1}$ (i.e. more than 200 times the detected level), and even if a person drank 2 litres per day, the daily dose would be equivalent to about '13.8 mg of lithium carbonate, which is less than two percent of the usual therapeutic dose for bipolar affective disorder (approximately 900 – 1200 milligrams per day for an adult)'. It should be added that Dr Lyons made a similar point in the TG4 programme. Applying Prof Kelly's calculation to the Li value reported previously at Tobar na nGealt (55.6 µg $l^{-1}$) would give only 0.1% of the usual therapeutic dose. The mean concentration of the four samples (i.e. two sets of duplicates – see Section 7.6.2) analysed for Li during this research was only 0.6 µg $l^{-1}$, which would provide only 0.001% of the therapeutic dose for someone consuming 2 litres of the water each day.

Kelly went on to say that such chemical analyses are not the best way to investigate the therapeutic value of the well. He argues that folk cures for mental illness 'find their true value as embedded elements of local traditions and beliefs, and reflect subtle, powerful cultural interpretations of mental illness and human suffering'. Other authors including Varner (2009) and Foley (2010) have made similar observations - see Section 8.1.1 – and the issue of holy wells as therapeutic landscapes will be addressed in Section 8.3.

### 8.2.4 Potential nutritional benefits of consuming water from holy wells

The potential nutritional benefits of drinking water from wells were reviewed in Section 8.1.2. Table 8.2 summarised the recommended daily intake (RDI) values for selected macro and micro nutrients for different groups of people (adults/children, males/females). Whilst most of the required daily nutrient intake is normally provided by food, the mineral content in water can make a useful contribution, especially for people having nutrient-poor diets (Hoque and Butler, 2016). This aspect is investigated further here, with respect to the chemical analysis results from the holy wells.

In Table 8.4 below, the contribution of selected ions and elements in the well water to the RDI is calculated, using both the median and 95%ile concentrations for those parameters. The calculations assume a daily water consumption of 2 litres per person (WHO, 2011), and are based on the 'typical' RDI figures in the right-hand column of Table 8.2. It can be seen from the table that for the two main macro nutrients Ca and Mg, the calculated contributions to the RDI based on the median sample concentrations would be approximately 14% and 4%, respectively, whilst for the wells with greater enrichment in these ions (i.e. using the 95%ile values), the contributions could be 31% and 14%, respectively. For the minor ions and trace elements, the calculated contributions of the well water to the RDI are much smaller. Nevertheless, certain wells might, for example, provide useful amounts of iron in individuals or groups where anaemia is an issue.

The concentrations of Ca, Mg and the other nutrients listed in Table 8.4 would obviously vary significantly across the country, especially in relation to lithology (see Sections 7.5.4 and 7.6.3). Table 8.5 shows the median and 95%ile values for the same nutrients for the seven lithological groups, along with the RDI values. Whilst the potential daily contributions of each nutrient to

the RDI are not calculated in the table, it can be easily seen, for example, that wells in carbonate aquifers (i.e. the impure and pure limestones, plus the sands and gravels and mixed bedrock and gravel groups) would potentially make larger dietary contributions of Ca, Mg and Fe than the waters from non-calcareous sedimentary, igneous or metamorphic aquifers.

Table 8.4 Median and 95%ile ionic and trace element concentrations and potential contributions to the recommended daily intakes (see Table 8.2 for further details about RDIs)

| Ion / element | RDI (mg $d^{-1}$) | Med well conc (mg $l^{-1}$) | 95%ile well conc (mg $l^{-1}$) | Contrib to RDI from well water | | | |
|---|---|---|---|---|---|---|---|
| | | | | Med | % | 95% | % |
| Ca | 1000 | 71.0 | 154.5 | 142 | 14.2 | 309 | 30.9 |
| Mg | 300 | 6.2 | 21.4 | 12.4 | 4.1 | 42.8 | 14.3 |
| Fe | 25 | 0.25 | 0.99 | 0.5 | 2 | 1.98 | 7.9 |
| Zn | 10 | 0.003 | 0.059 | 0.006 | 0.06 | 0.12 | 1.2 |
| Cu | 1 | 0.001 | 0.013 | 0.002 | 0.2 | 0.026 | 2.6 |
| Se | 0.03 | $4x10^{-5}$ | 0.0002 | $8x10^{-5}$ | 0.27 | 0.0004 | 1.3 |

Table 8.5 Median ionic and trace element concentrations (in mg $l^{-1}$) for different lithological groups compared with recommended daily intakes (see Table 8.2 for further details about RDIs)

| Ion / element | RDI (mg $d^{-1}$) | Impure lst | Pure lst | Non-calc sed | Igneous | Met | Snd & grvl | Mixed |
|---|---|---|---|---|---|---|---|---|
| Ca | 1000 | 133.0 | 113.3 | 33.0 | 17.4 | 29.6 | 128.8 | 125.5 |
| Mg | 300 | 6.9 | 8.8 | 5.3 | 5.1 | 5.8 | 10.5 | 5.8 |
| Fe | 25 | 0.43 | 0.31 | 0.17 | 0.12 | 0.12 | 0.40 | 0.39 |
| Zn | 10 | 0.002 | 0.003 | 0.001 | 0.003 | 0.003 | 0.003 | 0.004 |
| Cu | 1 | 0.001 | 0.001 | 0.001 | 0.003 | 0.001 | 0.0005 | 0.001 |
| Se | 0.03 | $5x10^{-5}$ | $4x10^{-5}$ | $3x10^{-5}$ | $6.7x10^{-5}$ | $2x10^{-5}$ | $6x10^{-5}$ | $7x10^{-5}$ |

The daily intakes of nutrients quoted here are *recommended* values for modern diets. At times in the past, diets amongst peasants in Ireland were much poorer than today, notably during the famine of the 1840s when an over-dependency on the potato led to mass starvation after that crop was blighted. At times of poor diet, it is reasonable to assume that mineral intakes from

well water supplies could have provided a higher proportion of daily nutrients than those suggested by Table 8.4. However, in other historical periods food sources were more varied. In a study of diets amongst peasants and commoners in early medieval Ireland (based on a review of 7th and 8th century law tracts and other literary sources), Peters (2015) found that available foods included, at times, fruit, fish and wild game, in addition to the staples of dairy products and cereals. Turning to a more recent era, Greaves (2018) considered differences in diet and health in 'the poor labouring population' across the UK in the late 19th century. He concluded that people living in rural regions such as the west of Ireland enjoyed more varied and nutritious diets (involving vegetables, milk, fish, whole grains as well as potatoes) than many people living in England, where white bread was the staple food. Crawford (1985) and Miller (2015), on the other hand, have pointed out that the more varied diet in late 19th and early 20th century Ireland compared to the pre-famine era did not improve the nutritional standard.

In Section 8.1.2 various studies were also reviewed which considered the benefits of Ca and Mg in potable water in relation to cardio-vascular health. Kozisek (2014), for example, reported that the minimum desirable concentrations in drinking water are 20-30 mg $l^{-1}$ for Ca and 10 mg $l^{-1}$ for Mg. The relative abundance of these two ions is also important for their optimum absorption by the body. Razowska-Jaworek (2014) suggests that the optimum Ca:Mg ratio is 2 (as a molar ratio), whilst Kozisek (2014) suggests a value of between 2 and 3 (units not given) and Hoque and Butler (2016) indicate that a Ca:Mg mass ratio above 2 is good for cardio-vascular health. Table 8.6 gives the median sample concentrations for Ca and Mg for wells in the seven lithological groups. The Ca:Mg ratios are also included.

Table 8.6 Median Ca and Mg concentrations and Ca:Mg molar ratios for different lithological groups

| | All data | Impure lst | Pure lst | Non-calc sed | Igneous | Met | Snd & grvl | Mixed |
|---|---|---|---|---|---|---|---|---|
| Ca (med conc in mg $l^{-1}$) | 71.0 | 133.0 | 113.3 | 33.0 | 17.4 | 29.6 | 128.8 | 125.5 |
| Mg (med conc in mg $l^{-1}$) | 6.2 | 6.9 | 8.8 | 5.3 | 5.1 | 5.8 | 10.5 | 5.8 |
| Ca:Mg molar ratio | 7.2 | 11.1 | 7.6 | 4.1 | 2.9 | 3.1 | 7.0 | 13.1 |

The highest median concentrations of Ca and Mg, and the highest Ca:Mg ratios are found in the groundwaters from the carbonate lithologies (including the sand and gravel and the mixed bedrock and gravel). However, the Ca:Mg ratios closest to 2 or the 2-3 optimal range mentioned

in the literature above, are found in the softer waters associated with the non-calcareous sedimentary, igneous and metamorphic lithologies.

A caveat must be included in relation to the discussion of nutritional benefits from water. As noted in the introduction to Section 8.2, water is not consumed at all holy wells, and where the well water is drunk, this often involves only small amounts taken as part of a ritual. Therefore, the calculations above are most applicable to situations where the main household water supply is from a well, and they only become relevant in the (probably rare) cases where holy wells are used as a regular source of drinking water.

### 8.2.5 Water chemistry results in relation to WHO and EU drinking water guidelines

The water chemistry results in relation to WHO and EU guidelines for drinking water are summarised in Table 8.7. The two columns on the right-hand side of the table show the number of wells sampled for a particular chemical parameter and the number of exceedances of the WHO and/or EU guideline value. Where the WHO and EU values differ, then the exceedances were counted with respect to the lower of the two guidelines (thus e.g. the EU MAC for Sb is lower than the WHO guideline value, and so was used in the comparison). Only those parameters determined during this research are included in the table. Hence, for example, ammonium, boron or nitrite are not included, although drinking water guidelines do exist (see Tables 6.2 and 6.3).

Overall, it can be seen in Table 8.7 that there are relatively few exceedances of drinking water guidelines for most parameters. The main exceptions are for Fe and, to a lesser extent, Mn, which are commonly found at relatively high concentrations in Irish groundwaters (Section 7.6). However, the WHO has not established a health-based guideline value for either Fe or Mn in drinking water, and the EU's guideline value for Fe mainly relates to the aesthetic quality of the water. High Mn in drinking water has been associated with neurological problems, but generally where it is present at concentrations above the 'acceptability' threshold of 0.1 mg $l^{-1}$ (WHO, 2011; see Section 6.2.3).

The major ions Na, $SO_4$ and Cl show a small number of exceedances, which all occur in samples from wells in coastal environments. The highest concentrations were found in a sample from St

Brendan's well Roskeen, which contained seawater and therefore was not potable (Section 7.5.5).

Table 8.7 Number of exceedances of WHO (WHO, 2011) and/or EU (European Commission, 1998) drinking water guidelines for those parameters analysed in samples from holy wells. See Table 6.2 and 6.3 for full WHO and EU guidelines

| Chemical | WHO guideline value (mg $l^{-1}$) | EU Directive 98/83/EC Drinking Water | | Holy wells results | |
|---|---|---|---|---|---|
| | | MAC (mg $l^{-1}$) | Guideline value (mg $l^{-1}$) | Nr of samples | Nr of exceedances |
| Aluminium | | | 0.2 | 147 | 5 |
| Antimony | 0.02 | 0.005 | | 155 | 0 |
| Arsenic | 0.01 (A, T) | 0.01 | | 156 | 1 |
| Barium | 0.7 | | | 156 | 0 |
| Cadmium | 0.003 | 0.005 | | 155 | 0 |
| Chloride | | | 250 | 167 | 3 |
| Chromium | 0.05 (P) | 0.05 | | 133 | 1 |
| Copper | 2 | 2 | | 156 | 0 |
| Fluoride | 1.5 | 1.5 | | 151 | 0 |
| Iron | | | 0.2 | 156 | 92 |
| Lead | 0.01 (A, T) | 0.01 | | 130 | 0 |
| Manganese | | | 0.05 | 150 | 17 |
| Nickel | 0.07 | 0.02 | | 156 | 0 |
| Nitrate | 50 | 50 | | 167 | 3 |
| Selenium | 0.04 (P) | 0.01 | | 100 | 0 |
| Sodium | | | 200 | 167 | 2 |
| Sulphate | | | 250 | 167 | 1 |
| Uranium | 0.03 (P) | | | 156 | 0 |

Notes: A, provisional guideline value because calculated guideline value is below the achievable quantification level; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

There are three wells where the WHO and EU nitrate level of 50 mg $l^{-1}$ (as $NO_3$ – this is equivalent to 11.3 mg $l^{-1}$ as N) was exceeded. As discussed in Section 7.2, samples for nitrate were often analysed in an external laboratory as well as in the TCD Environmental lab, with generally good agreement in the results (Section 7.3). In addition to the three exceedances, there were three other values that were close to the 50 mg $l^{-1}$ threshold; in fact, one of the two analyses of each

of these samples gave concentrations slightly above the threshold. In terms of health implications, nitrate is of value mainly as an *indicator* of anthropogenic pollution, although high concentrations can also be a direct health concern especially in relation to the condition in babies known as methaemoglobinaemia (Section 6.2.3).

In relation to trace elements:

a) The single exceedances of As and Cr were in samples from the non-potable seawater sample from St Brendan's well at Roskeen (Co Mayo).
b) There were five exceedances of the EU guideline value of 0.2 mg $l^{-1}$ (200 µg $l^{-1}$) for Al. Three of these were in samples from wells in metamorphic rock lithologies, with one each from igneous and non-calcareous sedimentary aquifers. The solubility of Al is strongly pH-dependent, and so Al concentrations tend to be lower in more buffered, carbonate-rich groundwaters. Although some studies have linked Al in drinking water with increased risks of Alzheimer's disease, the WHO (2011) highlights that there are difficulties taking account of confounding factors in such studies, and advises that Al occurs in drinking water below those of health concern (Section 6.2.4).

It is important to conclude this brief discussion by emphasising that only chemical aspects of water quality are considered here. In terms of human health risks, the most important factor is often the microbiological quality of the drinking water. For reasons explained in Section 7.1.2, it was outside the scope of this research to test the holy wells for their microbial water quality. However, a recent incident of microbial contamination of a holy well does highlight this concern. In January 2020, coliform bacteria were found in St Patrick's well near Clonmel in Co Tipperary[33]. The well water was analysed after two people were reported to have become ill after drinking water from the well. This is a karst limestone spring, where the groundwater vulnerability is classed as Extreme.

Although bacteriological analyses of water samples from holy wells are rare, studies of private well supplies in Ireland and elsewhere have found appreciable evidence of bacteriological contamination, especially where wells are located close to pollution sources such as farmyards and septic tank systems, and where the well headworks are poorly finished (Hynds *et al*., 2012;

[33] https://www.tipperarycoco.ie/news/press-release-relation-st-patrick%E2%80%99s-well-clonmel (accessed 19/5/2020)

Hynds *et al*., 2013; Misstear *et al*., 2017). It is therefore likely that many holy wells will be susceptible to microbial contamination, as they are generally shallow springs in areas with Extreme or High groundwater vulnerability, and where the widespread presence of nitrate above background levels indicate some anthropogenic influences on water quality.

## 8.3 The holy well as landscape, heritage and community resource

### 8.3.1 The Irish holy well as a therapeutic landscape

Apart from their reputations for yielding specific cures, wells have been associated with a more generic healing power. Health geographers in particular have identified holy wells as classic examples of what they term therapeutic landscapes, defined by Gesler (2003) as 'places that have achieved lasting reputations for providing physical, mental and spiritual healing', and are discussed as such in a number of recent Irish publications (Foley; 2010, 2011, 2015). The traditional healing reputation of the well was initially associated with the water itself, which was drunk in-situ or taken away for consumption elsewhere, or used for bathing aching limbs (Section 8.1.1). Equally, the places themselves were part of the cure.

Many wells are located in quiet rural landscape settings, often with calm natural surroundings within woods or by lakes or rivers. This idea of a calming place effect was also a reason why they were identified as therapeutic landscapes. Seen like this, mental health was also a significant part of their healing reputations for stress reduction, attention-restoration and socialisation, all recognised in contemporary healthy psychology as key ways in which nature works to promote human health and wellbeing. A classic example is Tobar na nGealt, or the 'well of the insane', in Co. Kerry, a holy well setting long associated with the treatment of mental illness (see Sections 5.4.1.3 and 8.2.3).

The combination of water, tree and stone is an important part of the holy well site. The topographical setting is also key to the therapeutic landscape and sense of wellbeing. Holy wells may be located in beautiful valleys, on mountainsides with spectacular views, in woodlands, by a lake, on along cliff paths or on the seashore. Two wells from Clonmel in Co Tipperary will serve as examples (Figure 8.7).



a) b)

Figure 8.7 Wells as therapeutic landscapes: a) St Patrick's well and b) Toberaheena, both in Clonmel, Co Tipperary. Photos by Bruce Misstear

The beautiful valley floor site of St Patrick's well in Clonmel is shown in Figure 8.7a. Here, the springs from the karstified limestone aquifer form a large pool, decorated with a medieval stone cross at its centre (see report in Appendix B). There are the ruins of a medieval church in the background. The spring well feeds the channel that enters the pond on the right of the picture. The performances of health include doing the rounds and drinking the well water (washing in the spring water has also been carried out, at least in the past). The water has a reputation for curing eyes, sore lips and other ailments, including a treatment for headaches[34]. The landscaping of the current site has been much changed since the 1950s.

An attendant at St Patrick's well mentioned to this researcher that it was traditional for locals to visit the well on all days of the week except Fridays, when they would visit the nearby Toberaheena (Friday's well) instead (Figure 8.7b). Toberaheena is beside a small stream fed by a spring (from an impure limestone aquifer), within a garden area which was being renovated (in 2017) as quiet space for people bereaved by suicide (the charitable group undertaking the renovations was C-SAW: South Tipperary Community Suicide Awareness). This project is therefore a good example of adopting a holy well site as a therapeutic landscape.

It should be mentioned here that the spiritual and psychological benefits of a therapeutic landscape might not match the actual chemical or microbiological attributes of the water itself.

[34] https://pilgrimagemedievalireland.com/2014/04/12/st-patricks-holy-well-at-marlfield-clonmel/ (accessed 20/5/2020)

As noted earlier (Section 8.2.5), coliform bacteria were recently discovered in St Patrick's well at Clonmel.

### 8.3.2 Heritage aspects

Although not all scholars accept that holy wells may date from early Christian or even pre-Christian times (Section 2.2.3), it is noteworthy that many well sites are located close to prehistoric monuments and burial sites and/or to early medieval churches and graveyards.

The Well of the White Cow on the east side of the Hill of Tara (Section 5.2.1.1) is within 200 m of standing stones, raths and passage tombs at this ancient site, whilst St Cuan's well at Mothel in Co Waterford is located close to a dolmen. Other wells are located inside old enclosures or raths: the holy well at 'the City' in Shrone in Co Kerry (Section 5.4.1.2) is beside the outer wall of a *cathair*, or ring fort, which is likely to have prehistoric origins (Kerry Co Co, 2015); and St Brigid's well at Shangarry in Co Limerick is within a rath (Ó Danachair, 1955) which, according to the signage at the well, may date from the 5$^{th}$ century CE.

Many of the wells surveyed in this research are located within or close to historic churches and graveyards. The approximate threshold of 100 m was used here to define 'close to' but, obviously, a well located further than this distance may still be linked to the church or graveyard. For example, St Ciaran's well at Clonmacnoise is approximately 700 m metres from the historic buildings and graveyards, but is likely associated with this site. Bearing in mind the limitations of this analysis it is interesting and possibly noteworthy that 67 of the 215 surveyed wells – 31% - are located within or close to graveyards or the grounds of old churches. Four examples of wells actually within church graveyards are shown in Figure 8.8.

Wells in or near the grounds of major religious buildings include: St Feidhlimidh's well in the grounds of the cathedral at Kilmore Upper in Co Cavan; and St Patrick's well Ballintubber, close to the grounds of the 13$^{th}$ century abbey, which is at the start of the pilgrimage trail that ends on the summit of Croagh Patrick (see Nugent [2020] for a recent account of this Tóchar Phádraig). Other wells that form part of a pilgrimage trail or *turas* include St Fachtna's well at Termon Co Clare (Section 5.3.1.1); St Ciaran's well Kilcar, Co Donegal; and St Colmcille's well Glencolmcille, also Co Donegal (Section 5.6.4).



a)



b)



c)



d)

Figure 8.8 Holy wells within graveyards: a) St MacCullin's well Grallagh, Co Fingal (Dublin); b) St Joseph's well Kilafarboy, Co Clare; c) St Colman's well Achill, Co Mayo; d) St Sedna's well Newtown, Co Tipperary. Photos by Bruce Misstear

Some holy wells are close to historic buildings not necessarily associated with religion: the Well of the Holy Cross at Gleninagh in Co Clare was once the water supply for the nearby 16th century tower house; St Catherine's well Killybegs is close to the 14th century St Kitt's castle (albeit there is a ruined church nearby also); St Patrick's well is within the grounds of Trinity College Dublin (a former monastic site); and St Brigid's well Morett in Co Laois is near the ruins of an old castle.

An ongoing heritage project led by Dr Fiona Beglane of Sligo IT is a good example of investigating the origins of an historical site – in this case the Disert site in Co Donegal (Section 5.4.3.1) - through archaeological and geophysical surveys, whilst engaging the local community in this work via the Disert Heritage Group (Beglane, 2018; Beglane *et al*., 2018). Archaeological findings

so far indicate that the site (which includes St Colmcille's holy well, a graveyard, a stone altar and a stone arch) dates back at least 1500 years, whilst folklore associations suggest a longer history (Beglane *et al*., 2016). A field archaeology course was planned for the summer of 2020 (before the Covid-19 outbreak)[35].

### 8.3.3 Holy wells as a community resource

Holy wells are important assets for local communities, both in terms of cultural heritage and local place memory (Foley, 2010; Misstear *et al*., 2018). Some wells, like St Brigid's well at Liscannor in Co Clare, are popular with tourists (Figure 8.9a). Yet, while many local enthusiasts, from a range of different perspectives, both spiritual and secular, do important work in maintaining sites and organising community events like walks and patterns, they are still neglected in significant ways. This is in part to do with their locations and ownership, but also how they are viewed in the 21st century. Many are on private land and largely inaccessible. Whilst holy wells included in the list of National Monuments should benefit from statutory protection, many of these 3000 wells have long since disappeared or been filled in or ploughed over.

But many other holy wells still represent important sites for community activity around the pattern day; places like Ardmore have a week-long festival dedicated to St Declan (Figure 8.9b), and Lady's Island in Co Wexford has seen gatherings of as many as 20,000 pilgrims on the pattern day in August, while St. Mullins in Co Carlow has a pattern that links the holy well to a large community event in the nearby graveyard; indeed St Moling's well is an example of a holy well with a long history of pilgrimage: it was visited by several thousands of pilgrims in the plague year 1348 (Clyn, 2007). At some holy well sites, chapels or altars have been provided for religious devotions e.g. at Ogulla well at Tulsk in Co Roscommon (Figure 8.9c). Sometimes large gatherings at a holy well have had a political as well as religious focus: about 10,000 people attended the pattern celebrations at St Kieran's well in Castlekeeran, Co Meath, in 1917 to listen to a speech by the prominent Republican Countess Markievicz (a stone plaque commemorating this event was erected near the entrance to the site in 2016; Figure 8.9d). Yet their traditional Catholic associations and a wider disregard as sites of superstition and ignorance have seen holy wells recede from view in many areas.

[35] https://ifrglobal.org/program/ireland-disert/ (accessed 4/6/2020)



a)




b)



c)




d)

Figure 8.9 Holy wells as popular destinations: a) some of the many objects left by tourists and pilgrims at St Brigid's well near Liscannor, Co Clare; b) a sign advertising the Ardmore pattern festival in July 2017; c) the hexagonal chapel at Ogulla well Tulsk in Co Roscommon; d) a plaque at St Kieran's well at Castlekeeran in Co Meath commemorating a large assembly to hear a speech by Countess Markiewicz in 1917. Photos by Bruce Misstear

Of the 215 holy wells surveyed in this research, some form of votive (rags, coins or a multitude of other items) was observed at 124 wells (58%), which gives some indication of their current usage. Moreover, at a number of wells there was evidence that votives are cleared away periodically e.g. at St Brigid's well in Tully Co Kildare most of the rags and other votive offerings - which this researcher had been observing for several years on the trees around the well - were removed prior to the St Brigid's day celebrations on 1st February 2017 (but new votives have been added subsequently). These examples should not be considered representative of the situation regarding the 3000 holy wells country wide, since the researcher was more likely to visit and record wells that are cared for and therefore accessible.

Apart from enhancing our understanding of the hydrogeology of holy wells, it is hoped that the documentation from the present research will help increase awareness amongst communities about groundwater issues more generally. Being out of sight and therefore out of mind, there is a low level of awareness about groundwater, both in Ireland and internationally. Indeed, many international water policy documents largely ignore groundwater, even though it provides drinking water to about half of the world's population, and sustains the flow of rivers through dry periods (UN Water, 2015). Engaging with communities about how their well or spring functions should help promote a wider awareness of issues such as the need to protect groundwater resources from pollution. (During sampling of a holy well at Templetown in the Cooley peninsula [Co Louth] in January 2018, this researcher was most impressed by the level of engagement and insightful questions asked by a group of primary school children who were visiting the well at the same time).

In this respect, the documentation from the present research will provide an additional resource to previous surveys of holy wells, including the Schools' Folklore Scheme from the 1930s (Irish Folklore Commission, 1937-38), and the website launched in 2017 by Dr Celeste Ray where members of the public can upload details about holy wells[36].

This researcher plans to pass on details of holy wells of particular hydrogeological interest to the Geological Survey of Ireland, so that they may be considered for inclusion in the national Geoheritage programme[37]. Hydrogeology is one of the 16 themes within this programme, and sites of hydrogeological interest – chosen mainly for their water chemistry – can be included in county audits and subsequently adopted in county development plans, with policies to protect them. At present, there are relatively few holy wells designated as County Geological Sites. In Co Meath, for example, two holy wells are included as County Geological Sites (Clarke *et al*., 2007) - St Gorman's spring (Section 5.9.3) and St Kieran's well at Castlekeeran (Section 5.3.3.2) - whereas there are no holy wells classified as County Geological Sites in Co Waterford (Parkes *et al*., 2012): St Declan's Stone in Ardmore is included, but not St Declan's well nearby (Section 5.4.1.1). Concerning spa wells, the Louisa Bridge warm spring in Co Kildare and the Drumod spa well in Swanlinbar in Co Cavan are designated as County Geological Sites (Parkes and Sheehan-Clarke, 2005; Parkes *et al*., 2013b), whilst the spa wells at Lisdoonvarna are not (Parkes *et al*., 2005). According to Parkes *et al*. (2012), 'County Geological Sites do not receive statutory

[36] https://ihwcbc.omeka.net/ (accessed 20/5/2020)
[37] https://www.gsi.ie/en-ie/programmes-and-projects/geoheritage/Pages/default.aspx (accessed 29/5/2020)

protection like Natural Heritage Areas (NHA) but receive an effective protection from their inclusion in the planning system'. Where sites are considered to be of national importance they can be formally proposed by the Geological Survey of Ireland for designation as NHAs by the National Parks and Wildlife Service 'after due survey and consultation with landowners'.

Yet documentation will only act as one part of a wider aim to preserve and encourage people to visit, use and conserve holy wells. The 2018 example of the reduction of a large holy well site at Warrenstown (Co Meath)[38] and ongoing issues with the safety of water drunk from wells, via pollution prevention, remain problematic. There are also local groups, such as the Wicklow Wells (Toibreacha Chill Mhantáin) who do important work in restoring holy wells[39]. Nevertheless, there is a need for a national organisation with a brief to manage holy wells, including protecting their water quality as well as physical infrastructure.

## 8.4 Concluding remarks

Of the 215 wells surveyed in this research, about 57% (n = 123) were associated with some healing reputation. A similar proportion of the wells sampled (96 out of 167, or 57%) also had reputations for cures. The most common of the named cures was for eye problems (27% of wells), followed by rheumatic and other joint ailments (11%), toothaches (8%) and headaches (7%). These figures were derived from a variety of written and verbal accounts, and so should be treated with caution.

The wells with reputations for cures are located in all seven of the main lithological groups, in similar proportion to the total number of wells sampled in that lithological group. Non-parametric Mann-Whitney U tests did not show significant differences between median concentrations for the majority of chemical parameters between wells with reputations for specific cures and other wells. Notably, however, sodium and chloride were found to differ significantly between eye wells and other wells, with the median concentrations of both ions being higher in the samples from the eye wells. This result is interesting because bathing sore eyes in a mildly saline solution is a recognised modern medical treatment (Ray, 2020c).

[38] https://www.independent.ie/irish-news/news/unbelievable-anger-over-drastic-changes-to-irish-pilgrimage-site-that-some-believe-has-cured-cancer-36917855.html (accessed 20/5/2020)
[39] https://www.facebook.com/Wicklow-Wells-Toibreacha-Chill-Mhant%C3%A1in-785652024788685/ (accessed 29/5/2020)

According to the well survey results, eye wells are more common close to the coast than the other wells, where rainfall and therefore recharge waters would be enriched in Na and Cl.

It was shown that obtaining a drinking water supply from a holy well could provide useful contributions to the recommended daily intakes of nutrients such as Ca (31%), Mg (14%) and Fe (8%), where the local groundwater was enriched in these ions (95%ile values from the sampling results were used in these calculations), and assuming people drank about 2 litres per day. However, it was also pointed out that holy wells are not usually used as a source of domestic water, and that the amount drunk as part of a ritual performed at a holy well would normally be very small, and much less than the normal daily water consumption of 2 litres.

In addition to the possible health benefits from consuming well water, some potential negative aspects were also considered. In the sampling results, there were relatively few exceedances of WHO and EU water guidelines. The main exceptions were for Fe and Mn (where 59% and 11% of sampled wells exceeded the EU guideline values, respectively), but these were at levels unlikely to be of health concern. Of most concern to health were the large number of nitrate values above background levels (i.e. 52% of wells with $NO_3 > 2$ mg $l^{-1}$ as N, as reported in Chapter 7). Even though only a few samples actually exceeded the drinking water guidelines, the presence of nitrate is an indicator of anthropogenic pollution and hence the possibility that the well may be susceptible to pollution from bacteria and other microbes.

The chapter ended with a brief discussion of the research into holy wells in the context of therapeutic landscapes, heritage and community involvement. Holy wells remain important today as a community resource and as part of our wider national heritage. The pattern day festivals may still attract large gatherings, many are close to or within sites of historical and archaeological significance, and the combination of the spiritual dimension with the attributes of their physical setting contribute to their ongoing role as therapeutic landscapes. Yet, many have disappeared over the years, and others are under threat from modern developments in farming and urbanisation. There is a need for some national agency to have responsibility for working with local communities to preserve these assets.

# 9 Conclusions and recommendations

## 9.1 Summary and conclusions

A comprehensive study of the hydrogeology of Irish holy wells has not been attempted previously. Moreover, this writer is not aware of any similar studies internationally.

In Chapter 1, the main research questions were identified as:

1. Are Irish holy wells more common in some physiographical, geological or hydrogeological settings than in others?
2. Are there aspects of the water chemistry of Irish holy wells that differ from the water chemistry of other wells in similar hydrogeological surroundings?
3. Are there any linkages between the water chemical characteristics of Irish holy wells and their reputed health benefits?

These research questions led to the following research objectives:

a) Investigate the hydrogeological settings of holy wells in Ireland using a combination of GIS applications and field surveys.
b) Sample and analyse the major ion and trace element water chemistry of holy wells in a variety of hydrogeological locations.
c) Compare water chemical characteristics of holy wells with chemistry data from other wells in Ireland, to see if there are any special characteristics in the water quality of holy wells.
d) Examine the relationship between the water chemistry of holy wells and the perceived benefits in terms of health and wellbeing.

In relation to objectives b) and c), it was expected that the research would provide valuable information on the hydrochemistry of shallow aquifer systems in Ireland, especially spring waters. However, as explained in Chapter 1, this was not a hydrochemistry research project *per se*, but rather a hydrogeological study of Irish holy wells, including their water chemical characteristics. A small number of spa wells were also studied.

In addition to these specific research questions and objectives, the research also considered some of the heritage issues surrounding holy wells.

The main conclusions regarding the research questions and objectives are presented in the following paragraphs.

### 9.1.1 Distribution of holy wells

An indicated in Chapter 2, several publications mention the number of holy wells in the Republic of Ireland as about 3000 (Logan, 1980; Foley, 2010; Ray; 2014). This figure is based on mapping carried out by the Ordnance Survey of Ireland in the 19$^{th}$ century. Basic details of wells including well name and townland are included in a National Monuments Service database, although grid references were not available for 320 of the wells. Moreover, many of the wells no longer exist, having been covered over or lost through various developments, and some holy wells that do exist are not included in the NMS database.

The first main research task was to carry out an analysis of the wells in the NMS database using ArcGIS (with ArcMap 10.3.2). The 2676 wells with grid references were analysed for their distribution according to county, topography (elevation and physiographic unit), lithology, aquifer class and groundwater vulnerability classification (Chapter 3). Not all of the wells were picked up in each analysis of the number of wells falling within a particular geological or hydrogeological category – this number varied from 48 to 107 wells, representing only 1.8% to 4% of the total. In most cases, these appeared to be wells on shorelines or other map boundaries. It should also be noted that the resolution of the digital maps and the original geological mapping would have had an influence on the accuracy of the analysis, as would the accuracy of the well locations. For example, the raster file with the elevation data had a cell size of 84 m x 84 m, whilst the bedrock geology layer in the GSI Groundwater Viewer was based on mapping at a scale of 1:100,000.

The largest number of wells was in County Cork (321), and the fewest in County Monaghan (8). When the data were normalised against area, the mean density of holy wells in the Republic of Ireland was about 9.4 holy wells per 250 km$^2$, with the frequency varying from 1.5 wells per 250 km$^2$ in Monaghan to a maximum of 25.5 wells per 250 km$^2$ in Dublin. A comparison was also made with historical population density, using data from the 1841 census, i.e. before the major depopulation caused by the Great Famine. Whilst population densities have obviously varied over the centuries, it was interesting to observe, for example, that whereas the highest well and

population densities were both found in Co Dublin, the lowest well frequency was in Co Monaghan which actually had a relatively high population density (at least in the mid 19th century). This suggests that other factors, including geology, have an important bearing on the distribution of holy wells.

In terms of topographical setting, an earlier author Ó Giolláin (2005) remarked that 'Other than those near the Medieval parish church, most wells are either on a height or by the seashore. Many are on the tops of hills or mountains'. However, the current GIS analysis suggested a more uniform topographical distribution, with 90% of wells lying between sea level and 150 m OD, and only 13 wells (0.5%) having elevations above 400 m (albeit, in relation to first part of Ó Giolláin's remark, many medieval parish churches probably lie in the elevation bands between 0 and 150 m containing the largest numbers of wells). The GIS analysis showed 19 wells having elevations below Ordnance Datum: all of these are shoreline wells. In addition, many of the 958 wells in the 0 - 50 m OD elevation range are at or close to shorelines. From a hydrogeological perspective, the location of wells close to the seashore, and often close to the high water level mark or in the intertidal zone, is unsurprising, since groundwater, being less dense than sea water, often discharges to the sea in such areas and hence is easily accessible as a spring. The significance of proximity to the coast in terms of water chemistry will be discussed in the next section.

The results of the GIS-based analysis showed that Irish holy wells occur in all the main lithological groupings and in all the main aquifer classes in Ireland. The six main lithological groups are impure limestones; pure limestones; non-calcareous sediments; igneous bedrock; metamorphic bedrock; and sands and gravels. When normalised according to area, in this case number of wells per 250 $km^2$, it was shown that the frequency of holy wells was somewhat higher in the pure limestone group (which might be expected, as these form some of Ireland's most productive aquifers), but also in the igneous rocks (which often have poor aquifer characteristics). Whilst the highest densities occur in the regionally important (Rf and Rkc) and locally important (Lk) bedrock aquifers, and in the regionally important sands and gravels (Rg), the majority of wells (1782, or 68% of the total) are located in the poorly productive aquifers (Ll, Pl and Pu categories) that underlie about 72% of the country.

This finding that Irish holy wells are almost as numerous in poorly productive aquifers as they are in regionally important aquifers may at first seem surprising. However, as explained in

Chapter 3, groundwater flow paths tend to be shorter in the more poorly productive bedrock aquifers, and hence springs (as locations of groundwater discharge) might be expected to be more numerous. In this respect, Mather (2016) reported that holy wells in England and Wales are more numerous in the less productive aquifers found in the west and southwest (especially Cornwall and Wales) compared with the higher yielding aquifers in the east and southeast. Mather attributed this pattern to water being more valued where it is scarcer (i.e. in the west and southwest), and hence more likely to be venerated, rather than to a higher frequency of springs in such areas. Additional non-geological explanations for this distribution might include the stronger legacy of Iron Age populations in the west and southwest of Britain, and possibly better survival rates of holy wells in these regions where there is less intensive agricultural development and less urbanisation than in the east and southeast.

Any desk study into the distribution of holy wells has several limitations, not least that local hydrogeological influences may not be detected, or that some of the wells in the database may no longer exist, or their locations may be inaccurate. Therefore, field surveys were considered an essential part of the research. A total of 215 holy wells and five spa wells were visited, their site details recorded on a proforma, and a summary report prepared on each well (Chapter 4). Each summary report described the well location, including grid references, the details of the well, including dimensions, and the superficial and bedrock geology at the site. Maps of geology, aquifer class and groundwater vulnerability were included, using the Geological Survey of Ireland's online Groundwater Data Viewer. The well reports also included the field measurements of physico-chemical parameters, and indicated whether a water sample was collected for full laboratory analysis (see Section 9.1.2 below). Examples of well survey reports are included in Appendix B.

In Chapter 4, the results of the field surveys were subjected to similar investigations using GIS as had been carried out for the full holy wells database in Chapter 3. The surveyed holy wells fell into all the main physiographical, lithological and aquifer categories identified in the earlier analysis for the full holy wells dataset. The distribution of the 215 surveyed wells was broadly representative of the full 2676 well dataset. At a confidence level of 95%, the calculated margin of error for the survey sample of 215 wells of the estimated total well population was approximately 6% (Section 4.1.1).

One new lithological and aquifer category was added to the GIS analysis of the surveyed wells based on the field surveys. This is a mixed bedrock and gravel category, where the groundwater source for the holy well is believed to be derived from a combined bedrock and sand and gravel source (Section 4.2.5). Thirteen wells were so categorised, but this is likely an underestimate because there are probably many more wells where there is a contribution to groundwater flow from the superficial deposits that overlie shallow bedrock and/or transition zone groundwater sources.

One clear trend in the distribution of holy wells in Ireland relates to groundwater vulnerability: the wells are more common in areas where the groundwater vulnerability is classed as Extreme or High, compared to Moderate or Low vulnerability areas: 77.5% of the surveyed wells, and 74.3% of the total wells, fall into areas classed as having Extreme or High vulnerability, compared to 5.1% and 9% in Low vulnerability areas, respectively. Areas with Extreme or High vulnerability are potentially at greater risk of contamination from activities such as farming and on-site wastewater disposal, and shallow wells and springs are especially susceptible.

The characteristics of individual wells were described in Chapter 5. Examples of wells within each of the seven lithological groups were given (33 wells), plus wells in confined aquifers (three wells) and coastal settings (four wells). The results of the five spa wells surveyed were also included. The most important finding from the overall field surveys in Chapter 4, and the individual well accounts in Chapter 5, is that the majority of holy wells are shallow spring wells (with a mean water depth of 0.34 m), sourced from shallow, unconfined bedrock aquifers (the transition zone is probably an important flow pathway in many cases), in areas with Extreme or High groundwater vulnerability. Outflows, where observed, were generally small (less than 0.5 l $s^{-1}$ and probably less than 0.1 l $s^{-1}$ in many cases). Exceptions include the large springs at Ogulla well in Roscommon and Tobernalt in Sligo, where flows of 10s of l $s^{-1}$ have been recorded. In contrast to the shallow spring wells, three of the four spa sites surveyed comprised boreholes that tap deep confined aquifer sources, sometimes producing more mineralised water with elevated temperatures. The exceptions were the Sulphur well and Twin wells at Lisdoonvarna, which are a hand dug well and a seepage zone, respectively.

Based on the findings of Chapters 3, 4 and 5, which relate to research objective a), the answer to the first of the posited research questions - *Are Irish holy wells more common in some*

*physiographical, geological or hydrogeological settings than in others?* - appears to be no: Irish holy wells are found in all the main landscape, geology and aquifer types examined.

### 9.1.2 Water chemistry

Following a review of relevant literature on groundwater chemistry in Chapter 6, the methods and results of the groundwater sampling programme conducted as part of this research were presented in Chapter 7. A total of 167 holy wells and five spa wells were sampled and tested for physico-chemical parameters EC, pH and temperature and the eight major ions Ca, Mg, Na, K, $HCO_3$, $SO_4$, Cl and $NO_3$. The element Si was also included with the major ions. 156 holy well samples plus the five spa well samples were also analysed for 51 minor ions and trace elements, including alkali metals, alkali earth elements, transition metals, post-transition metals and rare earth elements (REEs), although not all parameters were determined in every sample. Quality assurance measures included collecting and analysing blank samples, duplicate samples, repeat samples and calculating ion balance errors. The IBEs were in the range 0-5% for 81.4% of the 167 holy wells sampled.

The field measurements at holy well sites indicated that the majority of water samples were mildly acidic (84% samples had pH less than 7, with median pH = 6.5). There was a large range in EC values, from a minimum of 38 µS $cm^{-1}$ (an upland spring well) to a maximum of 61,150 µS $cm^{-1}$ (a seawater well), although only seven samples had EC above 1000 µS $cm^{-1}$. Water temperatures were typically between 9 and 13 $^{o}$C (70% of samples), but there was a wider range (from 3.8 to 16.3 $^{o}$C) in water temperature than would normally be encountered in groundwaters. This is because holy wells are generally shallow springs, often uncovered, and so respond to daily and seasonal air temperature variations to a greater extent than deeper groundwaters.

The major ion water chemistry was typically of a Ca-$HCO_3$ type. However, the water chemistry depends on the aquifer lithology and other factors such as proximity to the sea. Wells in non-carbonate lithologies (i.e. non-calcareous sedimentary, igneous and metamorphic groups) tended to be less mineralised and have softer water, with lower EC, Ca and $HCO_3$ concentrations. One-way analysis of variance (ANOVA) tests showed that the mean concentrations of these parameters were significantly different between the non-carbonate and carbonate lithological

groups (the latter comprising the impure and pure limestones, plus the sand and gravel and mixed bedrock and gravel groups).

Nitrate concentrations were above the natural background levels (NBLs) in 52% of the holy wells sampled, suggesting that anthropogenic influences are widespread. Summary statistics were therefore presented in Chapter 7 for low nitrate wells separately from the full dataset. Interestingly, there was very little association between the nitrate values and the groundwater vulnerability class: the mean $NO_3$ concentration exceeded the NBL across the five vulnerability classes (which range from X Extreme to Low – see Section 3.2 and Section 4.2.7), and an ANOVA test showed that the means were only significantly different between two of the vulnerability classes (High and Low). Whilst possibly surprising, this finding is in line with an earlier study of private wells in Ireland that showed similar or higher levels of bacteriological contamination in wells in Low vulnerability areas compared to areas with Extreme or High vulnerability (Hynds *et al*., 2012; 2013). Where wells are shallow, and do not have good protective headworks, they can be susceptible to pollution from nearby sources, including from surface runoff.

The distribution of several trace elements was also shown to be influenced by the aquifer lithology. For example, higher concentrations of Fe, Sr, Co and Mo were detected in the impure and pure limestones (and in the sand and gravel and mixed group) compared to the non-carbonate lithologies, whereas elevated concentrations of some other elements such as Cr, Li, As and Rb were found in the igneous group. The elevated Cr in the igneous wells is somewhat surprising, as the NBL study found lower levels of Cr in the igneous lithology (Tedd *et al*., 2017), and Cr mineral concentrations in granites are low (MacDonald *et al*., 2017). In contrast, elevated Rb in igneous rocks might be expected since Rb substitutes for K in mica and feldspar minerals and may be enriched in granites (Reimann and Birke, 2010). Although Li values were higher in the igneous group, concentrations in all lithologies were generally low, and lower than those reported in a study of Li concentrations in Co Carlow groundwaters, where the bedrock is mainly granite (Kavanagh *et al*., 2017).

Arsenic concentrations were also low (median = 0.3 µg $l^{-1}$), with the highest values again in the igneous lithological group. McGrory *et al*. (2017), in a national study of As in Irish groundwaters, concluded that elevated As was most likely to occur in Lower Palaeozoic metasediments, rhyolite volcanics and impure limestones. In this regard, one of the highest As values recorded in a holy well (albeit only 2.0 µg $l^{-1}$) was in a sample from a rhyolite volcanic aquifer in Co

Waterford (part of the igneous lithological group). Five (out of 156 samples) contained uranium above the NBL for the relevant lithology, of which four were taken from wells in the igneous group. The maximum U concentration (11.15 µg $l^{-1}$), however, was recorded in a sample from an impure limestone well.

Strontium levels were higher in the limestone lithologies. The solubility of Sr (which often substitutes for Ca and K in minerals such as calcite and dolomite) is seldom reached in groundwaters, making Sr a good indicator of groundwater residence times. The higher concentrations in the impure and pure limestones may therefore reflect longer flow paths in these aquifers (see Section 3.2).

ANOVA tests on trace element results for the seven lithological groups displayed a complex set of relationships. For most elements, significant differences in means were shown between one or more groups. In particular, significant differences were found between elements in one or more of the non-carbonate lithologies (non-calcareous sediments, igneous or metamorphic) with those in the impure limestone and pure limestone groups. For example, in the case of Al, Fe and Sr, their mean concentrations differed significantly between the three non-carbonate lithologies and the impure and pure limestones. For other elements such, as Be, Cs, Co, F, Mo, Tl and U, significant differences were found between two of the non-carbonate lithologies and the two limestone groups.

Comparisons of mean REE values normalised to Mud of Queensland sediment values (a proxy for weathered continental crust) showed greater relative abundances of REEs in the non-calcareous sedimentary, igneous and metamorphic lithologies compared to the limestones, sands and gravels and mixed bedrock and gravel groups. A slight depletion of light REEs relative to the heavier REEs was also observed, a trend explained in previous studies by the greater stability in solution of heavier REE-carbonate complexes (Smedley and Allen, 2004). There was a negative cerium anomaly for groundwaters in all seven lithological groups. Negative Ce anomalies have been linked with precipitation of Ce oxides in oxic groundwaters, and loss by adsorption (MacDonald *et al*., 2017).

The mobility of many elements is influenced by redox reactions and by the presence of iron and manganese oxyhydroxides. Most of the holy wells are open springs and so oxic conditions were expected. Elevated Fe and Mn concentrations were found to occur over a wide range of pH,

whilst no strong association was observed between these ions and nitrate (the presence of nitrate is an indicator of oxic conditions). Positive relationships were found between Fe and elements such as As and Co, suggesting that the mobility of these elements may be partly controlled by iron oxyhydroxide minerals. A positive relation was also indicated between As and Co concentrations, in line with results from a study by Russell *et al*. (2019), and probably reflects the presence of sulphide mineral phases enriched in Co-As.

The 31 wells in coastal settings (defined as wells within 500 m of the shoreline) had elevated concentrations of EC and several major ions – most notably Na and Cl - compared to the inland wells. ANOVA and non-parametric Mann-Whitney U tests showed that the mean and median values, respectively, of EC, Mg, Na, K, $SO_4$, Cl and Si were statistically different between samples from coastal and other wells. These results were as expected, since rainfall and hence recharge waters near the sea are enriched in these parameters. A coastal setting was also shown to have a strong influence on the minor ions and trace element distributions. Mann-Whitney U tests indicated significant differences in median values for 26 of the 51 parameters, with the concentrations being higher in the coastal setting for 25 of these, including 11 out of the 14 REEs.

As noted above, one of the objectives of this research was to see whether there were differences in the chemistry of waters in holy wells compared to other wells. The results were compared to the NBLs established by Tedd *et al*. (2017), using both the full holy wells dataset and the wells with low nitrate values. For the major ions, the percent holy well samples that exceeded the relevant NBL varied from 2% for Si and 6.6% for Mg, up to 52.1% for $NO_3$ and 54.5% for Cl. Mann-Whitney U tests confirmed that there were statistically significant differences in the median values of seven of the major ions, and pH and EC, between the two datasets. Considering only the data from the holy wells with low nitrate, there were still large numbers of exceedances for certain parameters, including Na (45%) and Cl (51.3%). When the statistical tests were repeated using only the data from the low nitrate holy wells instead of the full holy well dataset, these showed significant differences in median values for all the major ions except Ca and Mg. There were also many trace elements and minor ion values above the NBLs (albeit that NBLs have only been established for some of the 51 elements tested). The largest number of exceedances were for Fe (44% of samples), Ni (21%), Mn (17%), Mo (8%), As (5%) and Cu (4%). When the median concentrations of trace elements were compared between the full dataset and those from the low nitrate wells, it was found that more than half were

higher in the low nitrate well samples. This suggests that anthropogenic activities (or at least those associated with high nitrate) have not led to the elevated trace element values in the holy wells.

Based on these comparisons with NBLs, the initial answer to the second research question - *Are there aspects of the water chemistry of Irish holy wells that differ from the water chemistry of other wells in similar hydrogeological surroundings?* – appears to be yes, there are differences. However, the comparisons were limited by major differences in the nature of the two datasets. Firstly, the data used to establish the NBLs for the majority of parameters (including the major ions) came from monitoring records collected from a small number of (mainly) borehole sites (typically 21), after a screening process to remove boreholes liable to anthropogenic influences. In contrast, the holy wells dataset comprised one-off samples from 167 mainly shallow spring wells, many of which might be susceptible to contamination. Secondly, the monitoring boreholes used in the NBL study were generally located in productive (regionally and locally important) aquifers, whereas about 70% of the holy wells sampled were in poorly productive aquifers (in line with the national distribution of these aquifers – see Section 3.3.7 and Section 4.2.6). Therefore, it is more appropriate to conclude that this research question has not been answered fully, and that further research is required (see Section 9.2).

A limited amount of water chemistry monitoring was carried out as part of this research. Physico-chemical parameters, major ions, minor ions and trace elements were measured over a two-year period at four wells (see Chapter 5 for well descriptions). Bride's well at Calgath in Co Meath showed the least variation in pH, EC, water temperature and chemistry over the monitoring period. This was expected, because the well taps a confined aquifer (impure limestone lithology) with a relatively deep groundwater source and hence long flow path. St Brigid's well at Tully in Co Kildare also showed a fairly consistent major ion water chemistry, dominated by Ca and $HCO_3$, suggesting chemical equilibrium with the sand and gravel aquifer material. The well that exhibited the greatest seasonal variations was St Kieran's well at Castlekeeran in Co Meath. This is a spring well that issues from karstified limestone, and the water chemistry variations showed some links to rainfall. The sample with the highest mineralisation was collected during a relatively dry period during January 2017, whereas the sample with the lowest ionic concentration was taken following a wet period in April 2018. The igneous lithology well, St Moling's well in St Mullins, Co Carlow, exhibited a consistent water chemistry except for the final sample, which was more mineralised; this sample was collected

when the water level was recovering after the well had been drained. Nitrate levels were consistently low in the confined aquifer well (Bride's well), but above the NBL in the other three wells.

Concerning trace elements, generally only relatively small variations in concentration were observed throughout the monitoring period (albeit with the largest variations in those parameters present at the lowest concentrations). Bride's well, which is known as a chalybeate well, had elevated levels of Fe and, of the four monitoring wells, also gave the highest mean concentrations of several other elements including Mn, As, Sb, Li, Co, Zn and Sr. As noted above, Sr is an indicator of groundwater residence time, so it was unsurprising that this well, which taps a deep confined impure limestone aquifer, should show the highest Sr values whereas St Moling's well, which probably taps the shallow transition zone of a granite aquifer, had the lowest concentrations. St Moling's well gave the highest concentrations of REEs, consistent with the observation that this well had the lowest pH and the fact that minerals rich in REEs are commonly found in alkaline and granitic rocks. A noticeable feature of the hydrochemistry of St Kieran's well was the consistently high barium concentration compared to the other three wells throughout the monitoring period. The solubility of Ba depends mainly on its saturation with respect to barite, with high concentrations occurring when the $SO_4$ levels are low: at St Kieran's well the $SO_4$ concentrations were lower than those in two of the other wells, but slightly above that in St Moling's well.

The temporal variations observed in the four monitoring wells have implications on how the overall holy wells dataset should be interpreted. Most of the 167 wells were sampled only once, and hence the water sample provided only a snapshot of the water chemistry at that particular time. Given that the majority of holy wells tap shallow unconfined aquifers with short flow paths, and are located in areas where the groundwater vulnerability is generally Extreme or High, and where there are many potential contamination sources, it can be expected that water chemistry will vary at most of these wells. From the monitoring results collected in this research, seasonal variations in parameters such as pH, EC, nitrate, other major and minor ions and, of course, temperature are likely.

Whereas the majority of holy wells tap shallow unconfined aquifers (Bride's well being a notable exception), three of the five spa wells sampled during this research are supplied from confined aquifers. Two of these spa wells, Louisa Bridge at Leixlip in Co Kildare and, in particular, Lady's

well at Mallow in Co Cork, had spa reputations for their therapeutic warm waters. They also gave the highest water temperatures of any of the spa wells during this study (15.7 and 18.1 $^{o}$C, respectively). The groundwater at Louisa Bridge and in the Drumod Sulphur well at Swanlinbar in Co Cavan was quite mineralised, with EC values of 1865 and 1288 µS cm$^{-1}$, respectively. The major ion hydrochemistry at Louisa Bridge was enriched in Na and Cl, whilst the water sample collected from Drumod Sulphur well had high sulphate. It also contained elevated silicon, indicative of a long groundwater residence time. Mg and $SO_4$ concentrations in samples from all five of the spa wells were above the median values for the holy wells dataset. As indicated in Section 8.1.1, elevated magnesium and sulphur values are commonly found in spa groundwaters.

Strontium concentrations in four of the five spa wells were above the median and mean values for the holy wells, in line with generally longer residence times for the spa groundwaters. Barium concentrations were highest in the Lisdoonvarna wells, which was somewhat surprising as both wells have reputations for their sulphur content. However, the $SO_4$ concentrations for these wells were not particularly elevated when compared to the mean holy well values. Lithium concentrations exceeded the mean holy well value in the five spa wells (but only by a small amount in Lady's well), whilst the spa well with the most mineralised water, Louisa Bridge, gave the highest concentrations of several trace elements including Fe, Mn, Pb, Sb, As, Be, Cs, Cr and Li. The highest fluoride was encountered at Drumod spa, but this was below the drinking water limit.

It is believed that these findings satisfy the secondary objective of this research identified in Chapter 1, and restated in Section 9.1, which was to provide valuable information on the hydrochemistry of shallow aquifer systems in Ireland.

### 9.1.3 Relationship between chemical analysis results and reputed cures

The various reputations for cures associated with holy wells and spas were considered in Chapter 8. Reports of general cures or cures for specific ailments were found for 57% of the wells surveyed and sampled. The most common of the named cures was for eye problems (27% of wells surveyed), followed by rheumatic and other joint ailments (11%), toothaches (8%) and headaches (7%). However, there is a high degree of uncertainty about these figures, since they are based on a variety of sources, including 'grey literature' and verbal reports as well as more

formal documents. Therefore, extreme caution should be exercised when drawing any conclusions from this aspect of the research.

In relation to the number of wells sampled that have reputations for cures (96 out of 167), these were distributed in all the main lithological groups, in similar proportions to the proportion of wells within each group. Statistical analyses using Mann-Whitney U tests for non-parametric data did not find any links between reported cures and the water chemistry in the majority of tests. However, it was found that the major ions sodium and chloride were significantly different between eye wells and other wells, the median concentrations of both ions being higher in the samples from the eye wells. This finding is noteworthy, as bathing affected eyes in water enriched in sodium chloride is considered as a beneficial modern treatment for an eye irritation. The survey data also showed that eye wells are more common near the coast than the non-eye wells, so elevated Na and Cl values would be expected. There were also significant differences between eye wells and other wells for four trace elements (V, Cr, Se and Ba), three of which (V, Cr and Se) were also shown to be significantly different between coastal and non-coastal wells.

Mann-Whitney U tests were also performed on major ion and trace element data for wells with a number of the other reported cures, namely aches and pains; toothache; mental illness; and headaches. There were overlaps between some of the datasets e.g. nearly half the surveyed wells with reputations for treating aches and pains were also associated with eye cures. Nevertheless, in each case the Mann-Whitney U tests revealed very few statistically significant differences between the water chemistry in wells noted for a specific cure and the remaining wells. Of particular note, the median and mean lithium concentrations in those wells linked to mental health cures was found to be *lower* than the values for the other wells, although the number of samples from wells associated with mental health was very small (four). Two rounds of testing (summer and winter), with duplicates, failed to detect elevated lithium concentrations at Tobar na nGealt in Co Kerry, a well where a high Li value was reported in 2012.

The potential nutritional benefits of consuming water from holy wells was also examined. It was shown that up to 31%, 14% and 8% of the recommended daily intake of calcium, magnesium and iron, respectively, could be obtained by drinking 2 litres per day of water enriched in these ions (based on 95%ile concentration values). Whilst some evidence of people drinking water was found for about 27% of the wells surveyed, at the majority of sites the water consumption would be expected to be small, taken mainly as part of a ritual. These calculations of potential

nutrient intakes therefore are more applicable to domestic supply wells. It should be added that using a holy well for domestic purposes is often considered to bring bad luck (Ray, 2020c).

Possible negative effects of drinking water were also examined in Chapter 8. Comparisons between the water chemistry results and WHO and EU water guidelines (the guidelines are included in Chapter 6) indicated that there were relatively few exceedances. The main exceptions were for iron and manganese, but the EU guideline for Fe was primarily based on aesthetic considerations, whilst the WHO (2011) reported that Mn in groundwater is rarely at levels to cause health concerns. Of most relevance to potential health were the elevated values of nitrate in about half the wells sampled (even though only a few samples actually exceeded the drinking water guidelines). The presence of nitrate above background levels (i.e. above 2 mg $l^{-1}$ as N) is an indicator of anthropogenic pollution. Although sampling for microbial contaminants was beyond the scope of this research (see recommendation in Section 9.2 below), the presence of elevated nitrate does raise the possibility that these wells are susceptible to pollution from bacteria and other microbes.

Based on these results, the answer to the third research question - *Are there any linkages between the water chemical characteristics of Irish holy wells and their reputed health benefits?* – is generally no, or at least inconclusive. A notable finding, however, was the association between wells with reputations for eye cures and increased levels of sodium chloride.

### 9.1.4 Holy wells as part of heritage and a community resource

Chapter 8 also included a discussion of holy wells in the context of therapeutic landscapes, heritage and community involvement. In addition to any specific cures associated with holy wells, the combination of the spiritual dimension with the attributes of their physical setting can contribute to their role as therapeutic landscapes, described by health geographers as places with reputations for providing physical, mental and spiritual wellbeing. Many holy wells are set in peaceful rural settings, with attractive locations within woodlands or near to lakes and rivers, or along the seashore. A couple of examples of such well sites were described in Section 8.3.1, one of which (Toberaheena in Clonmel, Co Tipperary) has recently been restored as a quiet space for people bereaved by suicide.

About a third (31%) of the holy wells surveyed as part of this research are close to, or within, the grounds of historic churches and graveyards, whilst others are located at ancient sites such as raths and dolmens. Several prominent pilgrimage trails, or *turas*, feature holy wells, such as St Colmcille's well at Glencolmcille in Co Donegal and St Patrick's well near to the 13th century abbey at Ballintubber, Co Mayo, which is the start of the pilgrimage trail to Croagh Patrick. As part of the wider national heritage, holy wells remain important today as a community resource. Some evidence of votive offerings (such as rags, clothes, coins, religious medallions, etc) were encountered at 58% of the wells surveyed during this research, and there were many reports of the pattern day festivals still attracting large gatherings. Notwithstanding this level of interest, many holy wells have been covered over, filled in or subjected to unsympathetic renovation works over the years. There is a need for some national agency to have responsibility for working with local communities to preserve these community assets. There is also a need to build on current initiatives such as the archaeological investigations at the Disert site in Co Donegal, where academics from IT Sligo are working closely with a local community group to study this ancient site (which includes a holy well), and a website launched in 2017 (by the US academic Dr C Ray) where members of the public can upload details of holy wells (see Section 8.3 for details). The latter can be regarded partly as a follow up to the excellent Irish Folklore Commission 1937-38 archive known as the Schools' Folklore Collection.

The role of holy wells as sites of hydrogeological interest could be expanded through cooperation with the Geoheritage section of the Geological Survey of Ireland, to increase the number of holy wells designated as County Geological Sites (CGSs; see recommendations in Section 9.3). Currently, there are only a small number of such wells classed as CGSs (Section 8.3.3). Unlike Natural Heritage Areas (NHAs), CGSs do not receive statutory protection; however, they are afforded protection from their inclusion in the planning system. Moreover, the GSI can formally propose that CGSs of national importance should be designated as NHAs by the National Parks and Wildlife Service.

## 9.2 Recommendations for further research

Recommendations for future research include:

a) Compare the hydrochemistry of holy wells with similar shallow spring wells in the same area and lithology. This would add to our understanding in relation to research question 2 and objective c) above.

b) Carry out detailed investigations at a small number of holy well sites where the groundwater is believed to come from a combination of bedrock and superficial sources. The investigations would need to have the approval (and preferably involvement) of the local communities, and might include geophysical surveys and the installation of small diameter borehole clusters nearby, allowing water levels and water samples to be collected from different depths in the subsoil and shallow bedrock.

c) Sample wells for microbiological parameters, especially those wells that have elevated nitrate and are located in Extreme or High groundwater vulnerability areas. The analyses would focus on faecal coliforms (notably *E. coli*), but might also include viruses (e.g. rotavirus) and protozoa (e.g. *Cryptosporidium* and *Giardia*). A major challenge for such a study would be how to inform local people if a well was found to be contaminated. Understandably, this would be a very sensitive issue for people who drink water from a holy well as part of their ritual during a pilgrimage.

d) Test some of the many holy wells located in or near to graveyards for microbiological, organic and inorganic chemical parameters such as mercury, to see if there is any evidence of human impacts on the water quality. Again, communication of the findings would be a sensitive issue.

e) Carry out fingerprinting studies to identify the source of high nitrate in some of the holy wells. For example, techniques such as nitrogen isotopes and fluorescence emission excitation matrices (EEM) could be applied to samples from wells such as St Colman's well at Salterstown in Co Louth, where the source of a very high nitrate value recorded in this research was unclear (see Section 7.5.2).

f) Combine some of the trace element data collected in this research with the geochemistry and geophysical data from the Geological Survey of Ireland's Tellus project[40], to provide further insights into regional differences in groundwater chemistry.

[40] https://www.gsi.ie/en-ie/programmes-and-projects/tellus/Pages/default.aspx (accessed 31/7/2020)

## 9.3 Recommendations relating to well conservation and geological heritage

A national organisation should be established for the management and protection of holy wells. This would complement the work already being undertaken by local well and community groups, and by national bodies including the National Monuments Service (within the Office of Public Works) and the Geoheritage Section of the Geological Survey of Ireland. The new body could be formed as a non-governmental organisation (NGO), with volunteer representatives from local communities, academics, archaeologists, local historians, etc. A priority task would be to establish a comprehensive database of well sites, building on existing initiatives (see Section 9.1.4).

It is recommended that the protection of holy wells should be enhanced by designating more of these wells as County Geological Sites, for inclusion in County Development Plans. The GSI could also consider proposing some of the well sites as Natural Heritage Areas (NHAs). As happens at present, it would be necessary to involve landowners and the local community in the designation process. Seven examples of holy well sites recommended for consideration as CGSs, in the first instance, are given in Table 9.1 below (note that inclusion of a well in this table does not imply right of access). In addition to their hydrogeological and landscape setting, the physical characteristics of the well structure together with their history and current popularity, are factors in proposing these wells. These represent only a small sample of the interesting and important wells surveyed during this research (see list in Appendix A).

There are also some interesting holy wells located within areas already designated as CGSs, and it is recommended that the audit reports be expanded to include the wells. Examples include St Colman's well at Salterstown in Co Louth (Salterstown is a CGS primarily because of the good exposure of sulphide mineralisation in the local bedrock) and St Cronan's and St Fachtnas's wells in Co Clare (located within the karst Carran depression CGS).

Table 9.1 Holy wells recommended for consideration as County Geological Sites

| Well | County | Grid reference | Geology | Features of hydrogeological and other interest |
|---|---|---|---|---|
| St Moling's well St Mullins | Carlow | S 72911 38121 | Granite | The annual pilgrimage in late July draws large crowds. The well is in a very attractive garden site. The spring issues into a pond, which overflows into a well house (a former oratory), and thence to a stream channel (Section 5.5.1). The spring occurs at a change of slope and the groundwater source is probably the transition zone. The water is acidic (pH = 6.3), with EC around 200 µS $cm^{-1}$; the water type is Ca-$HCO_3$. The water contains some elevated trace elements, including REEs (Section 7.7). |
| Tubrid Millstreet | Cork | W 26006 90889 | Shales and sandstones (Namurian undiff.) | This spring forms a large teardrop shaped well which is both an important amenity as a holy well and also a source of water supply for the nearby town (with abstraction of 3200 $m^3$ $d^{-1}$). That this is such a large spring suggests that the groundwater source may be the Regionally Important Dinantian PUL aquifer that underlies the Namurian aquifer, rather than the Locally Important Namurian aquifer itself. The water type is Ca-$HCO_3$. |
| St Colmcille's well Glencolmcille | Donegal | G 52446 86100 | Slieve Tooey Quartzite Formation (Dalradian) | An important site on the *turas* in Glencolmcille. The well is in a side opening to a large cairn, formed by pilgrims carrying stones to the well (Section 5.6.4). Good exposures of transition zone material are visible in the area, and it is likely that this spring issues from the TZ. The well site may fall on a NNW-SSE lineament, which cuts the low hills immediately to the north. The water type is Na-Cl, and the water sample tested had elevated values of trace elements including REEs. |
| St Brigid's well Tully | Kildare | N 73125 10775 | Sand and gravel (Quat.) | Although the nearby St Brigid's well in the Japanese Gardens in included as a CGS, this well is possibly the best known and most visited holy well in the county. It is in a beautiful setting beside the Tully Stream, with several attractive features. The water is of Ca-$HCO_3$ type (Section 5.7.1.1 and 7.7). |
| Bride's well Calgath | Meath | N 89292 42475 | Limestone and shale (Calp) of the Lucan Formation (Dinantian) | This is one of the few examples of a holy well issuing from a confined aquifer (Section 5.9.1). The topographic setting is unusual, the well being close to the top of a small hill. It is reported to be one of the Leinster warm springs. It is known as a chalybeate well. Strontium levels were the highest among the four wells monitored in this research, consistent with a relatively long residence time for a confined aquifer source (see Section 7.7). |
| Tobernalt | Sligo | G 70955 32864 | Dartry Limestone Formation (Dinantian) | The well is part of a large karst spring that issues from the base of a limestone cliff (flow = 5000 $m^3$ $d^{-1}$). Located in a well-tended wooded site that includes statues of the holy family, a grotto and stations of the cross. Popular site for pilgrims. The water has a Ca-$HCO_3$ major ion chemistry. |
| St Declan's well Ardmore | Waterford | X 19801 77305 | Old Red Sandstone (Devonian) | Whereas St Declan's Stone (a glacial erratic) and the former Ardmore mine are included as CGSs, this holy well is not. The well is a famous pilgrimage site on the St Declan *turas*. It is a good example of a spring well on a sea cliff. The well is covered by a sandstone and mortar well house, topped with old stone carvings. The location of this well is possibly influenced by local faulting (Section 5.4.1.1). The water is slightly brackish, with an EC typically around 1000 µS $cm^{-1}$, with all major ions and several trace elements above NBLs. |

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# Appendix A List of well sites visited

Note that the inclusion of a well in this list does not imply right of access.

### Holy wells

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| St Moling's well St Mullins | Carlow | S72911 38121 | 672848E 638172N | N052.49009 | W006.927329 |
| Cranavane well Ballinvalley | Carlow | S86338 60589 | 686248E 660605N | N052.68997 | W006.72384 |
| Tullowphelim | Carlow | S 84822 73457 | 684771E 673487N | N052.80581 | W006.74296 |
| St Patrick's well Rathvilly | Carlow | S 88605 82570 | 688538E 682609N | N052.88706 | W006.68440 |
| St Laserian's well Old Leighlin | Carlow | S 65662 65407 | 665599E 665450N | N052.73615 | W007.02863 |
| St Fortchern's well Killoughternane | Carlow | S 77772 54218 | 677706E 654263N | N052.63402 | W006.85203 |
| St Kilian's well Mullagh | Cavan | N 66308 8501 | 666244E 785618N | N053.81587 | W006.99404 |
| St Brigid's well Raffony | Cavan | N 62850 89234 | 662788E 789251N | N053.84894 | W007.04578 |
| St Feidhlimidh's well Kilmore Upper | Cavan | H 38463 03454 | 638396E 803456N | N053.97905 | W007.41450 |
| St Patrick's well Curraghmore | Cavan | N 56697 90130 | 656632E 790146N | N053.85768 | W007.13915 |
| St Martin's well Ballinacally | Clare | R 27935 63405 | 527901E 663449N | N052.71734 | W009.06716 |
| St Brigid's well Kildysart | Clare | R 25852 59183 | 525819E 659228N | N052.67913 | W009.09701 |
| St Senan's well Mologha | Clare | R 04757 54362 | 504728E 654408N | N052.63252 | W009.40744 |
| St Kee's well (Tobar Chaoide) Foohagh | Clare | Q 85621 58949 | 485597E 58949N | N052.67003 | W009.69152 |
| St Flannan's well Drumanure | Clare | R 22282 84429 | 522252E 684469N | N052.90544 | W009.15579 |
| St Joseph's well Kilfarboy | Clare | R 08119 81541 | 508089E 681581N | N052.87726 | W009.36541 |
| St Brigid's well Ballysteen, Liscannor | Clare | R 04440 89960 | 504411E 689993N | N052.95225 | W009.42250 |
| Tobercornan Gleninagh North | Clare | M 20113 09804 | 520082E 709837N | N053.13306 | W009.19428 |
| Poll Insheen Gleninsheen | Clare | M 22993 02947 | 522960E 702983N | N053.07190 | W009.14962 |
| St Joseph's well Dulick Ennis | Clare | R 34261 79389 | 534223E 679427N | N052.86173 | W008.97681 |
| St Mochulla's well Tulla | Clare | R 49299 79756 | 549262E 679797N | N052.86668 | W008.75358 |
| Well of the holy cross Gleninagh North | Clare | M 19335 10323 | 519304E 710356N | N053.13762 | W009.20603 |
| St Cronan's well Termon | Clare | R 28900 99893 | 528866E 699930N | N053.04529 | W009.06085 |
| St Fachtna's well Termon (Coskeam) | Clare | M 30042 00472 | 530011E 700507N | N053.05062 | W009.04393 |
| Tobar Dearg Eanty Mor | Clare | M 25332 00480 | 5253901E 700513N | N053.05005 | W009.11415 |
| St Fanahan's well Mitchelstown | Cork | R82779 12346 | 582736E 612404N | N052.26307 | W008.25290 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| St Brigid's well Mountbridget | Cork | R 50398 11031 | 550357E 611086N | N052.24925 | W008.72698 |
| Tubrid well Millstreet | Cork | W 26006 90889 | 52597E 590947N | N052.06552 | W009.07965 |
| St John's well Mushera | Cork | W 32129 85672 | 532095E 585731N | N052.01943 | W008.98936 |
| St Olan's well Aghabullogue | Cork | W 44262 78435 | 544226E 578496N | N051.95575 | W008.81147 |
| Skour well Lough Hyne | Cork | W 09310 29403 | 509281E 529474N | N051.51059 | W009.30700 |
| Tobarin na Sul Lough Hyne | Cork | W 09326 29328 | 509297E 529399N | N051.50991 | W009.30675 |
| St Gobnait's well Ballyvourney | Cork | W 19858 76753 | 519810E 576810N | N051.93761 | W009.16623 |
| Well at St Gobnait's house Ballyvourney | Cork | W 19721 76821 | 519690E 576882N | N051.93824 | W009.16800 |
| St Finbarr's holy well Gougane Barra | Cork | W 09147 65979 | 509117E 566045N | N051.83923 | W009.31886 |
| Tobar Mhuire Titeskin | Cork | W 88517 64691 | 588471E 564755N | N051.83490 | W008.16729 |
| Trinity well Farrannagark | Cork | W 51499 45214 | 551461E 545282N | N051.65788 | W008.70155 |
| Wart well Timoleague | Cork | W 47210 43612 | 547173E 543680N | N051.64309 | W008.76329 |
| Tobar Mhuire Timoleague | Cork | W 46383 43214 | 546343E 543283N | N051.63944 | W008.77517 |
| Abbey well Kinsale | Cork | W 63487 50648 | 563447E 550715N | N051.70763 | W008.52889 |
| Trinity well Fort Hill Kinsale | Cork | W 65787 49460 | 565746E 549527N | N051.68709 | W008.49552 |
| St Fachtna's well Rosscarbery | Cork | W 28878 37116 | 528845E 537186N | N051.58270 | W009.02674 |
| St Catherine's well Killybegs | Donegal | G 71438 75645 | 571396E 875640N | N054.62817 | W008.44297 |
| St Ciaran's well Kilcar | Donegal | G 65135 75396 | 565094E 875594N | N054.62557 | W008.54054 |
| Well of the Holy Women Rinnakill | Donegal | G 58971 75332 | 558933E 875330N | N054.62453 | W008.63596 |
| St Colmcille's well Glencolmcille | Donegal | G 52446 86100 | 552426E 886095N | N054.72067 | W008.73842 |
| Abbey well Ballyshannon | Donegal | G 86767 62194 | 586718E 862193N | N054.50799 | W008.20508 |
| St Conal's well Bruckless | Donegal | G 75114 77569 | 575072E 877504N | N054.64567 | W008.38623 |
| St Colmcille's well Disert | Donegal | G 87980 87321 | 587935E 887317N | N054.73376 | W008.18734 |
| Doon well Kilmacrennan | Donegal | C 114400 19705 | 611390E 919693N | N055.04265 | W007.82187 |
| St Colmcille's well Carryblagh | Donegal | C 24079 42271 | 624026E 942254N | N055.22690 | W007.62236 |
| St Eigne's well Urris | Donegal | C 31897 43088 | 631843E 94070N | N055.23378 | W007.49949 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| St Patrick's well Trinity College | Dublin | O 16072 33907 | 716019E 733958N | N053.34312 | W006.25768 |
| St Begnet's well Dalkey Island | Dublin | O 27697 26369 | 727621E 726398N | N053.27254 | W006.08660 |
| Lady's well Flemington | Dublin (Fingal) | O 18243 64322 | 718169E 764343N | N053.61557 | W006.21398 |
| Lady's well Mulhuddart | Dublin (Fingal) | O 06999 40985 | 706929E 741011N | N053.40839 | W006.39175 |
| Patrick's well Robswalls | Dublin (Fingal) | O 24337 45062 | 724261E 745087N | N053.44121 | W006.12959 |
| St Brigid's well St Margarets | Dublin (Fingal) | O 12841 43629 | 712766E 743649N | N053.43091 | W006.30302 |
| St Catherine's well Fieldstown | Dublin (Fingal) | O 11686 50349 | 711613E 750373N | N053.49152 | W006.31800 |
| St Colmcille's well Swords | Dublin (Fingal) | O 18108 46553 | 718034E 746578N | N053.45603 | W006.22273 |
| St Doolagh's well Balgriffin | Dublin (Fingal) | O 21149 42126 | 721081E 742150N | N053.41559 | W006.17868 |
| St Mary's well Tobertown | Dublin (Fingal) | O 16734 64461 | 716661E 764482N | N053.61716 | W006.23673 |
| St Sylvester's well Malahide | Dublin (Fingal) | O 22623 46138 | 722548E 746163N | N053.45127 | W006.15495 |
| St Werburgh's well Swords | Dublin (Fingal) | O 18494 45798 | 718419E 745823N | N053.44916 | W006.21720 |
| Tobersool near Balbriggan | Dublin (Fingal) | O 16595 65581 | 716543E 765606N | N053.62725 | W006.23841 |
| St MacCullin's well Grallagh | Dublin (Fingal) | O 10718 56404 | 710647E 756424N | N053.54610 | W006.33045 |
| Lady's well Corbally | Dublin (South) | O 05593 25151 | 705521E 725180N | N053.26646 | W006.41818 |
| St Colmcille's well Oldcourt | Dublin (South) | O 11677 25427 | 711604E 725456N | N053.26769 | W006.32694 |
| St Patrick's well Boherboy | Dublin (South) | O 04365 26185 | 704294E 726214N | N053.27599 | W006.43623 |
| St Enda's well Barna | Galway | M 24513 23439 | 524481E 723470N | N053.25620 | W009.13178 |
| St Anna's well Gorumna Island | Galway | L 895 24160 | 489549E 724190N | N053.25656 | W009.65534 |
| Tobar Mhuire Kilkieran (Ardmore) | Galway | L 80472 29982 | 480451E 730011N | N053.30687 | W009.79381 |
| Tobar Mhuire Kilkieran (Ail na Bron) | Galway | L 84176 30637 | 484153E 730665N | N053.31359 | W009.73852 |
| St Chonaill's well Cashel | Galway | L 80765 43009 | 480744E 743036N | N053.42393 | W009.79433 |
| St Augustine's well Galway | Galway | M 30694 25586 | 530661E 725616N | N053.27633 | W009.03965 |
| Tobar Mhuire, Tobar Feichin Dooghta | Galway | M 02197 53192 | 502170E 75216N | N053.51890 | W009.47825 |
| St Joseph's well Leenaun | Galway | L 89439 63336 | 489416E 763358N | N053.60837 | W009.67108 |
| St Cummin's well Oughterard | Galway | M 13023 42279 | 512994E 742306N | N053.42369 | W009.30926 |
| St Cuan's well Bunatober | Galway | M 32227 42749 | 532196E 742777N | N053.43072 | W09.02036 |
| Our Lady's well Ballyheige | Kerry | Q 75711 28283 | 475693E 628333N | N052.39241 | W009.82641 |
| Tobar Daithleann Glendahalin | Kerry | Q 73506 31911 | 473487E 631967N | N052.42449 | W009.86020 |
| Tobar na Molt Ardfert | Kerry | Q 81897 20444 | 481875E 620495N | N052.32336 | W009.73288 |
| Tobar na nGealt Gleann na nGealt | Kerry | Q 67109 08362 | 467093E 608417N | N052.21148 | W009.94487 |
| Tobar Eoin Minard | Kerry | V 55400 99061 | 455384E 599118N | N052.12500 | W010.11210 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| Holy well at Shrone | Kerry | W 13841 88292 | 513812E 588350N | N052.04043 | W009.25636 |
| Our Lady's well Kenmare | Kerry | V 90710 571078 | 490694E 571078N | N051.88110 | W009.58780 |
| St Finian's well Kenmare | Kerry | V 92244 70295 | 492220E 570358N | N051.87498 | W009.56532 |
| Father Moore's well, Kildare | Kildare | N 75295 16359 | 675231E 716391N | N053.19264 | W006.87422 |
| St Brigid's well Japanese Gardens | Kildare | N 73496 10917 | 673431E 710950N | N053.14400 | W006.90238 |
| St Brigid's well Tully | Kildare | N 73125 10775 | 673057E 710806N | N053.14279 | W006.90796 |
| St Brigid's well Kilcullen | Kildare | N 84285 09469 | 684191E 709497N | N053.12936 | W006.74197 |
| St Patrick's well Glassely | Kildare | S 76107 98212 | 676043E 698248N | N052.02950 | W006.86636 |
| St Catherine's well Leixlip | Kildare | O 01691 36250 | 701620E 736277N | N053.36691 | W006.47308 |
| St Fiachra's well Ullard | Kilkenny | S 72378 48220 | 627314E 648266N | N052.5807 | W006.93299 |
| Ladywell Ballinakill | Kilkenny | S 45595 78931 | 645536E 678971N | N052.85973 | W007.32381 |
| St John's well Johnswell | Kilkenny | S 56187 61579 | 656117E 661627N | N052.70282 | W007.16954 |
| St Canice's well Kilkenny | Kilkenny | S 49980 656048 | 649922E 656048N | N052.65332 | W007.26218 |
| Tober Mogue Ennisnag | Kilkenny | S 52281 44109 | 652221E 644156N | N052.54623 | W007.23008 |
| St Moling's well Mullennakill | Kilkenny | S 60183 31343 | 660117E 631388N | N052.43067 | W007.11598 |
| St Columcille's well Inistioge | Kilkenny | S 63348 37889 | 663286E 637938N | N052.48918 | W007.06815 |
| St Nicholas well Killamery | Kilkenny | S 37694 36081 | 637644E 636128N | N052.47529 | W007.44599 |
| St Kieran's well Kilkieran | Kilkenny | S 42255 27470 | 642195E 627519N | N052.39759 | W007.37998 |
| St Fachtna's well Tybroughney | Kilkenny | S 44087 21432 | 644029E 621484N | N052.34318 | W007.35384 |
| Bastionfort well Gowran | Kilkenny | S 62699 53266 | 662638E 653311N | N052.62741 | W007.07480 |
| St Fintan's well Cromogue | Laois | S 39381 89746 | 639319E 689784N | N052.95740 | W007.41480 |
| St Kavan's well Annatrim | Laois | S 29473 92299 | 629423E 692337N | N052.98096 | W007.56194 |
| St Brigid's well Morett | Laois | N 54095 03133 | 654042E 703169N | N053.07640 | W007.19347 |
| Toberneeve Ballyadams | Laois | S 62233 90510 | 662171E 690547N | N052.96209 | W007.07460 |
| St Brigid's well Rosenallis | Laois | N 39707 09586 | 639650E 709619N | N053.13562 | W007.40745 |
| St John's well Toberboe | Laois | S 37759 74770 | 637702E 674811N | N052.82294 | W007.44061 |
| St Mary's well Killargue | Leitrim | G 86757 30988 | 586711E 830995N | N054.22766 | W008.20380 |
| St Patrick's well Tullaghan | Leitrim | G 75681 57327 | 575639E 857329N | N054.46387 | W008.37575 |
| Shaver's well Tullaghan | Leitrim | G 75527 57512 | 575485E 857513N | N054.46552 | W008.37815 |
| St Hugh's well Cleighran Beg | Leitrim | G 99020 20158 | 598972E 820164N | N054.13051 | W008.01573 |
| Black Dog holy well Kilmallock | Limerick | R 61766 27792 | 561725E 627844N | N052.40078 | W008.56246 |
| St Brigid's well Shangarry | Limerick | R 26558 32673 | 526524E 632724N | N052.44105 | W009.08072 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| Barrigone holy well | Limerick | R 28581 49965 | 528546E 650013N | N052.59669 | W009.05469 |
| St Patrick's well Knockpatrick | Limerick | R 24159 49605 | 524128E 649651N | N052.59284 | W009.11985 |
| Tobermurry Dromtrasna North | Limerick | R 16217 24295 | 516196E 624347N | N052.36428 | W009.23050 |
| St Patrick's well Ballyelan | Limerick | R 44258 33215 | 544221E 33215N | N052.44801 | W008.82055 |
| St Patrick's well Cartron | Longford | N 17358 84041 | 617306E 784059N | N053.80578 | W007.73726 |
| Lady well Legan | Longford | N 23547 63794 | 623493E 763816N | N053.62364 | W007.64487 |
| St Columbkille's well Ratharney | Longford | N 23283 61373 | 623230E 761387N | N053.60190 | W007.64905 |
| Toberpatrick Cornacullew | Longford | N 20031 93129 | 619978E 793145N | N053.88733 | W007.69612 |
| St Patrick's well Ballyduffy | Longford | N 23527 96699 | 623473E 796714N | N053.91926 | W007.64268 |
| Lady well Derrydarragh | Longford | N 02838 57480 | 602789E 757503N | N053.56742 | W007.95790 |
| St Colman's well Salterstown | Louth | O 11937 93258 | 711866E 793272N | N053.87681 | W006.29874 |
| Ladywell Dundalk | Louth | J 04838 06100 | 704767E 806112N | N053.99362 | W006.40224 |
| St Brigid's well Faughart | Louth | J 05895 12594 | 705823E 812608N | N054.05175 | W006.38387 |
| St Borchill's well Dysart | Louth | O 09872 88000 | 709799E 788016N | N053.83003 | W006.33203 |
| St Dennis's well Clogher | Louth | O 16196 84721 | 716123E 784738N | N053.79922 | W006.23726 |
| St Ronan's well Dromiskin | Louth | O 04770 97561 | 704695E 797570N | N053.91695 | W006.40622 |
| St James's well Carlingford | Louth | J 21670 09405 | 721596E 809417N | N054.01962 | W006.14441 |
| Lady well Templetown | Louth | J 21199 05810 | 721126E 805823N | N053.98745 | W006.15301 |
| St Attracta's well Attymas | Mayo | G 29195 11788 | 529167E 811800N | N054.05049 | W009.08170 |
| St Feichin's well Mullaghhawny | Mayo | G 27365 13345 | 527331E 813357N | N054.06421 | W009.11008 |
| Tobar Mhuire Rosserk | Mayo | G 25299 25020 | 525266E 825303N | N054.16880 | W009.14453 |
| St Cumin's well Kilcummin | Mayo | G 21208 37238 | 521177E 837244N | N054.27791 | W009.21034 |
| St Patrick's well Ballina | Mayo | G 24038 19736 | 524006E 819746N | N054.12114 | W009.16248 |
| St Deirbhle's well Belmullet | Mayo | F 61968 18684 | 461951E 818693N | N054.09879 | W010.11072 |
| St Colman's well Slievemore Achill | Mayo | F 64006 07195 | 463987E 807206N | N053.99617 | W010.07446 |
| St Brendan's well Roskeen | Mayo | L 91322 95739 | 491296E 795750N | N053.89977 | W09.65406 |
| Tobar Ri an Dhomhnaigh Kilgeever | Mayo | L 83653 80736 | 483630E 780753N | N053.76337 | W09.76500 |
| Tobar Mhuire Balla | Mayo | M 25440 84556 | 525408E 784577N | N053.80536 | W09.13244 |
| St Patrick's well Ballintubber | Mayo | M 15512 79156 | 515481E 779174N | N053.75532 | W09.28164 |
| Bride's well Calgath | Meath | N 89292 42475 | 689225E 742512N | N053.42507 | W006.65752 |
| Our Lady's well Killyon | Meath | N 68366 49090 | 668302E 749115N | N053.48761 | W006.97082 |
| St Brigid's well Ardsallagh | Meath | N 89704 63493 | 689636E 763515N | N053.61379 | W006.64532 |
| St Columcille's well Skryne | Meath | N 95076 60686 | 695007E 760709N | N053.58736 | W006.56503 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| St Finian's well Clonard | Meath | N 66832 45510 | 666769E 745566N | N053.45565 | W006.99468 |
| St Kieran's well Castlekeeran | Meath | N 68782 77073 | 668718E 777092N | N053.73894 | W006.95838 |
| St Colmcille's well Kells | Meath | N 73460 75754 | 673395E 775774N | N053.72646 | W006.88782 |
| St Patrick's well Carlanstown | Meath | N 76366 79624 | 676301E 779643N | N053.76083 | W006.282 |
| St Gorman's well | Meath | N 74071 44193 | 647006E 744219N | N053.44285 | W006.88604 |
| St Dympna's well Kildalkey | Meath | N 72574 59043 | 672508E 759068N | N053.57647 | W006.90513 |
| St Anne's well Randalstown | Meath | N 84069 71406 | 684002E 771427N | N053.68581 | W006.72830 |
| Well of the White Cow Tara | Meath | N 92157 59694 | 692088E 759717N | N053.57925 | W006.60939 |
| Planxty well Smithborough | Monaghan | H 60300 29925 | 660239E 82993N | N054.21475 | W007.07645 |
| St Dympna's well Caldavnet | Monaghan | H 61582 42555 | 661521E 842558N | N054.32804 | W007.05420 |
| St Muadan's well Errigal Truagh | Monaghan | H 66062 49203 | 666003E 849207N | N054.38720 | W006.98384 |
| Seven Blessed Wells of Killeigh | Offaly | N 36280 18269 | 636224E 718301N | N053.21389 | W007.45766 |
| St Anthony's well Killina | Offaly | N 272231 23828 | 627177E 723858N | N053.26437 | W007.59264 |
| St Manchin's well Lemanaghan | Offaly | N 17210 26943 | 617158E 726973N | N053.29278 | W007.74264 |
| St Saran's well Moystown | Offaly | N 04051 20697 | 604002E 720727N | N053.23691 | W007.94006 |
| St Kieran's well Seir Kieran | Offaly | N 14109 01701 | 614057E 701736N | N053.06607 | W007.79027 |
| St Molua's well Roscomroe | Offaly | S 16592 97578 | 616538E 697614N | N053.02895 | W007.75345 |
| St Ciaran's well Clonmacnoise | Offaly | N 00442 30040 | 600393E 730069N | N053.32089 | W007.99410 |
| St Brigid's well Drum | Roscommon | M 98110 38719 | 598062E 738748N | N053.39888 | W008.02914 |
| St Ronan's well Taughmaconnell | Roscommon | M 90347 37120 | 590302E 737149N | N053.38442 | W008.14577 |
| Ogulla well Tulsk | Roscommon | M 81840 80890 | 581799E 780912N | N053.77744 | W008.27618 |
| St Brigid's well Brideswell | Roscommon | M 94165 44722 | 594114E 744749N | N053.45278 | W008.08861 |
| St Lasair's well Lough Meelagh | Roscommon | G 89832 12196 | 589786E 812207N | N054.05891 | W008.15600 |
| Tobernalt Carraroe | Sligo | G 70955 32864 | 570913E 832871N | N054.24386 | W008.44626 |
| St Patrick's well Dromard | Sligo | G 57113 29209 | 557074E 829218N | N054.21007 | W008.65805 |
| St Attracta's well Clogher | Sligo | G 66659 98846 | 566619E 798855N | N053.93801 | W008.50840 |
| St Ciaran's well Kilmacteige | Sligo | G 39427 10630 | 539392E 810641N | N054.04138 | W008.92534 |
| St Patrick's well Aughris | Sligo | G 50286 36838 | 550250E 836842N | N054.27797 | W008.76393 |
| St Patrick's well Clonmel | Tipperary | S 16900 22875 | 616846E 622928N | N052.35766 | W007.75266 |
| Toberaheena Clonmel | Tipperary | S 18863 22206 | 618809E 622258N | N052.35159 | W007.72391 |
| St Patrick's well Carrigatogher | Tipperary | R 80373 76717 | 580321E 676759N | N052.84141 | W008.29210 |
| St Sedna's well Newtown | Tipperary | R 87220 29415 | 587180E 629470N | N052.41655 | W008.18855 |
| St Peacaun's holy well Toureen | Tipperary | S 00572 28465 | 600523E 628516N | N052.40816 | W007.99231 |

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| St Brigid's and other wells Kilrossanty | Waterford | S 31514 03380 | 631459E 603436N | N052.18183 | W007.53998 |
| St Declan's well Ardmore | Waterford | X 19801 77305 | 619749E 577366N | N051.94804 | W007.71272 |
| St Bartholomew's well Kinsalebeg | Waterford | X 13244 79169 | 613194E 579230N | N051.96499 | W007.80800 |
| St Declan's well Toor | Waterford | X 15509 87652 | 615457E 587712N | N052.04117 | W007.77469 |
| St Cuan's well Mothel | Waterford | S 41236 17864 | 641178E 617917N | N052.31135 | W007.39610 |
| St Cathaldus well Canty | Waterford | X 18408 94134 | 618356E 594189N | N052.09931 | W007.73209 |
| St Mochua's well Clashmore | Waterford | X 12175 84150 | 612119E 584202N | N052.00977 | W007.82339 |
| St Brigid's well Killare | Westmeath | N 27755 48375 | 627702E 748402N | N053.48489 | W007.58264 |
| St Menaghan's well | Westmeath | N 10654 36057 | 610603E 736085N | N053.3748 | W007.84065 |
| Sunday's well Ballymore | Westmeath | N 22744 49750 | 622691E 749775N | N053.49749 | W007.65801 |
| St Brigid's well Cullion | Westmeath | N 42923 55754 | 642865E 755778N | N053.55017 | W007.35316 |
| Tobernacogany Fore | Westmeath | N 51031 70532 | 650974E 770553N | N053.68222 | W007.22843 |
| St Mogue's well Ferns | Wexford | T 02259 49885 | 702189E 649922N | N052.59096 | W006.49180 |
| St David's well Ballynaslaney | Wexford | S 99991 29702 | 699922E 629752N | N052.41015 | W006.53132 |
| Our Lady's well Lady's Island | Wexford | T 11118 07360 | 711047E 607415N | N052.20731 | W006.37521 |
| Lady's Island well | Wexford | T 10543 07417 | 710472E 607470N | N052.20793 | W006.38364 |
| St Anne's well Killann | Wexford | S 84916 41706 | 684849E 641754N | N052.52054 | W006.74974 |
| St Machain's well Kilmuckridge | Wexford | T 16592 39643 | 716518E 639691N | N052.49617 | W006.28402 |
| St James's well Tomhaggard | Wexford | T 02943 08059 | 702875E 608114N | N052.21518 | W006.49453 |
| St Anne's well Tomhaggard | Wexford | T 02999 08061 | 702927E 608120N | N052.21518 | W006.49475 |
| Trinity well Tinnacurra | Wexford | S 95239 16693 | 695170E 616746N | N052.29413 | W006.60481 |
| St Munn's well Brownscastle | Wexford | S 91248 21784 | 691179E 621836N | N052.34054 | W006.66193 |
| St Kevin's well Glasnamullen | Wicklow | O 20455 09216 | 720380E 709249N | N053.12019 | W006.20155 |
| Holy Trinity well Ashford | Wicklow | T 27058 99160 | 726981E 699195N | N053.02835 | W006.10696 |
| Our Lady's well Arklow | Wicklow | T 25113 77838 | 725035E 671322N | N052.77838 | W006.14665 |
| Our Lady's well Ballymanus | Wicklow | T 22316 93835 | 722243E 693877N | N052.98168 | W006.17957 |
| Our Lady's well Ballymoney | Wicklow | T 15490 85246 | 715416E 685283N | N052.90599 | W006.28424 |
| St Aidan's well Preban | Wicklow | T 07972 77305 | 707829E 677341N | N052.83625 | W006.39960 |
| St Kevin's well Glendalough | Wicklow | T 12636 96640 | 712563E 696676N | N053.00895 | W006.32268 |
| St Patrick's well Blessington | Wicklow | N 98359 14292 | 698298E 714324N | N053.17031 | W006.52989 |
| St Nicholas's well Dunlavin | Wicklow | N 87293 00525 | 687227E 700563N | N053.04860 | W006.69904 |
| Tober Eoin Rathdangan | Wicklow | S 97877 86506 | 697807E 686544N | N052.92081 | W006.54553 |
| St Michael's well Rathdrum | Wicklow | T 18987 88607 | 718913E 688648N | N052.93543 | W006.23107 |

## Spa wells

| Well | County | Irish Grid Ref | ITM | Latitude | Longitude |
|---|---|---|---|---|---|
| Drumod Spa well Swanlinbar | Cavan | H 20038 26604 | 619984E 826615N | N054.18806 | W007.69379 |
| Lisdoonvarna spa - main Sulphur well | Clare | R 13552 97945 | 513529E 697982N | N053.02553 | W009.28910 |
| Lisdoonvarna spa - Twin wells: sulphur well | Clare | R 12877 980023 | 512847E 698060N | N053.02612 | W009.29918 |
| Spa well Mallow | Cork | W 56309 98549 | 556270E 598606N | N052.13758 | W008.63882 |
| Louisa Bridge Spa well Leixlip | Kildare | N 99451 36635 | 699388E 736651N | N053.37070 | W006.50649 |

## Appendix B Examples of well survey reports

Three examples of the survey reports completed for the 215 holy wells and five spa wells are included here: St Declan's well Ardmore (Co Waterford), Cranavane holy well (Co Carlow) and St Patrick's well Clonmel (Co Tipperary).

**Well name: St Declan's well Ardmore, Co Waterford**

| | | | | |
|---|---|---|---|---|
| Location / Townland | | Dysert townland, Ardmore, Co Waterford | | |
| Grid reference | Irish Grid | X 19801 77305 | | |
| | ITM | 619749E 577366N | | |
| Latitude / Longitude (degrees) | | N051.94804 W007.71272 | OSI Discovery Map Nr | 82 |
| Date(s) visited | | 14/04/2017 (12.20 hrs); 18/05/2017 (10.05 hrs); 27/06/2017 (15.00 hrs); 7/02/2018 (13.30 hrs); 9/10/2018 (11.15 hrs); 27/03/2019 (14.45 hrs) | | |
| Access | | The well is beside the old church ruins, close to the start of the Cliff walk southeast of Ardmore.<br>Although the well is not shown on the OSI Discovery map, it is marked on the historical 6 inch and 25 inch maps, along with the ruins of Dysert church. | | |
| Well description | | The well is within a sandstone and mortar block well house, which has two rectangular portals – the one on the right measures 0.85 m high by 0.6 m wide, whilst the entrance on the left is 1.15 m high by 0.55 m wide. The well house is topped with a couple of old carved stones showing the crucifixion (there was apparently formerly a third cross, which is now missing).<br>The well dimensions are 1.95 m wide and 0.6 m from front to rear. There are loose stones in the base of the well, which contained about 0.1 m of water when visited in April 2017 (or about 0.05 to 0.08 m in October 2018, the base of the well being uneven).<br>The well discharges via a rough channel, 0.3 m wide, which drains towards the church ruins and then to the sea. There was only a trickle of water at time of the visits in April, May and June 2017, and in October 2018.<br>There were no votives in or at the well, but there were some statues and ribbons in the old altar area of the church ruins observed during most visits (although these had been removed by the visit in March 2019). | | |

| | | |
|---|---|---|
| Reputed cures | | Eyesight (http://irelandsholywells.blogspot.ie/2011/08/saint-declans-well-ardmore.html; accessed 2/7/2020). Foley (2010), quoting Logan (1980), also mentions sprains, wounds and rheumatism. Broderick (2016), citing Ó Cadhla (2002), recounts a story of a crippled man being cured after washing his feet and hands in the well. |
| Topography | | The well is on the cliff pathway, about 25 m above the shoreline. |
| Elevation (m above OD) | | 23 |
| Geology | Superficial | Rock outcrop is at or close to the surface in the vicinity of the well. On the relatively flat cliff top above the well there is till derived from Devonian sandstones (TDSs). |
| | Bedrock | Sandstone outcrops are visible along the shoreline below the well, and around the headland. These appear to strike approximately east-west, consistent with the main Hercynian structural trend. At the well the rock formation is the Ardmore Member of the Old Red Sandstone (GYam), described on the geology map as grey to red sandstone and grey siltstone. In the Groundwater Rock Unit classification, the bedrock is described simply as Devonian Old Red Sandstone (DORS). |
| | Structural features | There is an embayment in the shoreline immediately below the well, raising the possibility of a (north-south) fracture influencing the well location.<br>The sandstones on the cliff south of Ardmore, where St Declan's well is located, represent the southern limb of an east-west trending syncline, with the town of Ardmore being underlain by younger Dinantian strata. |
| Hydrogeology | Description | The ORS is a locally important (Ll) aquifer. As mentioned above, the rocks along the coastline are highly fractured and the occurrence of the spring well at this location might be related to a north-south fracture that results in an indentation in the shoreline below the well site – this is seen more clearly on the 2010 OSI Ortho image than on the OSI Digital Globe image.<br>There were formerly two mine workings in the vicinity, one of which, known as the "Putty Hole", was in the cliff directly below the well site. The mine was worked in the 17$^{th}$ and 18$^{th}$ centuries for iron, copper, lead and silver (Parkes et al., 2013). The name Putty Hole relates to the "heavy mud" which occurs in the cave/mine adit (Suipéil, 2019); the presence of such weathered material would be consistent with faulting here (although this is just speculation on the part of this researcher).<br>The water is slightly brackish, with an EC typically around 1,000 µS cm$^{-1}$. |
| | Depth to water<br>(m below ref point) | 0.36 m below the entrance portal on the left (14/4/17); |

| | | |
|---|---|---|
| | | 0.37 m below the entrance portal on the left (18/5/17);<br>0.36 m below the entrance portal on the left (27/6/17);<br>0.36 m below the entrance portal on the left (9/10/18);<br>0.35 m below the entrance portal on the left (27/3/19). |
| | Aquifer class | Ll |
| | Vulnerability | X Extreme |
| Water quality | EC (µS $cm^{-1}$) | 995 (14/4/17); 1004 (18/5/17); 1039 (27/6/17); 1002 (9/10/18); 985 (27/3/19) |
| | Temperature (°C) | 11 (14/4/17); 11.3 (18/5/17); 13.4 (27/6/17); 12.4 (9/10/18); 10.0 (27/3/19) |
| | pH | 6.67 (14/4/17); 6.65 (18/5/17); 6.37 (27/6/17); 6.1 (but rising, 9/10/18); 7.01 (27/3/19) |
| | Sample collected? | Y (18/5/17) – SHW78 and 79 (duplicate) |
| | Sample appearance | Clear |
| | Weather conditions | Clear, 13.5 °C (14/4/17); sunny, 12 °C (18/5/17); sunny, 18 °C (27/6/17); dry 15 °C (9/10/18); sunny, 13 °C (27/3/19) |
| Potential pollution sources nearby? | | Public path. Some housing on cliff above (west of well) |
| Additional comments | | St Declan founded a monastery in Ardmore in about the year 416 CE and thus reportedly pre-dates St Patrick as the person who first brought Christianity to Ireland, albeit his travels and influence weren't as widespread (http://www.ardmorewaterford.com/st-declans-well-ardmore/; accessed 2/7/2020). The saint's feast day is 24th July, when a pattern is held each year (the celebrations begin on the eve of the saint's day and continue over the following week). Foley (2010) and Broderick (2016) describe the traditions surrounding the well and other sites associated with St Declan in Ardmore, including at St Declan's stone (a conglomerate erratic) on the foreshore, which is said to have travelled across the sea to Ardmore carrying St Declan's bell. The rituals included drinking water from the well.<br><br>There is a second holy well in the area which is named after a priest, Father O'Donnell; this well is located along the cliff walk south of St Declan's well. The stone well house/grotto at Father O'Donnell's well (see photos) was constructed by a Mr O'Rahilly in 1928 (Keane, 2018). Like St Declan's well, Fr O'Donnell's well is a spring that issues from Old Red Sandstone bedrock. The water has a similar EC and temperature to the water in St Declan's well (986 µS $cm^{-1}$ and 10.3 °C, respectively, on 27/3/19), and the flow in March 2019 was estimated as approximately 0.1-0.2 L $s^{-1}$. |

Photos:



St Declan's well. The sandstone well house has two portals and is topped by two carved crucifixion scenes



Outcrops of Old Red Sandstone in the cliffs near the well



The rear of the well house, with the ruined church in the background (14/4/17)



Votives in an alcove within the church ruins (14/4/17)



The cliff path, walking west towards the church ruins and Ardmore (14/4/17)



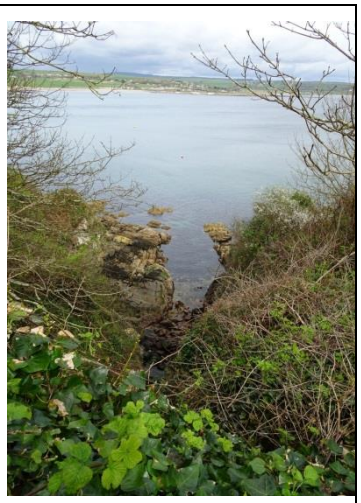

Advertising the 2017 Ardmore Pattern Festival



Inside the left portal of the wellhouse (14/4/17)



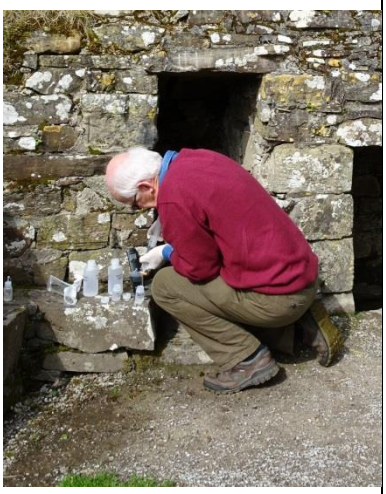
The narrow chanel that drains away from the well (14/4/17)

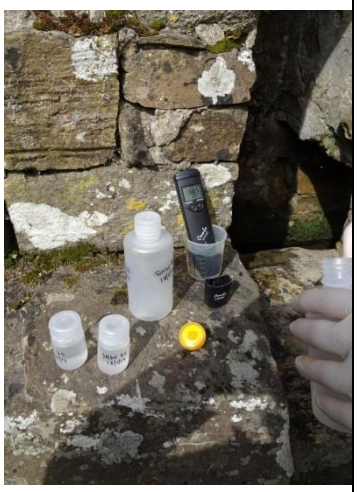


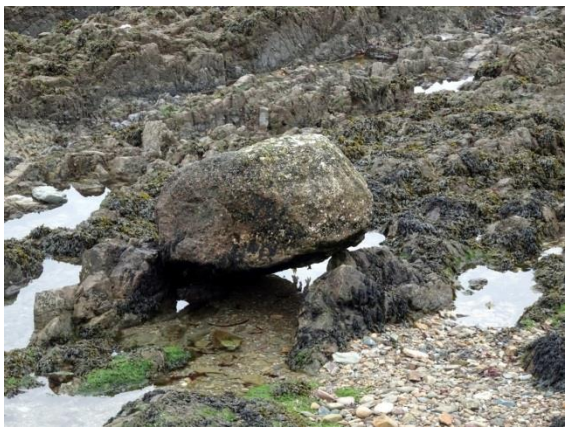
View from the well site to the shoreline below, with its outcrops of fractured sandstone rocks



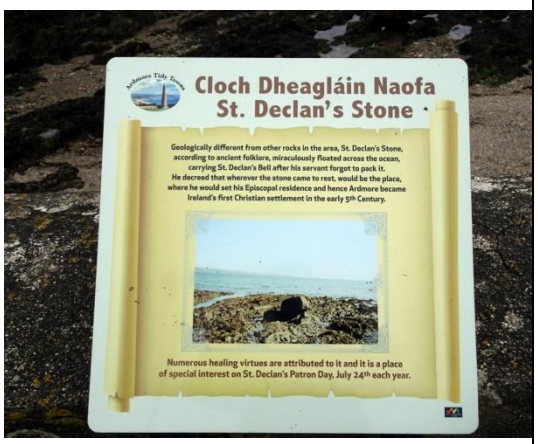
Sampling the well 18/5/2017







St Declan's stone (a glacial erratic) on the foreshore at Ardmore (7/2/18).




The legend of St Declan's stone



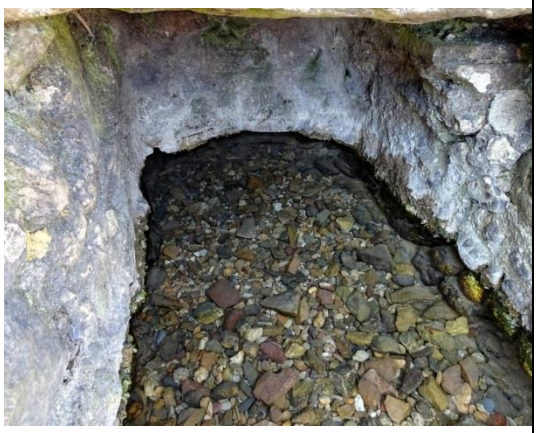
St Declan's well in February 2018



Eroded sandstone where crosses have been scratched into the wall of the old church ruins (7/2/18)



The rather elaborate stone struture that surrounds Father O'Donnell's well (27/3/19)



The interior of the Father O'Donnell's well



Fr O'Donnell's well can be seen in the centre distance: it is in a slight deperession, about four-fifths of the way up the hill slope



The spring discharges into the concrete chamber and then in into a drain that leads down towards the sea.

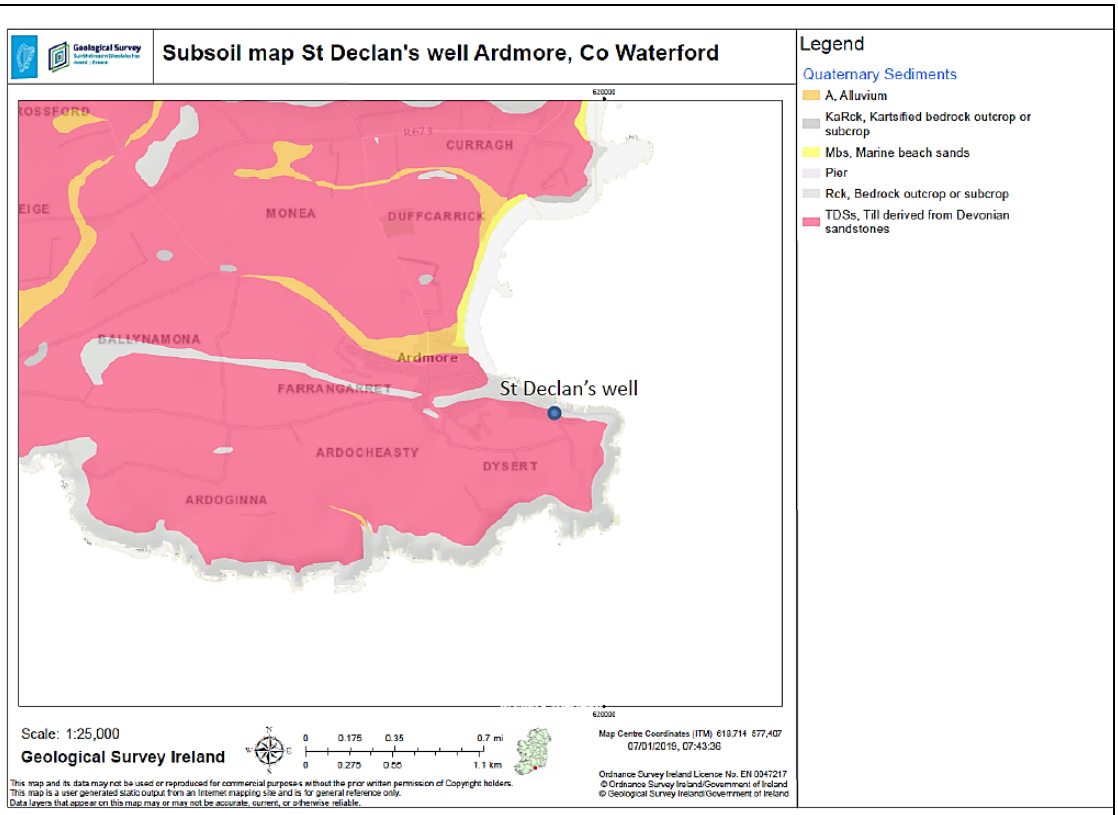
## Maps

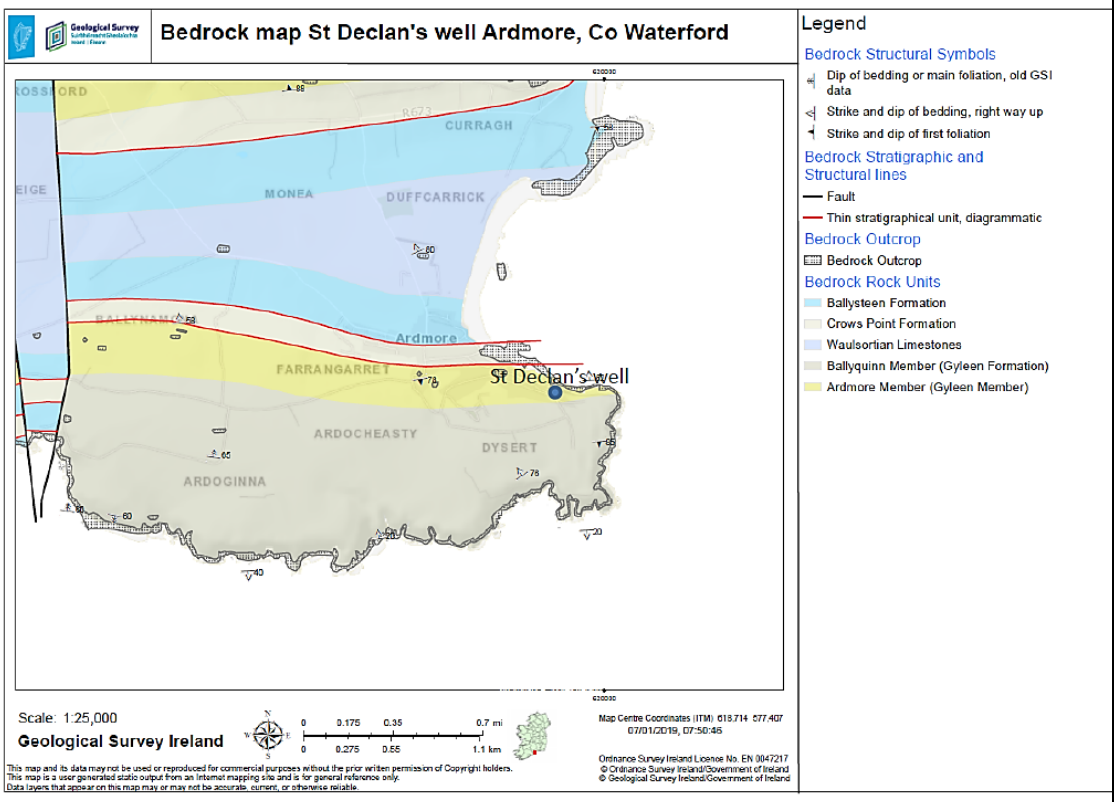


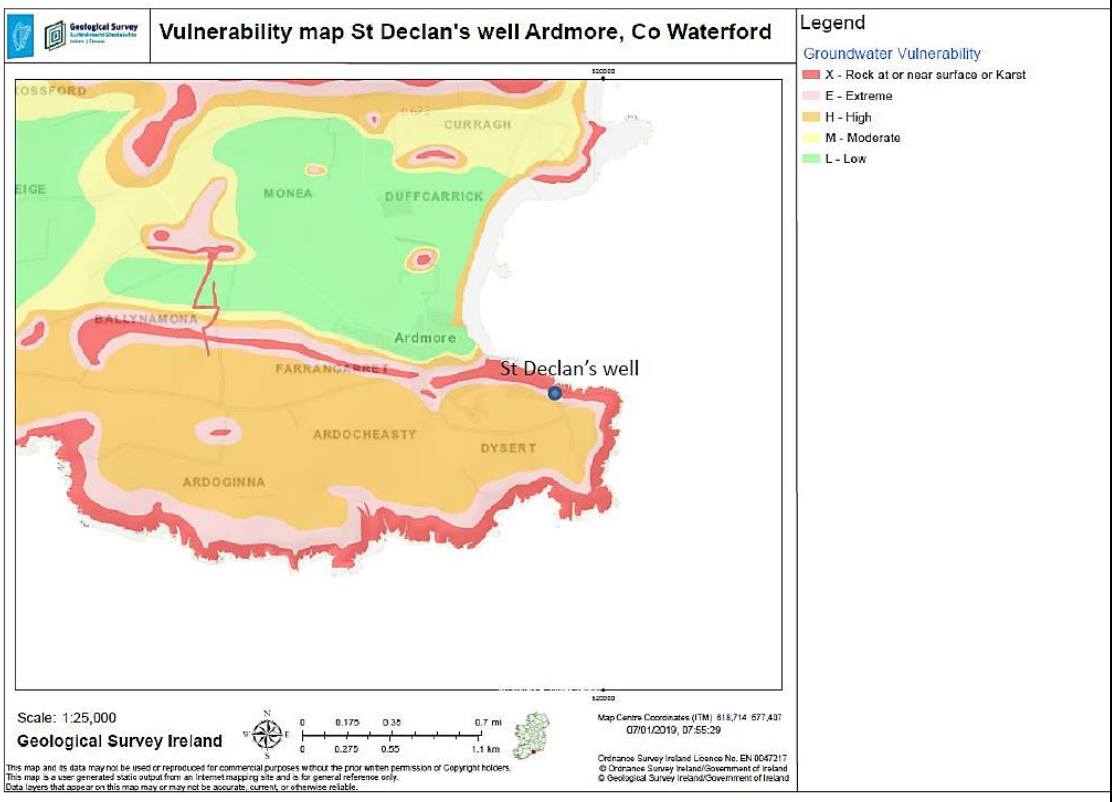

(Image produced using the GSI Groundwater Viewer)

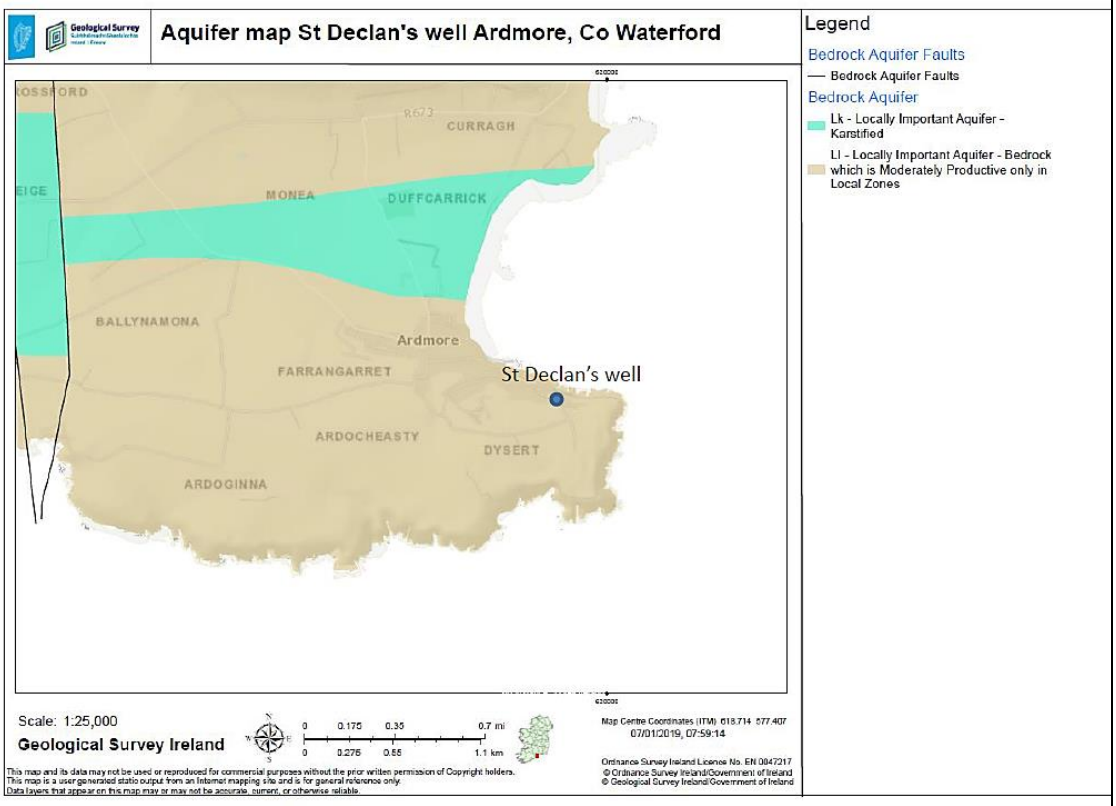



(Image produced using the GSI Groundwater Viewer)


Subsoil map St Declan's well Ardmore, Co Waterford
Legend
Quaternary Sediments
A, Alluvium
KaRck, Kartsified bedrock outcrop or subcrop
Mbs, Marine beach sands
Pier
Rck, Bedrock outcrop or subcrop
TDSs, Till derived from Devonian sandstones
CURRAGH
MONEA
DUFFCARRICK
BALLYNAMONA
Ardmore
FARRANGARRET
St Declan's well
ARDOCHEASTY
DYSERT
ARDOGINNA
Scale: 1:25,000
Geological Survey Ireland
Map Centre Coordinates (ITM) 618,714 577,407
07/01/2019, 07:43:36
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Bedrock map St Declan's well Ardmore, Co Waterford
Legend
Bedrock Structural Symbols
Dip of bedding or main foliation, old GSI data
Strike and dip of bedding, right way up
Strike and dip of first foliation
Bedrock Stratigraphic and Structural lines
Fault
Thin stratigraphical unit, diagrammatic
Bedrock Outcrop
Bedrock Outcrop
Bedrock Rock Units
Ballysteen Formation
Crows Point Formation
Waulsortian Limestones
Ballyquinn Member (Gyleen Formation)
Ardmore Member (Gyleen Member)
CURRAGH
MONEA
DUFFCARRICK
Ardmore
FARRANGARRET
St Declan's well
ARDOCHEASTY
DYSERT
ARDOGINNA
Scale: 1:25,000
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Vulnerability map St Declan's well Ardmore, Co Waterford
Legend
Groundwater Vulnerability
X - Rock at or near surface or Karst
E - Extreme
H - High
M - Moderate
L - Low
CURRAGH
MONEA
DUFFCARRICK
BALLYNAMONA
Ardmore
FARRANGARRET
St Declan's well
ARDOCHEASTY
DYSERT
ARDOGINNA
Scale: 1:25,000
Geological Survey Ireland
Map Centre Coordinates (ITM) 618,714 577,497
07/01/2019, 07:55:29


Aquifer map St Declan's well Ardmore, Co Waterford
Legend
Bedrock Aquifer Faults
Bedrock Aquifer Faults
Bedrock Aquifer
Lk - Locally Important Aquifer - Karstified
Ll - Locally Important Aquifer - Bedrock which is Moderately Productive only in Local Zones
CURRAGH
MONEA
DUFFCARRICK
BALLYNAMONA
Ardmore
FARRANGARRET
St Declan's well
ARDOCHEASTY
DYSERT
ARDOGINNA
Scale: 1:25,000
Geological Survey Ireland
Map Centre Coordinates (ITM) 618,714 577,497
07/01/2019, 07:59:14

**Well name: Cranavane holy well, Co Carlow**

| | | | |
|---|---|---|---|
| Location / Townland | | Ballinvalley townland, west of Kildavin | |
| Grid reference | Irish Grid | S 86315 60561 (lower well); S 86338 60589 (upper well) | |
| | ITM | 686248E 660605N (lower well); 686273E 660634N (upper well) | |
| Latitude / Longitude (degrees) | | N052.68972 W006.72421 (lower well); N052.68997 W006.72384 (upper well) | OSI Discovery map Nr 61 |
| Date(s) visited: | | 5/11/2016 (09.00 hrs); 10/11/2016 (15.30 hrs) | |
| Access | | The Cranavane site is on the north side of the R724, about 3 km west of Kildavin. The (lower) well is about 135 m from the road, accessible by a good track. The upper well is the one shown on the 1:50,000 OSI map and on the historical 25 inch map, whilst the lower well is marked on the historical 6 inch map. The well is referred to as Tobercranan on the historical maps. | |
| Well description | | There are two wells at this attractive site, a lower well which discharges into a "coffin trough" and an upper well about 30 m north (upslope). The lower well is contained within a large dry stone wall structure, measuring roughly 6 m long x 3m wide x 1.5 m high. The portal to the well chamber is 1.1 m high and 0.5 m wide, and the well inside measures approximately 0.3 m wide and 0.6 m from front to back. At the time of the visits in November 2016, it contained only a few cm of water.<br>The coffin trough immediately below the lower well is about 5 m long and 1.2 m wide at its maximum width.<br>The upper well is in the northeast corner of a dry stone walled area, with a laurel tree growing over it (the area around the wells is rich with trees – ash, hawthorn, blackthorn, scots pine, birch). The upper well measures roughly 1.1 x 1.2 m and is lined with large stones. It contained about 10 cm of water on 5/11/16 (but there were a lot of leaves and mud, so this depth is very approximate). | |
| Reputed cures | | The signboard at the entrance to the site refers to "soreness of eyes, pains and hurt limbs, and other body ailments". | |
| Topography | | The land slopes to the south to a river about 200 m away, on the south side of the R724. | |
| Elevation (m above OD) | | 126 (lower well); 128 (upper well). | |
| Geology | Superficial | Granite till (TGr), but with bedrock close to surface (Rck). | |
| | Bedrock | According to the geology map, the site is on Ordovician metasediments (slates, schists and phyllites belonging to the Maulin Formation), but close to the contact with granites immediately to the north. These formations are referred to as Ordovician Metasediments (OM) and Granites and other Igneous Intrusive rocks (GII), respectively, in the Groundwater Rock Unit classification. | |

| | | |
|---|---|---|
| | Structural features | The bedding strike is ENE-WSW. There is a NW-SE fault southeast of the well site (and which is aligned with the well location if it continues to the NW). The metasediments and granites in the area are also cross cut by north-south faulting. |
| Hydrogeology | Description | The lower well is presumably fed by the same source as the upper well (although there was no evidence visible of a direct pipe connection between the two wells).<br>The upper well is close to the contact between the Ordovician metasediments and the granite intrusion further upslope, and so this contact may have a bearing on the hydrogeology. As noted above, the well is also on the same alignment as a NW-SE fault shown on the map southeast of the well site, which might also be an influence on the well hydrogeology (if it extends further in that direction).<br>Two boreholes in Ballinvalley in the vicinity of the holy well are shown in the GSI's Groundwater Viewer. One was drilled in 1972 to 37.8 m (the depth to rock is not recorded), and yielded 49 $m^3$ $d^{-1}$; the second was drilled in 1974 to 28 m and gave a yield of 25 $m^3$ $d^{-1}$. The locational accuracy of the wells is 500m and 1 km, respectively, and so it is not known whether they tapped the metasediments or granites. |
| | Depth to water<br>(m below ref point) | 0.27 m below the stone floor in the well chamber (lower well) (5/11/16).<br>0.05 m below the lowermost stone on the left side of the well (upper well) (5/11/16 and 10/11/16). |
| | Aquifer class | Ll (metasediments), Pl (granites) |
| | Vulnerability | X Extreme (near boundary with E Extreme) |
| Water quality | EC (µS $cm^{-1}$) | 204 (upper well, 5/11/16); 223 (coffin trough, 5/11/16).<br>204 (upper well, 10/11/16) |
| | Temperature ($^oC$) | 7.0 (upper well); 5.2 (coffin trough – similar to air temperature), (5/11/16).<br>8.4 (upper well, 10/11/16) |
| | pH | 6.2 (upper well); 6.4 (coffin trough); but meter reading slow to stabilise for both measurements (5/11/16).<br>5.54 (upper well, 10/11/16) |
| | Sample collected? | Y, from upper well (10/11/16) – SHW 15 |
| | Sample appearance | Clear (but some leaf debris) |
| | Weather conditions | Dry, 5 $^oC$ (5/11/16); dry, 7 $^oC$, but heavy rain 2 days previously (10/11/16) |
| Potential pollution sources nearby? | | The site is surrounded by fields |

| | |
|---|---|
| Additional comments | The signboard mentions that the well name derives from *Crann a Bhán*, white tree. The patron day is 3rd May. The pilgrimage was banned in 1798, but recommenced in the early 19th century until it was banned again by a priest in the 1870s owing to some disturbances. The restoration of this site began in 1998, and included the building of stone cairns, benches, etc. Some further details are available at: https://pilgrimagemedievalireland.com/2016/07/13/cranavane-holy-well-co-carlow/ (accessed 2/7/2020) This website mentions that the well has no patron, but that it was probably dedicated at one time to St Finian. The tradition of dipping coffins in the trough before burial at the nearby Barragh graveyard is also mentioned. |

Photos:




Sign to Cranavane well at side of R724 road



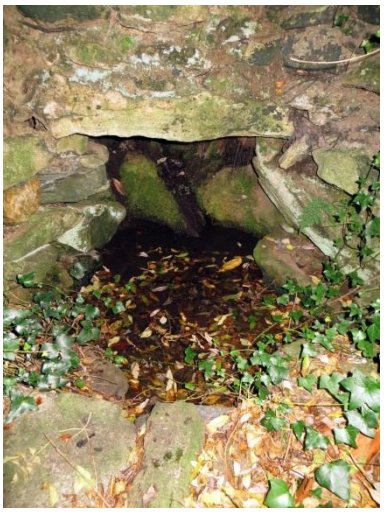
View of well site from the south. The wells are in the copse of trees in the centre of the picture, accessed by the tree-lined track



The well house containing the lower well, which discharges into the coffin trough



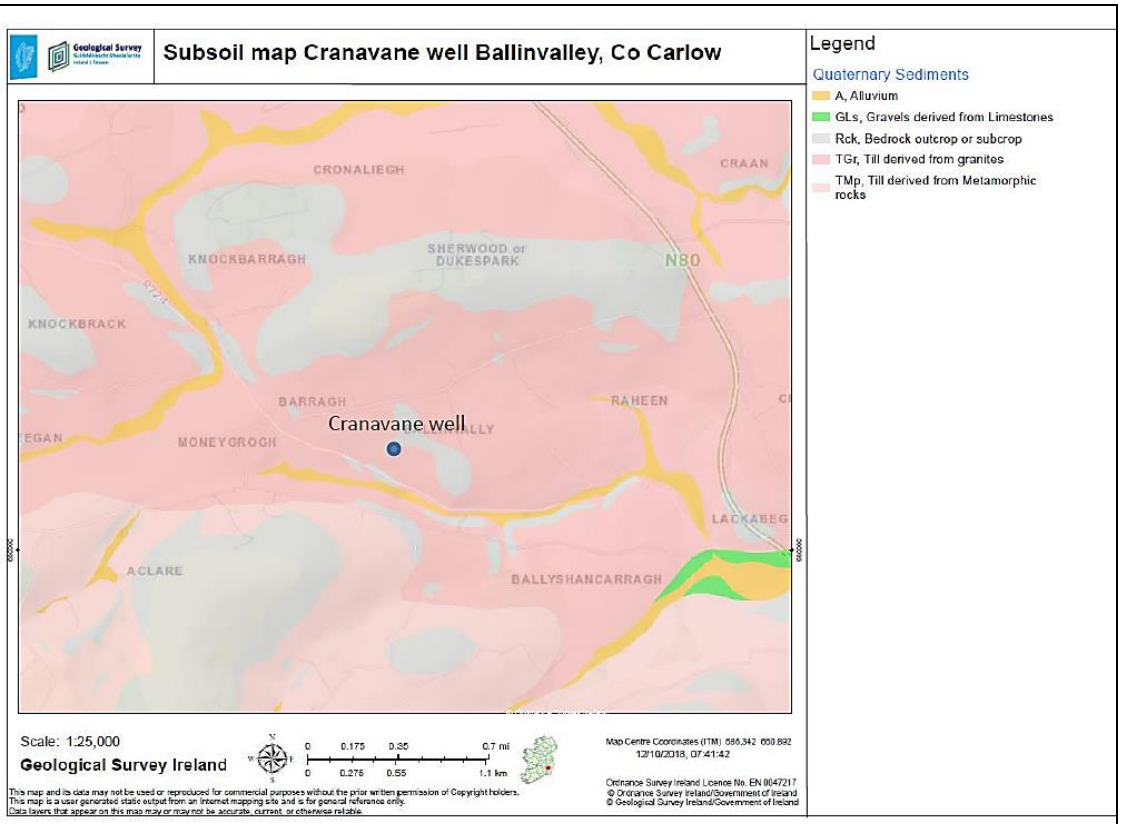
The rear of the well house of the lower well

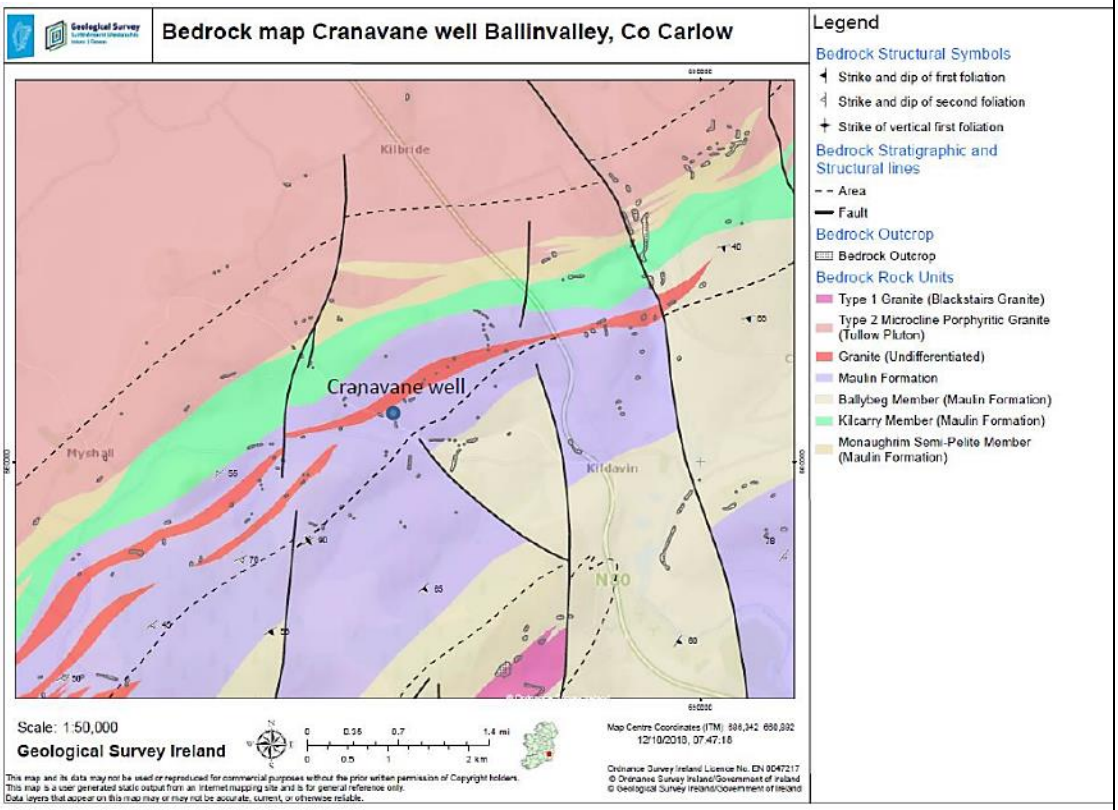
| | | |
|---|---|---|
|  |  |  |
| The coffin trough | The upper well | The upper well |

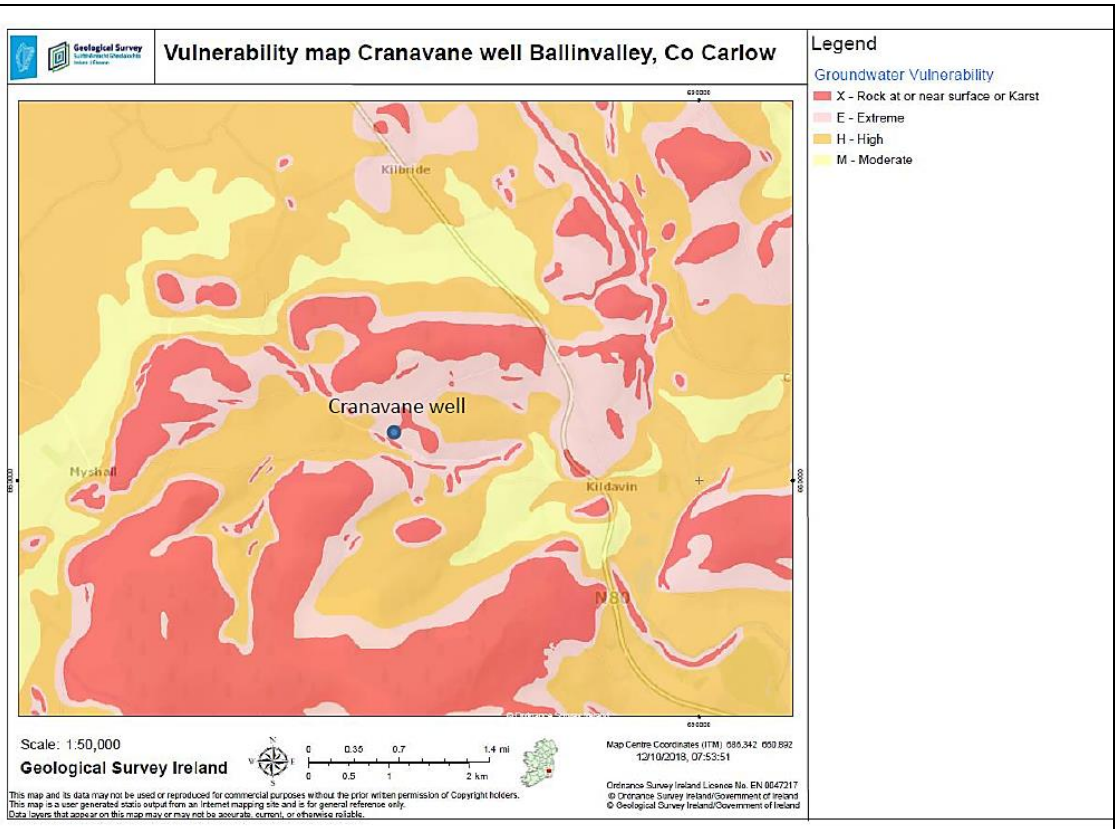
Maps:

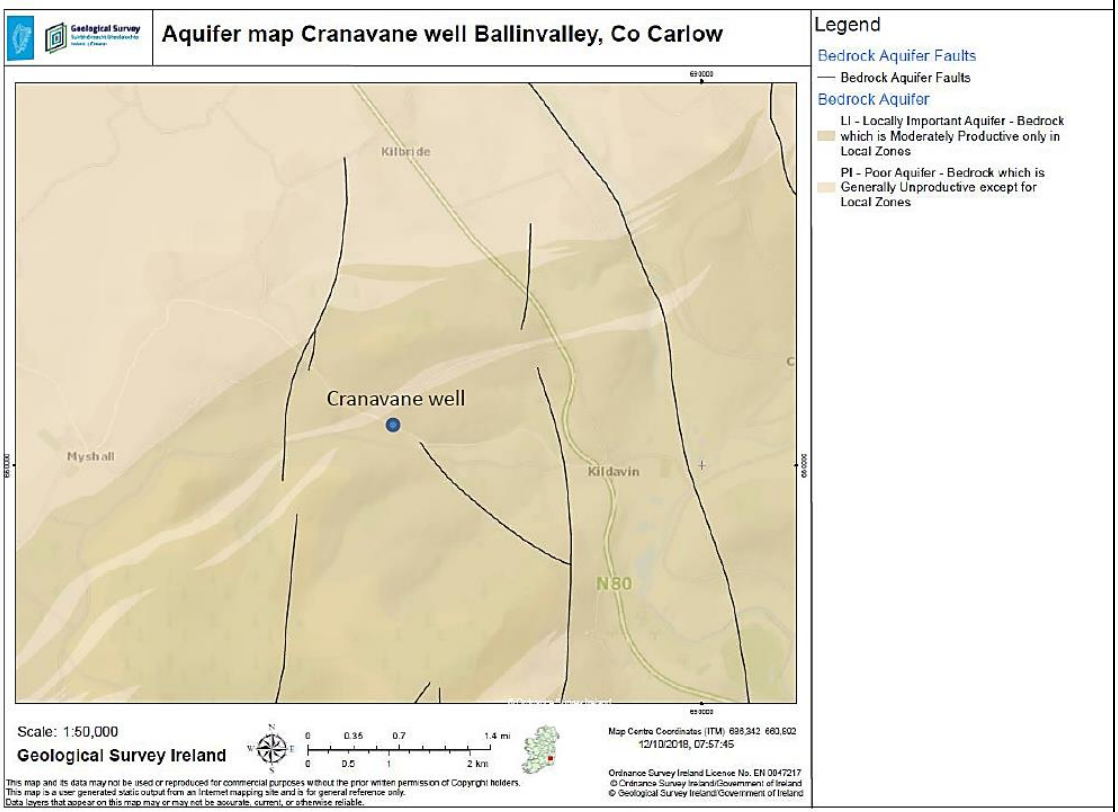



(Image produced using the GSI Groundwater Viewer)


Subsoil map Cranavane well Ballinvalley, Co Carlow
Legend
Quaternary Sediments
A, Alluvium
GLs, Gravels derived from Limestones
Rck, Bedrock outcrop or subcrop
TGr, Till derived from granites
TMp, Till derived from Metamorphic rocks
CRONALIEGH
CRAAN
KNOCKBARRAGH
SHERWOOD or DUKESPARK
N80
KNOCKBRACK
BARRAGH
RAHEEN
Cranavane well
MONEYGROGH
LACKABEG
ACLARE
BALLYSHANCARRAGH
Scale: 1:25,000
Geological Survey Ireland
Map Centre Coordinates (ITM): 686,342 660,892
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Bedrock map Cranavane well Ballinvalley, Co Carlow
Legend
Bedrock Structural Symbols
Strike and dip of first foliation
Strike and dip of second foliation
Strike of vertical first foliation
Bedrock Stratigraphic and Structural lines
Area
Fault
Bedrock Outcrop
Bedrock Outcrop
Bedrock Rock Units
Type 1 Granite (Blackstairs Granite)
Type 2 Microcline Porphyritic Granite (Tullow Pluton)
Granite (Undifferentiated)
Maulin Formation
Ballybeg Member (Maulin Formation)
Kilcarry Member (Maulin Formation)
Monaughrim Semi-Pelite Member (Maulin Formation)
Kilbride
Cranavane well
Myshall
Kildavin
N80
Scale: 1:50,000
Geological Survey Ireland
Map Centre Coordinates (ITM): 686,342 660,892
12/10/2018, 07:47:18
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Vulnerability map Cranavane well Ballinvalley, Co Carlow
Legend
Groundwater Vulnerability
X - Rock at or near surface or Karst
E - Extreme
H - High
M - Moderate
Kilbride
Cranavane well
Myshall
Kildavin
N80
Scale: 1:50,000
Geological Survey Ireland
0 0.35 0.7 1.4 mi
0 0.5 1 2 km
Map Centre Coordinates (ITM) 686,342 660,892
12/10/2018, 07:53:51
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Aquifer map Cranavane well Ballinvalley, Co Carlow
Legend
Bedrock Aquifer Faults
Bedrock Aquifer Faults
Bedrock Aquifer
Ll - Locally Important Aquifer - Bedrock which is Moderately Productive only in Local Zones
Pl - Poor Aquifer - Bedrock which is Generally Unproductive except for Local Zones
Kilbride
Cranavane well
Myshall
Kildavin
N80
Scale: 1:50,000
Geological Survey Ireland
0 0.35 0.7 1.4 mi
0 0.5 1 2 km
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Data layers that appear on this map may or may not be accurate, current, or otherwise reliable.

**Well name: St Patrick's well Clonmel, County Tipperary**

| | | | |
|---|---|---|---|
| Location / Townland | | Patrickswell townland, Clonmel | |
| Grid reference | Irish Grid | S 16900 22875 | |
| | ITM | 616846E 622928N | |
| Latitude / Longitude (degrees) | | N052.35766 W007.75266 | OSI Discovery Map Nr: 74 |
| Date(s) visited | | 15/04/2017 (11.00 hrs); 18/05/2017 (13.00 hrs) | |
| Access | | The well is signposted off the Clonmel to Cahir road. It is about 300 m north of Patrickswell crossroads, and is accessed via a gate and steps from the road down into the well site in the valley below.<br>Although not marked on the OSI Discovery map, St Patrick's well is shown on the historical 6 inch and 25 inch maps. | |
| Well description | | The valley bottom site contains a very large oval pond fed by limestone springs (bubbles can be seen rising in the water). The well is to the northwest of the pond and discharges into it.<br>The well is surrounded by a low stone wall and there is a (locked) iron gate at the point of outflow. The well is about 4 m long and up to 2.5 m in width; it has an approximate teardrop shape. The well contained 0.4 m of water when measured in April 2017. The discharge from the spring well occurs via two hollowed rocks (similar to those at St Brigid's well in Kildare) towards the pond; the flow was probably several litres per second, whilst the outflow from the southern end of the pond (through two arched channels in the boundary wall) to the nearby river (a tributary of the Suir) was probably several tens of litres per second in April 2017.<br>The site also contains a large statue of St Patrick alongside the steps leading down from the road, a stone cross in the centre of the pond (5th century according to a local leaflet about the site), and a ruined church (15th century) at the southwest end of the pond. There are stations of the cross around the boundary wall of the site. | |
| Reputed cures | | In the 19th century the well was known for curing sore lips, eyes and other ailments, by drinking or washing in its waters (https://pilgrimagemedievalireland.com/2014/04/12/st-patricks-holy-well-at-marlfield-clonmel/; accessed 19/4/17). | |
| Topography | | Bottom of a north-south oriented glaciated valley, about 2 km from the main valley of the River Suir. | |
| Elevation (m above OD) | | 41 | |
| Geology | Superficial | Karstified limestone bedrock (KaRck) outcrops at the site. The subsoils are alluvium plus tills derived from Namurian sandstones and shales (TNSSs). | |

| | | |
|---|---|---|
| | Bedrock | Massive grey limestone outcrop (with beds up to a metre thick) is visible at the site, especially alongside and behind the statue of St Patrick near the access pathway. The limestones belong to the Kilsheelan Formation (KS), referred to as Dinantian Pure Bedded Limestones (DPBL) in the Groundwater Rock Unit classification. |
| | Structural features | The beds dip gently to the WSW and are cut by sets of steeply dipping joints striking north-south and at 70 degrees. The well site is near the "fork" where a northwest-southeast fault joins (and is cut off by) a NNW-SSE fault (see map). |
| Hydrogeology | Description | The Dinantian PBL is a regionally important karstified aquifer. However, the karst features option in the GSI Groundwater Viewer does not show any karst features at this site. Nor are there any boreholes shown in in the immediate vicinity. The local topography and the presence of the springs here may be influenced by the bedrock faulting.<br>This is designated as a County Geological Site, being 'an excellent example of a limestone spring, in this case housed within a holy well site' (GSI, Geoheritage Report TY049). |
| | Depth to water<br>(m below ref point) | 0.26 m below the surround at the western edge of the well (opposite a small carved panel of the saint) (15/4/17);<br>0.28 m below the surround at the western edge of the well (18/5/17). |
| | Aquifer class | Rkd |
| | Vulnerability | E Extreme and X Extreme |
| Water quality | EC (µS $cm^{-1}$) | 698 (15/4/17); 710 (18/5/17) |
| | Temperature ($^oC$) | 11.3 (15/4/17); 12.2 (18/5/17) |
| | pH | 6.84 (15/4/17); 6.6 (18/5/17) |
| | Sample collected? | Y (18/5/17) – SHW82 (from outflow below entrance gate to well) |
| | Sample appearance | Clear |
| | Weather conditions | Cool, 9 $^oC$ (15/4/17); dry, 13 $^oC$ (18/5/17) |
| Potential pollution sources nearby? | | Pasture in surrounding fields. |
| Additional comments | | There were some coins in the well. Otherwise, the votives were placed at a statue of St Patrick within the old church ruins.<br>An attendant at the site provided a leaflet about the well, which refers to it as a place of pilgrimage since pre-Christian times, before Patrick came to the site and baptised people here. The |

| | |
|---|---|
| | well is in the former parish of Inishlounaght, and in the present day parish of St Mary's Irishtown. The leaflet describes the performances associated with the rounds, which include drinking the well water. The attendant mentioned that it was traditional for locals to visit this well on all days of the week except Fridays, when they would visit the nearby Toberaheena (Friday's well) instead.<br><br>Some further information about the site and its history is given at http://irelandsholywells.blogspot.ie/2012/06/saint-patricks-well-clonmel.html (accessed 12/4/17) and especially at https://pilgrimagemedievalireland.com/2014/04/12/st-patricks-holy-well-at-marlfield-clonmel/ (accessed 19/4/17). The latter includes an interesting photo from the early 20th century that shows the well before the more recent landscaping works: there is an ash tree growing out of the well, which is surrounded by a rough stone wall. The water can be seen discharging through the two hollowed stones. The website refers to the modern landscaping works as dating mainly from the late 1960s. |

Photos:



The large pond fed by limestone springs, including St Patrick's well (the stone enclosure on the right of the picture)



Water from St Patrick's well discharges through two hollowed rocks (which can be seen below the iron gate)



The steps down to St Patrick's well site (the walled enclosure surrounding the well can be seen through the trees, on the far side of the pond)



A statue of St Patrick in front of beds of massive grey limestone



The channel leading away from the well



Discharge from the southern end of the pond to the nearby river



The teardrop shape of the well



Looking from the well outflow towards the large pond

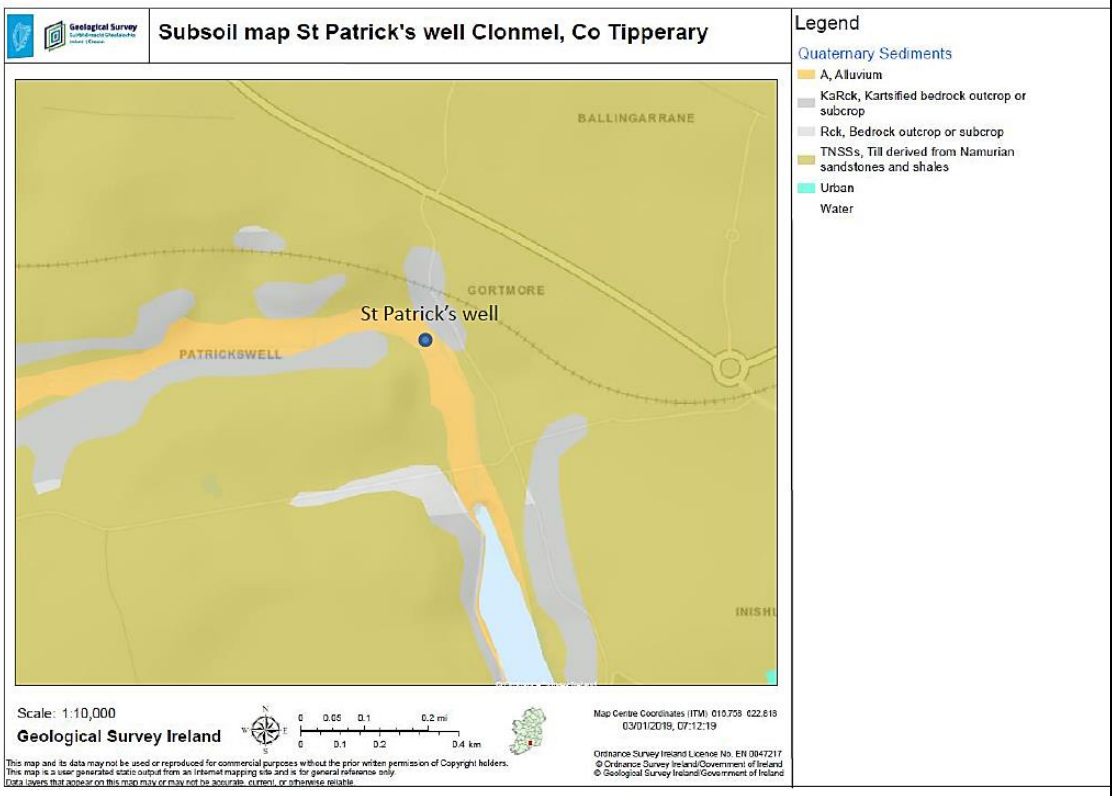


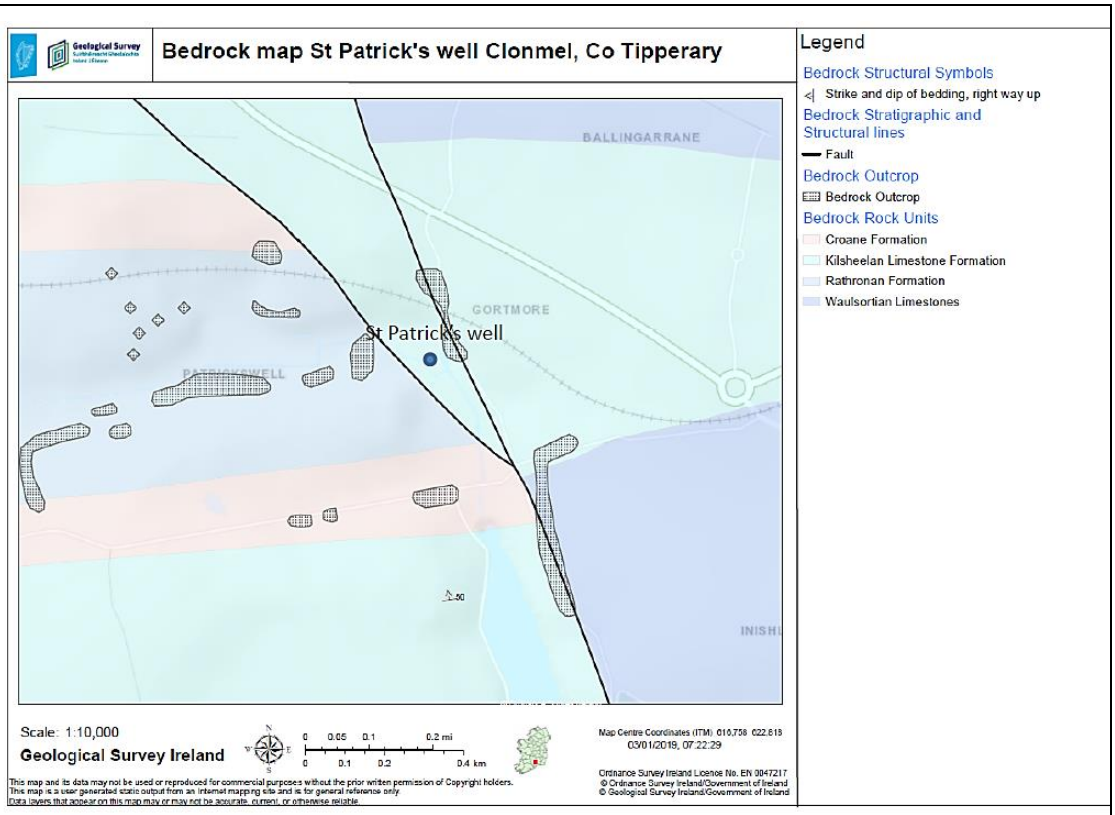

Plaque acknowledging some of the funding for the restoration work at St Patrick's well

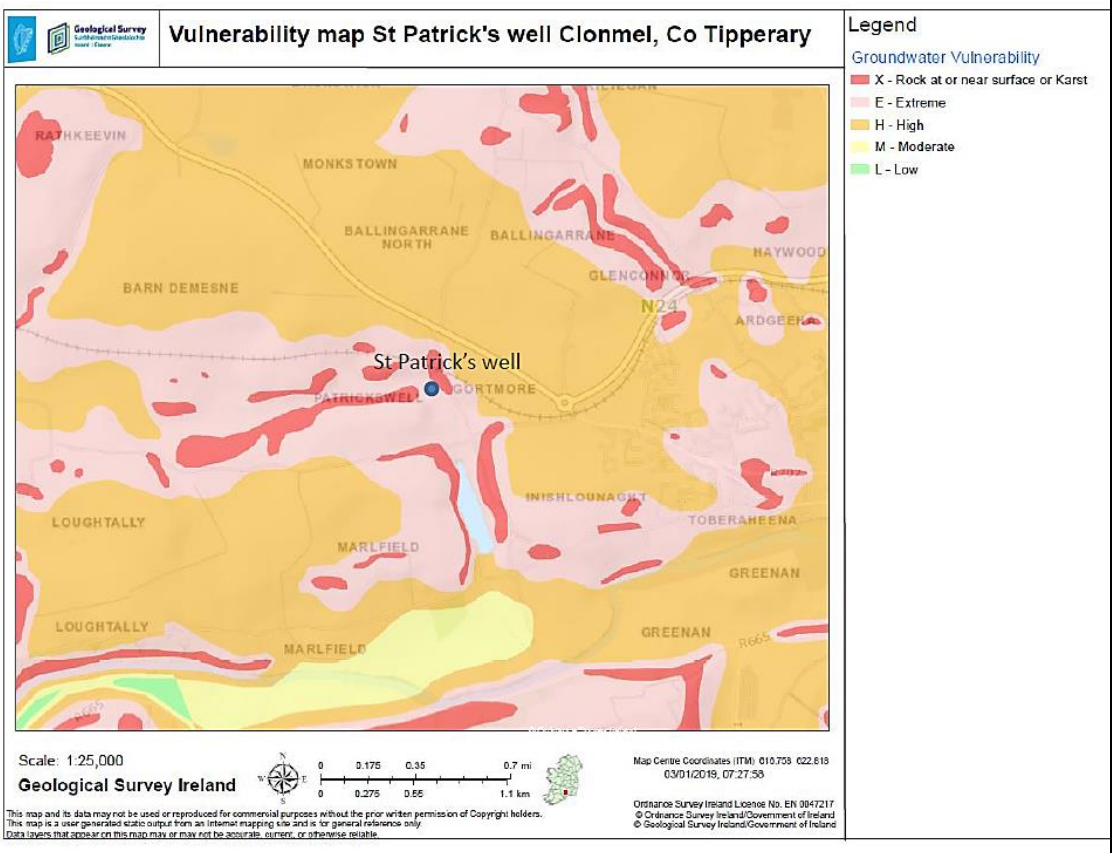
## Maps

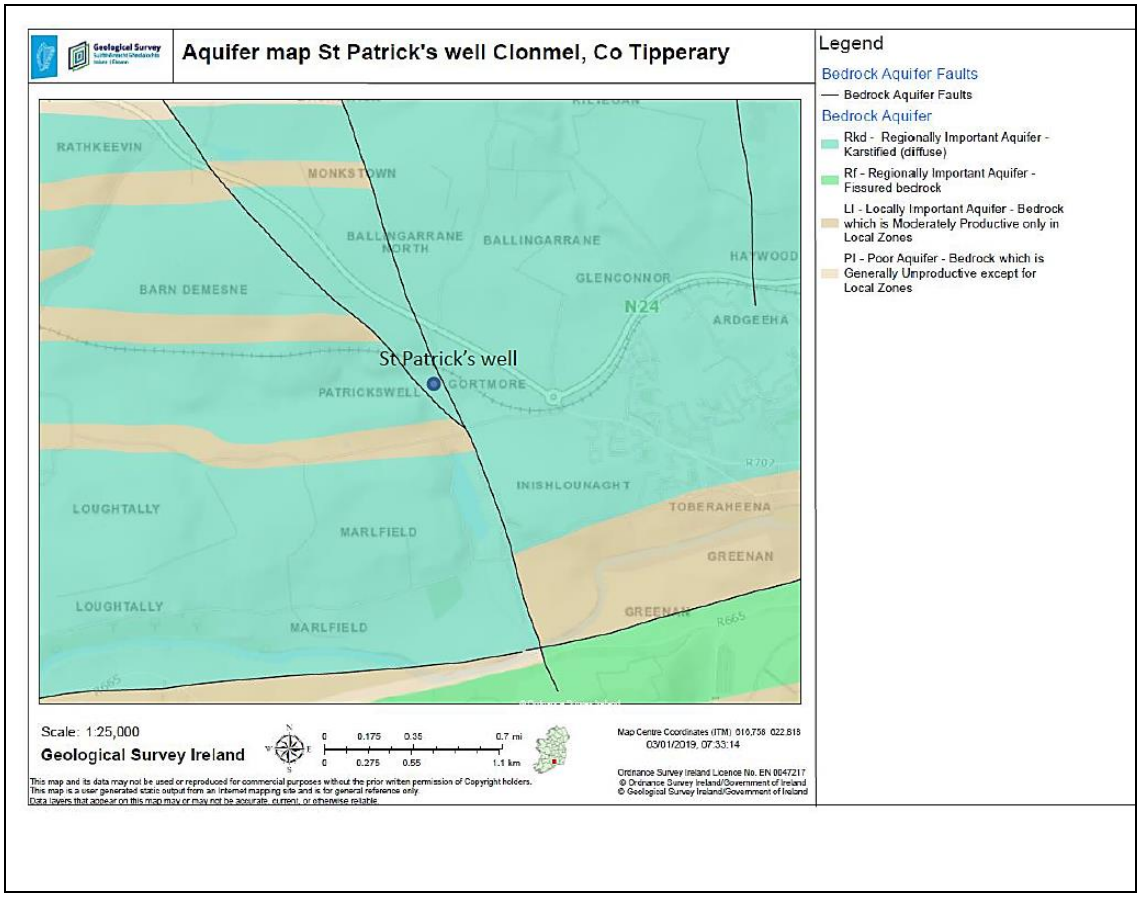



(Image produced using the GSI Groundwater Viewer)




Bedrock map St Patrick's well Clonmel, Co Tipperary
Legend
Bedrock Structural Symbols
Strike and dip of bedding, right way up
Bedrock Stratigraphic and Structural lines
Fault
Bedrock Outcrop
Bedrock Outcrop
Bedrock Rock Units
Croane Formation
Kilsheelan Limestone Formation
Rathronan Formation
Waulsortian Limestones
BALLINGARRANE
GORTMORE
St Patrick's well
PATRICKSWELL
Scale: 1:10,000
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Map Centre Coordinates (ITM): 610,758 622,618
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Vulnerability map St Patrick's well Clonmel, Co Tipperary
Legend
Groundwater Vulnerability
X - Rock at or near surface or Karst
E - Extreme
H - High
M - Moderate
L - Low
RATHKEEVIN
MONKSTOWN
BALLINGARRANE NORTH
BALLINGARRANE
HAYWOOD
GLENCONNOR
BARN DEMESNE
N24
ARDGEEHA
St Patrick's well
GORTMORE
PATRICKSWELL
INISHLOUNAGHT
TOBERAHEENA
LOUGHTALLY
MARLFIELD
GREENAN
LOUGHTALLY
MARLFIELD
GREENAN
R665
Scale: 1:25,000
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Aquifer map St Patrick's well Clonmel, Co Tipperary
Legend
Bedrock Aquifer Faults
Bedrock Aquifer Faults
Bedrock Aquifer
Rkd - Regionally Important Aquifer - Karstified (diffuse)
Rf - Regionally Important Aquifer - Fissured bedrock
Ll - Locally Important Aquifer - Bedrock which is Moderately Productive only in Local Zones
Pl - Poor Aquifer - Bedrock which is Generally Unproductive except for Local Zones
RATHKEEVIN
MONKSTOWN
BALLINGARRANE NORTH
BALLINGARRANE
HATWOOD
GLENCONNOR
BARN DEMESNE
N24
ARDGEEHA
St Patrick's well
PATRICKSWELL
GORTMORE
INISHLOUNAGHT
TOBERAHEENA
LOUGHTALLY
MARLFIELD
GREENAN
LOUGHTALLY
MARLFIELD
GREENAN
Scale: 1:25,000
Geological Survey Ireland
0 0.175 0.35 0.7 mi
0 0.275 0.55 1.1 km
Map Centre Coordinates (ITM) 610,758 622,818
03/01/2019, 07:33:14
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# Appendix C Hydrochemical data

Tables C.1 to C.7 present the summary descriptive statistics for minor ions and trace elements for each lithological group, whilst Table C.8 to C.14 include the rare earth element statistics.

Table C.1 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.8) for the **impure limestone** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 23 | 0.165 | 0.533 | 1.279 | 0.012 | 0.015 | 0.28 | 3.86 | 22.66 | 33.49 |
| Antimony (Sb) | ng $l^{-1}$ | 26 | 0.75 | 1.83 | 4.03 | 1.039 | 12.41 | 78.31 | 86.72 | 126.7 | 475.4 |
| Arsenic (As)[a] | µg $l^{-1}$ | 26 | 0.013 | 0.018 | 0.027 | 0.073 | 0.116 | 0.38 | 0.66 | 1.76 | 3.50 |
| Barium (Ba) | µg $l^{-1}$ | 26 | 0.011 | 0.016 | 0.027 | 6.921 | 9.583 | 40.94 | 62.97 | 244.7 | 301.7 |
| Beryllium (Be) | ng $l^{-1}$ | 26 | 0.165 | 0.391 | 0.851 | 0.155 | 0.406 | 1.59 | 4.86 | 20.58 | 32.5 |
| Cadmium (Cd) | ng $l^{-1}$ | 25 | 0.1 | 0.29 | 0.67 | 1.211 | 1.659 | 17.81 | 23.52 | 114.2 | 137.4 |
| Caesium (Cs) | ng $l^{-1}$ | 26 | 0.06 | 0.1 | 0.19 | 0.302 | 0.85 | 3.89 | 13.73 | 30.9 | 196.3 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 21 | 0.158 | 0.194 | 0.269 | 0.089 | 0.103 | 0.33 | 0.389 | 0.79 | 1.49 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 26 | 0.006 | 0.008 | 0.011 | 0.041 | 0.087 | 0.18 | 0.355 | 0.87 | 3.25 |
| Copper (Cu) | µg $l^{-1}$ | 26 | 0.015 | 0.023 | 0.039 | 0.164 | 0.202 | 1.09 | 1.30 | 3.47 | 4.58 |
| Fluoride (F) | µg $l^{-1}$ | 26 | | 100 | | 34.0 | 39.3 | 89.6 | 104.9 | 205 | 517 |
| Gallium (Ga) | ng $l^{-1}$ | 26 | 0.25 | 0.45 | 0.86 | 0.024 | 0.133 | 0.876 | 3.58 | 20.4 | 28.0 |
| Hafnium (Hf) | ng $l^{-1}$ | 21 | 0.070 | 0.140 | 0.300 | 0.028 | 0.03 | 0.247 | 1.19 | 6.66 | 8.31 |
| Indium (In) | ng $l^{-1}$ | 21 | 0.050 | 0.140 | 0.320 | 0.006 | 0.007 | 0.028 | 0.07 | 0.31 | 0.46 |
| Iron (Fe) | µg $l^{-1}$ | 26 | 8.761 | 9.046 | 9.624 | 95.9 | `126.6 | 426.1 | 719 | 1150 | 5154 |
| Lead (Pb) | ng $l^{-1}$ | 19 | 4.320 | 15.99 | 39.68 | 0.385 | 2.241 | 10.85 | 51.6 | 203.7 | 395 |
| Lithium (Li) | µg $l^{-1}$ | 26 | 0.122 | 0.137 | 0.167 | 0.148 | 0.299 | 1.28 | 2.86 | 4.7 | 37.1 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 26 | 0.046 | 0.063 | 0.10 | 0.01 | 0.03 | 1.16 | 71.13 | 215.7 | 1062 |
| Molyb'num (Mo) | ng $l^{-1}$ | 26 | 0.50 | 1.44 | 3.33 | 34.16 | 41.99 | 330.4 | 594.6 | 1508 | 3937 |
| Nickel (Ni) | µg $l^{-1}$ | 26 | 0.007 | 0.014 | 0.028 | 0.535 | 0.836 | 1.978 | 2.33 | 5.53 | 7.71 |
| Niobium (Nb) | ng $l^{-1}$ | 25 | 0.110 | 0.210 | 0.400 | 0.039 | 0.082 | 0.372 | 1.820 | 10.12 | 17.3 |
| Phosphorus (P) | µg $l^{-1}$ | 23 | 22.38 | 23.96 | 27.18 | 1.534 | 2.228 | 49.66 | 125.3 | 558.7 | 710.9 |
| Rubidium (Rb) | µg $l^{-1}$ | 26 | 0.001 | 0.001 | 0.002 | 0.146 | 0.224 | 0.800 | 1.14 | 2.79 | 2.96 |
| Scandium (Sc) | µg $l^{-1}$ | 26 | 0.046 | 0.049 | 0.055 | 0.239 | 0.309 | 0.767 | 0.760 | 1.19 | 1.38 |
| Selenium (Se) | ng $l^{-1}$ | 14 | 7.421 | 10.62 | 17.13 | 7.01 | 13.08 | 45.62 | 55.95 | 122.9 | 133.7 |
| Strontium (Sr) | µg $l^{-1}$ | 26 | 0.039 | 0.049 | 0.067 | 93.7 | 123.2 | 297.8 | 405.7 | 908.8 | 2007 |
| Tantalum (Ta) | ng $l^{-1}$ | 18 | 0.020 | 0.050 | 0.100 | 0.0000 | 0.0008 | 0.016 | 0.033 | 0.128 | 0.265 |
| Thallium (Tl) | ng $l^{-1}$ | 26 | 0.230 | 0.350 | 0.600 | 0.640 | 0.839 | 2.89 | 12.46 | 69.2 | 103.2 |
| Thorium (Th) | ng $l^{-1}$ | 26 | 0.030 | 0.130 | 0.340 | 0.015 | 0.023 | 0.1 | 1.03 | 2.06 | 17.1 |
| Tin (Sn) | ng $l^{-1}$ | 22 | 2.780 | 4.900 | 9.200 | 0.333 | 0.409 | 2.12 | 4.34 | 14.9 | 17.3 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 26 | 0.056 | 0.095 | 0.174 | 0.114 | 0.124 | 0.357 | 0.62 | 2.16 | 2.96 |
| Tungsten (W) | ng $l^{-1}$ | 15 | 1.010 | 1.490 | 2.460 | 0.032 | 0.062 | 0.452 | 3.65 | 18.9 | 21.6 |
| Uranium (U) | ng $l^{-1}$ | 26 | 0.330 | 0.440 | 0.660 | 78.93 | 119.6 | 772.9 | 1251 | 2707 | 11150 |
| Vanadium (V)[a] | µg $l^{-1}$ | 20 | 0.042 | 0.053 | 0.074 | 0.003 | 0.004 | 0.320 | 0.337 | 0.733 | 0.82 |
| Yttrium (Y) | ng $l^{-1}$ | 26 | 0.105 | 0.421 | 1.064 | 7.716 | 11.46 | 66.6 | 92.97 | 299.6 | 508 |
| Zircon (Zr) | ng $l^{-1}$ | 25 | 0.800 | 1.400 | 2.630 | 1.509 | 2.919 | 13.49 | 54.87 | 321.2 | 449 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 11 | 0.088 | 0.287 | 0.692 | 0.033 | 0.104 | 1.795 | 3.95 | 15.59 | 26.9 |

Note: [a] Results prone to chloride interferences

Table C.2 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.9) for the **pure limestone** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 34 | 0.165 | 0.533 | 1.279 | 0.006 | 0.022 | 1.13 | 4.51 | 13.07 | 81.9 |
| Antimony (Sb) | ng $l^{-1}$ | 35 | 0.75 | 1.83 | 4.03 | 17.87 | 19.94 | 48.92 | 68.11 | 140.1 | 374.2 |
| Arsenic (As)[a] | µg $l^{-1}$ | 35 | 0.013 | 0.018 | 0.027 | 0.103 | 0.121 | 0.296 | 1.08 | 1.68 | 23.5 |
| Barium (Ba) | µg $l^{-1}$ | 35 | 0.011 | 0.016 | 0.027 | 1.387 | 1.604 | 14.51 | 30.77 | 122.6 | 256.9 |
| Beryllium (Be) | ng $l^{-1}$ | 35 | 0.165 | 0.391 | 0.851 | 0.438 | 0.835 | 2.175 | 2.68 | 4.81 | 13.95 |
| Cadmium (Cd) | ng $l^{-1}$ | 35 | 0.1 | 0.29 | 0.67 | 2.095 | 3.766 | 15.7 | 18.34 | 47.1 | 53.5 |
| Caesium (Cs) | ng $l^{-1}$ | 35 | 0.06 | 0.1 | 0.19 | 0.354 | 0.639 | 3.046 | 16.04 | 46.4 | 302.1 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 31 | 0.158 | 0.194 | 0.269 | 0.113 | 0.158 | 0.417 | 2.54 | 1.52 | 63.4 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 35 | 0.006 | 0.008 | 0.011 | 0.047 | 0.076 | 0.129 | 0.184 | 0.34 | 1.13 |
| Copper (Cu) | µg $l^{-1}$ | 35 | 0.015 | 0.023 | 0.039 | 0.137 | 0.364 | 0.828 | 2.323 | 10.97 | 20.3 |
| Fluoride (F) | µg $l^{-1}$ | 33 | | 100 | | 16.8 | 22.4 | 80.9 | 98.9 | 271.6 | 486 |
| Gallium (Ga) | ng $l^{-1}$ | 35 | 0.25 | 0.45 | 0.86 | 0.295 | 0.364 | 1.201 | 3.001 | 9.51 | 34.9 |
| Hafnium (Hf) | ng $l^{-1}$ | 31 | 0.070 | 0.140 | 0.300 | 0.036 | 0.068 | 0.293 | 0.461 | 1.50 | 2.22 |
| Indium (In) | ng $l^{-1}$ | 28 | 0.050 | 0.140 | 0.320 | 0.001 | 0.009 | 0.046 | 2.701 | 0.190 | 74.0 |
| Iron (Fe) | µg $l^{-1}$ | 35 | 8.761 | 9.046 | 9.624 | 126.6 | 147.5 | 312.1 | 447.6 | 1108.7 | 1570 |
| Lead (Pb) | ng $l^{-1}$ | 31 | 4.320 | 15.99 | 39.68 | 0.068 | 0.469 | 12.09 | 25.95 | 82.99 | 183.9 |
| Lithium (Li) | µg $l^{-1}$ | 35 | 0.122 | 0.137 | 0.167 | 0.040 | 0.085 | 0.732 | 9.37 | 3.19 | 293.7 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 33 | 0.046 | 0.063 | 0.10 | 0.028 | 0.039 | 0.974 | 11.09 | 53.75 | 70.9 |
| Molyb'num (Mo) | ng $l^{-1}$ | 35 | 0.50 | 1.44 | 3.33 | 17.78 | 43.45 | 150.6 | 495.8 | 1143.9 | 9373 |
| Nickel (Ni) | µg $l^{-1}$ | 35 | 0.007 | 0.014 | 0.028 | 0.434 | 0.540 | 1.301 | 1.706 | 3.59 | 8.32 |
| Niobium (Nb) | ng $l^{-1}$ | 32 | 0.110 | 0.210 | 0.400 | 0.071 | 0.099 | 0.416 | 0.687 | 1.76 | 3.99 |
| Phosphorus (P) | µg $l^{-1}$ | 30 | 22.38 | 23.96 | 27.18 | 1.296 | 3.334 | 16.33 | 133.6 | 81.68 | 3299 |
| Rubidium (Rb) | µg $l^{-1}$ | 35 | 0.001 | 0.001 | 0.002 | 0.210 | 0.224 | 0.725 | 4.11 | 4.02 | 108.2 |
| Scandium (Sc) | µg $l^{-1}$ | 35 | 0.046 | 0.049 | 0.055 | 0.041 | 0.085 | 0.479 | 0.526 | 1.02 | 1.55 |
| Selenium (Se) | ng $l^{-1}$ | 18 | 7.421 | 10.62 | 17.13 | 8.60 | 10.90 | 41.36 | 60.34 | 186.2 | 193.5 |
| Strontium (Sr) | µg $l^{-1}$ | 35 | 0.039 | 0.049 | 0.067 | 18.36 | 70.21 | 192.6 | 430.2 | 809.2 | 6647 |
| Tantalum (Ta) | ng $l^{-1}$ | 23 | 0.020 | 0.050 | 0.100 | 0.001 | 0.001 | 0.015 | 0.023 | 0.085 | 0.101 |
| Thallium (Tl) | ng $l^{-1}$ | 35 | 0.230 | 0.350 | 0.600 | 1.067 | 1.343 | 6.368 | 26.38 | 33.63 | 626.9 |
| Thorium (Th) | ng $l^{-1}$ | 34 | 0.030 | 0.130 | 0.340 | 0.009 | 0.035 | 0.217 | 0.902 | 4.55 | 8.01 |
| Tin (Sn) | ng $l^{-1}$ | 33 | 2.780 | 4.900 | 9.200 | 0.273 | 0.841 | 1.98 | 6.69 | 29.49 | 49.0 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 35 | 0.056 | 0.095 | 0.174 | 0.085 | 0.094 | 0.219 | 1.101 | 0.787 | 29.0 |
| Tungsten (W) | ng $l^{-1}$ | 22 | 1.010 | 1.490 | 2.460 | 0.042 | 0.073 | 0.436 | 1.90 | 9.55 | 13.3 |
| Uranium (U) | ng $l^{-1}$ | 35 | 0.330 | 0.440 | 0.660 | 14.88 | 139.31 | 670.7 | 823.1 | 2110 | 2647 |
| Vanadium (V)[a] | µg $l^{-1}$ | 29 | 0.042 | 0.053 | 0.074 | 0.012 | 0.033 | 0.220 | 1.116 | 1.307 | 23.7 |
| Yttrium (Y) | ng $l^{-1}$ | 35 | 0.105 | 0.421 | 1.064 | 9.462 | 17.13 | 58.19 | 81.72 | 218.0 | 348.9 |
| Zircon (Zr) | ng $l^{-1}$ | 34 | 0.800 | 1.400 | 2.630 | 4.107 | 4.366 | 14.07 | 21.82 | 61.95 | 94.9 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 15 | 0.088 | 0.287 | 0.692 | 0.051 | 0.927 | 2.764 | 9.92 | 39.77 | 77.6 |

Note: [a] Results prone to chloride interferences

Table C.3 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.10) for the **non-calcareous sedimentary** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 31 | 0.165 | 0.533 | 1.279 | 0.049 | 0.089 | 5.51 | 21.93 | 99.0 | 294 |
| Antimony (Sb) | ng $l^{-1}$ | 32 | 0.75 | 1.83 | 4.03 | 1.585 | 3.977 | 20.25 | 71.67 | 245.4 | 675.6 |
| Arsenic (As)[a] | µg $l^{-1}$ | 33 | 0.013 | 0.018 | 0.027 | 0.068 | 0.073 | 0.227 | 0.409 | 1.16 | 2.43 |
| Barium (Ba) | µg $l^{-1}$ | 33 | 0.011 | 0.016 | 0.027 | 0.728 | 1.624 | 12.57 | 36.97 | 140.7 | 374.5 |
| Beryllium (Be) | ng $l^{-1}$ | 33 | 0.165 | 0.391 | 0.851 | 0.211 | 0.451 | 4.467 | 12.88 | 59.7 | 125.4 |
| Cadmium (Cd) | ng $l^{-1}$ | 33 | 0.1 | 0.29 | 0.67 | 0.167 | 1.08 | 4.89 | 21.04 | 54.4 | 302.7 |
| Caesium (Cs) | ng $l^{-1}$ | 33 | 0.06 | 0.1 | 0.19 | 0.518 | 0.949 | 11.83 | 50.10 | 206.0 | 340 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 33 | 0.158 | 0.194 | 0.269 | 0.140 | 0.168 | 0.487 | 1.108 | 1.66 | 18.6 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 33 | 0.006 | 0.008 | 0.011 | 0.010 | 0.020 | 0.083 | 0.141 | 0.318 | 1.14 |
| Copper (Cu) | µg $l^{-1}$ | 33 | 0.015 | 0.023 | 0.039 | 0.064 | 0.096 | 0.719 | 3.035 | 10.40 | 41.7 |
| Fluoride (F) | µg $l^{-1}$ | 29 | | 100 | | 9.10 | 13.74 | 33.3 | 47.5 | 103.4 | 133 |
| Gallium (Ga) | ng $l^{-1}$ | 30 | 0.25 | 0.45 | 0.86 | 0.166 | 0.287 | 0.914 | 2.858 | 14.40 | 21.3 |
| Hafnium (Hf) | ng $l^{-1}$ | 30 | 0.070 | 0.140 | 0.300 | 0.006 | 0.032 | 0.164 | 0.660 | 2.27 | 8.09 |
| Indium (In) | ng $l^{-1}$ | 28 | 0.050 | 0.140 | 0.320 | 0.002 | 0.012 | 0.036 | 0.057 | 0.164 | 0.34 |
| Iron (Fe) | µg $l^{-1}$ | 33 | 8.761 | 9.046 | 9.624 | 6.681 | 16.60 | 165.7 | 210.8 | 750.4 | 1094 |
| Lead (Pb) | ng $l^{-1}$ | 28 | 4.320 | 15.99 | 39.68 | 0.732 | 1.232 | 8.208 | 37.57 | 67.02 | 585.5 |
| Lithium (Li) | µg $l^{-1}$ | 33 | 0.122 | 0.137 | 0.167 | 0.128 | 0.169 | 0.587 | 1.063 | 3.03 | 6.22 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 31 | 0.046 | 0.063 | 0.10 | 0.033 | 0.121 | 2.791 | 26.36 | 85.96 | 379.6 |
| Molyb'num (Mo) | ng $l^{-1}$ | 33 | 0.50 | 1.44 | 3.33 | 0.474 | 2.766 | 25.67 | 106.6 | 392.9 | 925.5 |
| Nickel (Ni) | µg $l^{-1}$ | 33 | 0.007 | 0.014 | 0.028 | 0.048 | 0.140 | 0.719 | 1.094 | 2.42 | 5.85 |
| Niobium (Nb) | ng $l^{-1}$ | 27 | 0.110 | 0.210 | 0.400 | 0.020 | 0.047 | 0.285 | 0.519 | 1.73 | 2.15 |
| Phosphorus (P) | µg $l^{-1}$ | 27 | 22.38 | 23.96 | 27.18 | 0.043 | 1.483 | 12.14 | 51.40 | 220.1 | 544.9 |
| Rubidium (Rb) | µg $l^{-1}$ | 33 | 0.001 | 0.001 | 0.002 | 0.086 | 0.160 | 0.911 | 1.307 | 3.69 | 5.44 |
| Scandium (Sc) | µg $l^{-1}$ | 33 | 0.046 | 0.049 | 0.055 | 0.082 | 0.221 | 0.484 | 0.458 | 0.812 | 0.844 |
| Selenium (Se) | ng $l^{-1}$ | 27 | 7.421 | 10.62 | 17.13 | 8.766 | 11.21 | 29.69 | 75.69 | 250.8 | 845.8 |
| Strontium (Sr) | µg $l^{-1}$ | 33 | 0.039 | 0.049 | 0.067 | 11.44 | 19.68 | 74.82 | 128.8 | 318.7 | 672.9 |
| Tantalum (Ta) | ng $l^{-1}$ | 16 | 0.020 | 0.050 | 0.100 | 0.002 | 0.002 | 0.013 | 0.014 | 0.029 | 0.031 |
| Thallium (Tl) | ng $l^{-1}$ | 33 | 0.230 | 0.350 | 0.600 | 0.217 | 0.689 | 1.400 | 2.682 | 10.21 | 17.9 |
| Thorium (Th) | ng $l^{-1}$ | 33 | 0.030 | 0.130 | 0.340 | 0.004 | 0.034 | 0.478 | 1.145 | 3.74 | 12.8 |
| Tin (Sn) | ng $l^{-1}$ | 20 | 2.780 | 4.900 | 9.200 | 0.003 | 0.055 | 2.251 | 3.590 | 10.90 | 19.6 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 33 | 0.056 | 0.095 | 0.174 | 0.038 | 0.054 | 0.159 | 0.364 | 1.213 | 1.76 |
| Tungsten (W) | ng $l^{-1}$ | 19 | 1.010 | 1.490 | 2.460 | 0.005 | 0.016 | 0.375 | 2.597 | 10.76 | 12.9 |
| Uranium (U) | ng $l^{-1}$ | 33 | 0.330 | 0.440 | 0.660 | 4.965 | 8.185 | 104.0 | 384.8 | 1528.6 | 2995 |
| Vanadium (V)[a] | µg $l^{-1}$ | 29 | 0.042 | 0.053 | 0.074 | 0.006 | 0.040 | 0.279 | 0.616 | 3.30 | 5.66 |
| Yttrium (Y) | ng $l^{-1}$ | 33 | 0.105 | 0.421 | 1.064 | 9.048 | 12.42 | 92.0 | 375.7 | 1091.5 | 6047 |
| Zircon (Zr) | ng $l^{-1}$ | 31 | 0.800 | 1.400 | 2.630 | 0.823 | 1.256 | 8.73 | 25.3 | 78.3 | 274.5 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 12 | 0.088 | 0.287 | 0.692 | 0.621 | 0.639 | 1.350 | 3.128 | 7.25 | 7.36 |

Note: [a] Results prone to chloride interferences

Table C.4 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.11) for the **igneous** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 14 | 0.165 | 0.533 | 1.279 | 0.107 | 0.211 | 7.567 | 43.14 | 204.1 | 384.3 |
| Antimony (Sb) | ng $l^{-1}$ | 14 | 0.75 | 1.83 | 4.03 | 1.700 | 2.145 | 31.98 | 73.91 | 223.9 | 241.6 |
| Arsenic (As)[a] | µg $l^{-1}$ | 14 | 0.013 | 0.018 | 0.027 | 0.173 | 0.188 | 0.916 | 1.389 | 3.81 | 5.28 |
| Barium (Ba) | µg $l^{-1}$ | 14 | 0.011 | 0.016 | 0.027 | 1.601 | 3.804 | 12.25 | 37.53 | 157.2 | 308.8 |
| Beryllium (Be) | ng $l^{-1}$ | 14 | 0.165 | 0.391 | 0.851 | 1.191 | 1.730 | 16.00 | 39.69 | 126.9 | 152.4 |
| Cadmium (Cd) | ng $l^{-1}$ | 14 | 0.1 | 0.29 | 0.67 | 1.615 | 3.802 | 14.23 | 20.55 | 61.1 | 94.3 |
| Caesium (Cs) | ng $l^{-1}$ | 14 | 0.06 | 0.1 | 0.19 | 2.452 | 7.709 | 23.28 | 79.39 | 281.7 | 308.4 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 13 | 0.158 | 0.194 | 0.269 | 0.245 | 0.257 | 0.896 | 1.354 | 3.89 | 6.54 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 14 | 0.006 | 0.008 | 0.011 | 0.016 | 0.017 | 0.078 | 0.122 | 0.316 | 0.346 |
| Copper (Cu) | µg $l^{-1}$ | 14 | 0.015 | 0.023 | 0.039 | 0.207 | 0.304 | 2.785 | 9.38 | 33.40 | 58.3 |
| Fluoride (F) | µg $l^{-1}$ | 9 | | 100 | | 14.2 | 20.48 | 55.8 | 58.39 | 110.1 | 126 |
| Gallium (Ga) | ng $l^{-1}$ | 14 | 0.25 | 0.45 | 0.86 | 0.000 | 0.073 | 3.957 | 10.65 | 39.6 | 68.5 |
| Hafnium (Hf) | ng $l^{-1}$ | 12 | 0.070 | 0.140 | 0.300 | 0.006 | 0.030 | 0.517 | 1.084 | 2.88 | 3.71 |
| Indium (In) | ng $l^{-1}$ | 11 | 0.050 | 0.140 | 0.320 | 0.002 | 0.006 | 0.100 | 0.173 | 0.551 | 0.80 |
| Iron (Fe) | µg $l^{-1}$ | 14 | 8.761 | 9.046 | 9.624 | 12.14 | 22.92 | 115.7 | 216.0 | 715.5 | 983.3 |
| Lead (Pb) | ng $l^{-1}$ | 12 | 4.320 | 15.99 | 39.68 | 1.000 | 2.372 | 36.33 | 182.2 | 806.5 | 1131 |
| Lithium (Li) | µg $l^{-1}$ | 14 | 0.122 | 0.137 | 0.167 | 0.138 | 0.200 | 2.619 | 6.17 | 23.81 | 50.0 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 14 | 0.046 | 0.063 | 0.10 | 0.038 | 0.052 | 3.340 | 22.73 | 98.56 | 201.9 |
| Molyb'num (Mo) | ng $l^{-1}$ | 14 | 0.50 | 1.44 | 3.33 | 6.263 | 6.402 | 57.11 | 2167 | 11463 | 23600 |
| Nickel (Ni) | µg $l^{-1}$ | 14 | 0.007 | 0.014 | 0.028 | 0.316 | 0.318 | 0.876 | 2.085 | 6.400 | 11.3 |
| Niobium (Nb) | ng $l^{-1}$ | 14 | 0.110 | 0.210 | 0.400 | 0.100 | 0.113 | 0.875 | 4.182 | 18.65 | 22.4 |
| Phosphorus (P) | µg $l^{-1}$ | 13 | 22.38 | 23.96 | 27.18 | 3.189 | 3.679 | 32.74 | 79.25 | 303.3 | 670.7 |
| Rubidium (Rb) | µg $l^{-1}$ | 14 | 0.001 | 0.001 | 0.002 | 0.143 | 0.268 | 2.351 | 4.831 | 17.52 | 37.1 |
| Scandium (Sc) | µg $l^{-1}$ | 14 | 0.046 | 0.049 | 0.055 | 0.067 | 0.081 | 0.409 | 0.680 | 1.667 | 2.04 |
| Selenium (Se) | ng $l^{-1}$ | 11 | 7.421 | 10.62 | 17.13 | 8.404 | 10.54 | 67.25 | 71.35 | 172.9 | 178.2 |
| Strontium (Sr) | µg $l^{-1}$ | 14 | 0.039 | 0.049 | 0.067 | 23.16 | 36.86 | 70.71 | 130.2 | 365.4 | 676.8 |
| Tantalum (Ta) | ng $l^{-1}$ | 8 | 0.020 | 0.050 | 0.100 | 0.015 | 0.022 | 0.122 | 0.162 | 0.426 | 0.504 |
| Thallium (Tl) | ng $l^{-1}$ | 14 | 0.230 | 0.350 | 0.600 | 0.027 | 0.382 | 3.68 | 4.01 | 8.06 | 8.51 |
| Thorium (Th) | ng $l^{-1}$ | 14 | 0.030 | 0.130 | 0.340 | 0.059 | 0.095 | 1.051 | 10.25 | 51.32 | 94.5 |
| Tin (Sn) | ng $l^{-1}$ | 13 | 2.780 | 4.900 | 9.200 | 0.026 | 0.438 | 1.764 | 19.63 | 88.05 | 152.5 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 14 | 0.056 | 0.095 | 0.174 | 0.070 | 0.088 | 0.322 | 0.562 | 1.402 | 1.50 |
| Tungsten (W) | ng $l^{-1}$ | 11 | 1.010 | 1.490 | 2.460 | 0.080 | 0.123 | 2.342 | 49.31 | 255.6 | 467.5 |
| Uranium (U) | ng $l^{-1}$ | 14 | 0.330 | 0.440 | 0.660 | 3.515 | 5.602 | 353.5 | 1496 | 7055 | 8969 |
| Vanadium (V)[a] | µg $l^{-1}$ | 14 | 0.042 | 0.053 | 0.074 | 0.083 | 0.094 | 0.499 | 0.753 | 2.55 | 2.74 |
| Yttrium (Y) | ng $l^{-1}$ | 14 | 0.105 | 0.421 | 1.064 | 13.42 | 16.17 | 138.9 | 211.5 | 714.6 | 800.2 |
| Zircon (Zr) | ng $l^{-1}$ | 13 | 0.800 | 1.400 | 2.630 | 1.437 | 1.700 | 27.85 | 32.29 | 75.75 | 76.7 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 12 | 0.088 | 0.287 | 0.692 | 0.251 | 0.312 | 3.197 | 7.512 | 25.73 | 26.7 |

Note: [a] Results prone to chloride interferences

Table C.5 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.12) for the **metamorphic** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 31 | 0.165 | 0.533 | 1.279 | 0.040 | 0.136 | 3.747 | 51.10 | 365.5 | 622.6 |
| Antimony (Sb) | ng $l^{-1}$ | 33 | 0.75 | 1.83 | 4.03 | 4.312 | 5.193 | 41.87 | 68.79 | 316.7 | 347.7 |
| Arsenic (As)[a] | µg $l^{-1}$ | 33 | 0.013 | 0.018 | 0.027 | 0.027 | 0.045 | 0.300 | 0.638 | 1.363 | 7.82 |
| Barium (Ba) | µg $l^{-1}$ | 33 | 0.011 | 0.016 | 0.027 | 1.531 | 1.634 | 14.94 | 40.68 | 88.1 | 538.3 |
| Beryllium (Be) | ng $l^{-1}$ | 33 | 0.165 | 0.391 | 0.851 | 0.099 | 0.534 | 3.266 | 18.99 | 68.05 | 313.6 |
| Cadmium (Cd) | ng $l^{-1}$ | 33 | 0.1 | 0.29 | 0.67 | 0.842 | 1.195 | 6.041 | 111.5 | 316.1 | 2725 |
| Caesium (Cs) | ng $l^{-1}$ | 33 | 0.06 | 0.1 | 0.19 | 0.142 | 0.380 | 6.706 | 34.59 | 142.0 | 488.8 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 26 | 0.158 | 0.194 | 0.269 | 0.151 | 0.270 | 0.506 | 0.615 | 1.173 | 2.03 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 33 | 0.006 | 0.008 | 0.011 | 0.015 | 0.019 | 0.103 | 0.191 | 0.536 | 1.60 |
| Copper (Cu) | µg $l^{-1}$ | 33 | 0.015 | 0.023 | 0.039 | 0.072 | 0.098 | 1.464 | 4.107 | 19.51 | 36.4 |
| Fluoride (F) | µg $l^{-1}$ | 28 | | 100 | | 16.0 | 19.6 | 49.0 | 51.0 | 88.7 | 90.0 |
| Gallium (Ga) | ng $l^{-1}$ | 30 | 0.25 | 0.45 | 0.86 | 0.0000 | 0.081 | 1.170 | 4.740 | 24.63 | 48.7 |
| Hafnium (Hf) | ng $l^{-1}$ | 27 | 0.070 | 0.140 | 0.300 | 0.008 | 0.017 | 0.236 | 1.132 | 3.62 | 15.0 |
| Indium (In) | ng $l^{-1}$ | 29 | 0.050 | 0.140 | 0.320 | 0.007 | 0.012 | 0.046 | 0.125 | 0.576 | 0.98 |
| Iron (Fe) | µg $l^{-1}$ | 33 | 8.761 | 9.046 | 9.624 | 1.973 | 16.20 | 120.7 | 212.7 | 670.2 | 833.8 |
| Lead (Pb) | ng $l^{-1}$ | 30 | 4.320 | 15.99 | 39.68 | 0.235 | 1.552 | 17.27 | 113.8 | 646.3 | 927.2 |
| Lithium (Li) | µg $l^{-1}$ | 33 | 0.122 | 0.137 | 0.167 | 0.017 | 0.161 | 0.919 | 1.266 | 2.82 | 4.11 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 33 | 0.046 | 0.063 | 0.10 | 0.011 | 0.080 | 3.73 | 23.76 | 56.0 | 482.8 |
| Molyb'num (Mo) | ng $l^{-1}$ | 33 | 0.50 | 1.44 | 3.33 | 1.290 | 1.903 | 65.3 | 155.3 | 299.2 | 2488 |
| Nickel (Ni) | µg $l^{-1}$ | 33 | 0.007 | 0.014 | 0.028 | 0.235 | 0.262 | 0.953 | 1.450 | 4.70 | 8.0 |
| Niobium (Nb) | ng $l^{-1}$ | 29 | 0.110 | 0.210 | 0.400 | 0.005 | 0.080 | 0.359 | 1.288 | 3.79 | 15.1 |
| Phosphorus (P) | µg $l^{-1}$ | 28 | 22.38 | 23.96 | 27.18 | 0.226 | 2.249 | 14.71 | 56.21 | 120.5 | 982.5 |
| Rubidium (Rb) | µg $l^{-1}$ | 33 | 0.001 | 0.001 | 0.002 | 0.044 | 0.093 | 0.912 | 1.464 | 3.937 | 10.5 |
| Scandium (Sc) | µg $l^{-1}$ | 33 | 0.046 | 0.049 | 0.055 | 0.104 | 0.265 | 0.658 | 0.706 | 1.266 | 1.82 |
| Selenium (Se) | ng $l^{-1}$ | 21 | 7.421 | 10.62 | 17.13 | 4.383 | 10.47 | 24.71 | 35.50 | 67.36 | 186.4 |
| Strontium (Sr) | µg $l^{-1}$ | 33 | 0.039 | 0.049 | 0.067 | 5.496 | 22.32 | 101.0 | 159.4 | 343.8 | 1285.0 |
| Tantalum (Ta) | ng $l^{-1}$ | 22 | 0.020 | 0.050 | 0.100 | 0.001 | 0.002 | 0.018 | 0.070 | 0.186 | 0.71 |
| Thallium (Tl) | ng $l^{-1}$ | 33 | 0.230 | 0.350 | 0.600 | 0.083 | 0.392 | 2.015 | 2.873 | 9.04 | 10.4 |
| Thorium (Th) | ng $l^{-1}$ | 33 | 0.030 | 0.130 | 0.340 | 0.002 | 0.035 | 0.427 | 3.733 | 16.71 | 51.6 |
| Tin (Sn) | ng $l^{-1}$ | 24 | 2.780 | 4.900 | 9.200 | 0.122 | 0.290 | 3.126 | 5.457 | 12.98 | 35.3 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 33 | 0.056 | 0.095 | 0.174 | 0.044 | 0.061 | 0.238 | 0.612 | 1.643 | 8.16 |
| Tungsten (W) | ng $l^{-1}$ | 26 | 1.010 | 1.490 | 2.460 | 0.015 | 0.040 | 0.706 | 2.213 | 7.22 | 8.44 |
| Uranium (U) | ng $l^{-1}$ | 33 | 0.330 | 0.440 | 0.660 | 3.905 | 5.307 | 90.80 | 263.9 | 821.7 | 2000.1 |
| Vanadium (V)[a] | µg $l^{-1}$ | 26 | 0.042 | 0.053 | 0.074 | 0.016 | 0.066 | 0.225 | 0.351 | 1.159 | 1.23 |
| Yttrium (Y) | ng $l^{-1}$ | 33 | 0.105 | 0.421 | 1.064 | 8.456 | 13.66 | 122.5 | 353.8 | 950.5 | 3358 |
| Zircon (Zr) | ng $l^{-1}$ | 31 | 0.800 | 1.400 | 2.630 | 0.123 | 0.413 | 9.553 | 37.08 | 90.08 | 622.0 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 21 | 0.088 | 0.287 | 0.692 | 0.016 | 0.163 | 2.671 | 39.37 | 296.1 | 350.8 |

Note: [a] Results prone to chloride interferences

Table C.6 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.13) for the **sand and gravel** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 6 | 0.165 | 0.533 | 1.279 | 0.164 | 0.173 | 0.387 | 0.450 | 0.85 | 0.92 |
| Antimony (Sb) | ng $l^{-1}$ | 6 | 0.75 | 1.83 | 4.03 | 14.61 | 17.35 | 46.33 | 53.01 | 94.45 | 96.3 |
| Arsenic (As)[a] | µg $l^{-1}$ | 6 | 0.013 | 0.018 | 0.027 | 0.102 | 0.105 | 0.183 | 0.235 | 0.466 | 0.52 |
| Barium (Ba) | µg $l^{-1}$ | 6 | 0.011 | 0.016 | 0.027 | 13.33 | 18.12 | 64.99 | 60.22 | 93.31 | 93.9 |
| Beryllium (Be) | ng $l^{-1}$ | 6 | 0.165 | 0.391 | 0.851 | 0.703 | 0.703 | 1.078 | 1.14 | 1.66 | 1.68 |
| Cadmium (Cd) | ng $l^{-1}$ | 6 | 0.1 | 0.29 | 0.67 | 1.572 | 2.433 | 10.83 | 9.15 | 13.64 | 13.95 |
| Caesium (Cs) | ng $l^{-1}$ | 6 | 0.06 | 0.1 | 0.19 | 0.413 | 0.520 | 2.937 | 5.45 | 13.03 | 13.29 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 4 | 0.158 | 0.194 | 0.269 | 0.366 | 0.445 | 0.910 | 0.780 | 0.93 | 0.93 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 6 | 0.006 | 0.008 | 0.011 | 0.121 | 0.125 | 0.142 | 0.163 | 0.222 | 0.225 |
| Copper (Cu) | µg $l^{-1}$ | 6 | 0.015 | 0.023 | 0.039 | 0.304 | 0.327 | 0.469 | 0.870 | 2.33 | 2.87 |
| Fluoride (F) | µg $l^{-1}$ | 6 | | 100 | | 58.6 | 59.4 | 78.6 | 74.6 | 87.0 | 89.0 |
| Gallium (Ga) | ng $l^{-1}$ | 6 | 0.25 | 0.45 | 0.86 | 1.093 | 1.128 | 1.403 | 1.611 | 2.65 | 3.03 |
| Hafnium (Hf) | ng $l^{-1}$ | 5 | 0.070 | 0.140 | 0.300 | 0.004 | 0.053 | 0.122 | 0.140 | 0.235 | 0.244 |
| Indium (In) | ng $l^{-1}$ | 4 | 0.050 | 0.140 | 0.320 | 0.014 | 0.016 | 0.053 | 0.050 | 0.078 | 0.078 |
| Iron (Fe) | µg $l^{-1}$ | 6 | 8.761 | 9.046 | 9.624 | 259.0 | 287.6 | 397.4 | 504.2 | 814.7 | 830.4 |
| Lead (Pb) | ng $l^{-1}$ | 4 | 4.320 | 15.99 | 39.68 | 18.28 | 18.91 | 32.65 | 34.48 | 52.6 | 54.3 |
| Lithium (Li) | µg $l^{-1}$ | 6 | 0.122 | 0.137 | 0.167 | 0.943 | 0.958 | 1.196 | 1.329 | 2.09 | 2.36 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 5 | 0.046 | 0.063 | 0.10 | 0.214 | 0.218 | 0.258 | 2.636 | 9.39 | 11.5 |
| Molyb'num (Mo) | ng $l^{-1}$ | 6 | 0.50 | 1.44 | 3.33 | 42.40 | 43.74 | 79.77 | 183.3 | 457.3 | 489.6 |
| Nickel (Ni) | µg $l^{-1}$ | 6 | 0.007 | 0.014 | 0.028 | 0.629 | 0.764 | 1.246 | 1.325 | 2.09 | 2.34 |
| Niobium (Nb) | ng $l^{-1}$ | 6 | 0.110 | 0.210 | 0.400 | 0.126 | 0.143 | 0.257 | 0.424 | 1.10 | 1.34 |
| Phosphorus (P) | µg $l^{-1}$ | 3 | 22.38 | 23.96 | 27.18 | 3.98 | 4.22 | 6.38 | 6.50 | 8.87 | 9.14 |
| Rubidium (Rb) | µg $l^{-1}$ | 6 | 0.001 | 0.001 | 0.002 | 0.103 | 0.127 | 0.453 | 0.602 | 1.281 | 1.36 |
| Scandium (Sc) | µg $l^{-1}$ | 6 | 0.046 | 0.049 | 0.055 | 0.603 | 0.609 | 0.884 | 0.860 | 1.101 | 1.12 |
| Selenium (Se) | ng $l^{-1}$ | 4 | 7.421 | 10.62 | 17.13 | 34.8 | 35.67 | 61.1 | 69.9 | 116.4 | 122.6 |
| Strontium (Sr) | µg $l^{-1}$ | 6 | 0.039 | 0.049 | 0.067 | 164.4 | 171.8 | 203.6 | 202.1 | 229.5 | 235.4 |
| Tantalum (Ta) | ng $l^{-1}$ | 5 | 0.020 | 0.050 | 0.100 | 0.002 | 0.003 | 0.012 | 0.010 | 0.016 | 0.016 |
| Thallium (Tl) | ng $l^{-1}$ | 6 | 0.230 | 0.350 | 0.600 | 0.733 | 0.777 | 1.002 | 1.346 | 2.25 | 2.29 |
| Thorium (Th) | ng $l^{-1}$ | 6 | 0.030 | 0.130 | 0.340 | 0.053 | 0.054 | 0.090 | 0.098 | 0.153 | 0.16 |
| Tin (Sn) | ng $l^{-1}$ | 5 | 2.780 | 4.900 | 9.200 | 1.374 | 1.459 | 2.324 | 2.716 | 4.64 | 5.04 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 6 | 0.056 | 0.095 | 0.174 | 0.159 | 0.163 | 0.394 | 0.532 | 1.104 | 1.18 |
| Tungsten (W) | ng $l^{-1}$ | 5 | 1.010 | 1.490 | 2.460 | 0.210 | 0.210 | 1.177 | 8.955 | 33.64 | 41.7 |
| Uranium (U) | ng $l^{-1}$ | 6 | 0.330 | 0.440 | 0.660 | 287.4 | 361.1 | 859.8 | 798.0 | 1099.8 | 1100.0 |
| Vanadium (V)[a] | µg $l^{-1}$ | 5 | 0.042 | 0.053 | 0.074 | 0.036 | 0.049 | 0.173 | 0.242 | 0.529 | 0.58 |
| Yttrium (Y) | ng $l^{-1}$ | 6 | 0.105 | 0.421 | 1.064 | 14.36 | 15.97 | 29.52 | 35.91 | 66.03 | 71.4 |
| Zircon (Zr) | ng $l^{-1}$ | 6 | 0.800 | 1.400 | 2.630 | 0.674 | 1.552 | 5.452 | 7.572 | 16.03 | 17.2 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 1 | 0.088 | 0.287 | 0.692 | | | 2.79 | | | |

Note: [a] Results prone to chloride interferences

Table C.7 Summary descriptive statistics for minor ions and trace elements (excluding the REEs, which are shown in Table C.14) for the **mixed gravel and bedrock** lithological group

| | Unit | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium (Al) | µg $l^{-1}$ | 8 | 0.165 | 0.533 | 1.279 | 0.086 | 0.097 | 0.294 | 3.317 | 11.61 | 12.6 |
| Antimony (Sb) | ng $l^{-1}$ | 9 | 0.75 | 1.83 | 4.03 | 38.65 | 49.42 | 97.1 | 725.5 | 3304.8 | 4642 |
| Arsenic (As)[a] | µg $l^{-1}$ | 9 | 0.013 | 0.018 | 0.027 | 0.155 | 0.157 | 0.447 | 0.748 | 2.21 | 2.57 |
| Barium (Ba) | µg $l^{-1}$ | 9 | 0.011 | 0.016 | 0.027 | 9.921 | 11.07 | 52.02 | 50.30 | 99.58 | 108.6 |
| Beryllium (Be) | ng $l^{-1}$ | 9 | 0.165 | 0.391 | 0.851 | 0.722 | 0.724 | 0.981 | 1.410 | 2.90 | 3.07 |
| Cadmium (Cd) | ng $l^{-1}$ | 9 | 0.1 | 0.29 | 0.67 | 3.154 | 4.977 | 11.55 | 19.86 | 52.85 | 60.37 |
| Caesium (Cs) | ng $l^{-1}$ | 9 | 0.06 | 0.1 | 0.19 | 0.428 | 0.596 | 3.459 | 16.87 | 68.27 | 87.0 |
| Chromium (Cr)[a] | µg $l^{-1}$ | 5 | 0.158 | 0.194 | 0.269 | 0.131 | 0.139 | 0.791 | 1.136 | 2.87 | 3.26 |
| Cobalt (Co)[a] | µg $l^{-1}$ | 9 | 0.006 | 0.008 | 0.011 | 0.105 | 0.112 | 0.224 | 0.216 | 0.382 | 0.43 |
| Copper (Cu) | µg $l^{-1}$ | 9 | 0.015 | 0.023 | 0.039 | 0.551 | 0.553 | 0.841 | 2.071 | 6.42 | 8.2 |
| Fluoride (F) | µg $l^{-1}$ | 9 | | 100 | | 54.5 | 55.4 | 104.0 | 148.0 | 388.4 | 516.0 |
| Gallium (Ga) | ng $l^{-1}$ | 9 | 0.25 | 0.45 | 0.86 | 0.306 | 0.461 | 1.249 | 8.764 | 28.12 | 28.9 |
| Hafnium (Hf) | ng $l^{-1}$ | 5 | 0.070 | 0.140 | 0.300 | 0.080 | 0.085 | 0.209 | 0.355 | 0.769 | 0.82 |
| Indium (In) | ng $l^{-1}$ | 7 | 0.050 | 0.140 | 0.320 | 0.006 | 0.007 | 0.040 | 0.132 | 0.400 | 0.42 |
| Iron (Fe) | µg $l^{-1}$ | 9 | 8.761 | 9.046 | 9.624 | 194.1 | 228.4 | 393.1 | 548.2 | 913.4 | 957.0 |
| Lead (Pb) | ng $l^{-1}$ | 6 | 4.320 | 15.99 | 39.68 | 3.738 | 4.520 | 20.12 | 362.1 | 1577.4 | 2094 |
| Lithium (Li) | µg $l^{-1}$ | 9 | 0.122 | 0.137 | 0.167 | 0.557 | 0.572 | 0.976 | 6.51 | 28.97 | 42.0 |
| Mang'ese (Mn)[a] | µg $l^{-1}$ | 8 | 0.046 | 0.063 | 0.10 | 0.033 | 0.065 | 0.712 | 5.54 | 18.66 | 20.8 |
| Molyb'num (Mo) | ng $l^{-1}$ | 9 | 0.50 | 1.44 | 3.33 | 43.26 | 48.64 | 346.5 | 2116 | 9851 | 15650 |
| Nickel (Ni) | µg $l^{-1}$ | 9 | 0.007 | 0.014 | 0.028 | 0.847 | 1.044 | 1.459 | 2.467 | 5.38 | 5.52 |
| Niobium (Nb) | ng $l^{-1}$ | 9 | 0.110 | 0.210 | 0.400 | 0.158 | 0.165 | 0.345 | 0.491 | 1.18 | 1.51 |
| Phosphorus (P) | µg $l^{-1}$ | 8 | 22.38 | 23.96 | 27.18 | 3.029 | 3.736 | 26.85 | 48.2 | 152.9 | 193.4 |
| Rubidium (Rb) | µg $l^{-1}$ | 9 | 0.001 | 0.001 | 0.002 | 0.102 | 0.111 | 0.436 | 1.931 | 7.91 | 11.6 |
| Scandium (Sc) | µg $l^{-1}$ | 9 | 0.046 | 0.049 | 0.055 | 0.512 | 0.541 | 0.716 | 0.730 | 0.98 | 1.04 |
| Selenium (Se) | ng $l^{-1}$ | 5 | 7.421 | 10.62 | 17.13 | 15.96 | 25.60 | 68.79 | 126.4 | 339.4 | 404.7 |
| Strontium (Sr) | µg $l^{-1}$ | 9 | 0.039 | 0.049 | 0.067 | 135.2 | 149.4 | 301.9 | 306.4 | 496.3 | 501.2 |
| Tantalum (Ta) | ng $l^{-1}$ | 6 | 0.020 | 0.050 | 0.100 | 0.001 | 0.001 | 0.009 | 0.008 | 0.013 | 0.014 |
| Thallium (Tl) | ng $l^{-1}$ | 9 | 0.230 | 0.350 | 0.600 | 0.931 | 1.597 | 5.448 | 25.84 | 96.94 | 103.3 |
| Thorium (Th) | ng $l^{-1}$ | 9 | 0.030 | 0.130 | 0.340 | 0.048 | 0.053 | 0.091 | 0.150 | 0.394 | 0.51 |
| Tin (Sn) | ng $l^{-1}$ | 6 | 2.780 | 4.900 | 9.200 | 2.106 | 2.308 | 4.064 | 13.65 | 48.83 | 63.3 |
| Titanium (Ti)[a] | µg $l^{-1}$ | 9 | 0.056 | 0.095 | 0.174 | 0.177 | 0.190 | 0.300 | 0.939 | 2.95 | 3.62 |
| Tungsten (W) | ng $l^{-1}$ | 8 | 1.010 | 1.490 | 2.460 | 0.063 | 0.064 | 1.410 | 26.36 | 131.6 | 200.0 |
| Uranium (U) | ng $l^{-1}$ | 9 | 0.330 | 0.440 | 0.660 | 445.5 | 549.7 | 1467 | 1577 | 3025 | 3320 |
| Vanadium (V)[a] | µg $l^{-1}$ | 9 | 0.042 | 0.053 | 0.074 | 0.004 | 0.007 | 0.140 | 0.508 | 2.032 | 2.97 |
| Yttrium (Y) | ng $l^{-1}$ | 9 | 0.105 | 0.421 | 1.064 | 14.31 | 14.81 | 25.56 | 27.53 | 40.75 | 43.1 |
| Zircon (Zr) | ng $l^{-1}$ | 9 | 0.800 | 1.400 | 2.630 | 1.726 | 1.809 | 6.973 | 13.98 | 44.74 | 48.2 |
| Zinc (Zn)[a] | µg $l^{-1}$ | 5 | 0.088 | 0.287 | 0.692 | 0.434 | 0.501 | 3.885 | 5.074 | 10.52 | 10.8 |

Note: [a] Results prone to chloride interferences

Table C.8 Summary descriptive statistics for lanthanide rare earth elements for the **impure limestone** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 26 | 0.080 | 0.340 | 0.880 | 1.210 | 2.096 | 11.06 | 28.87 | 145.8 | 208.7 |
| Cerium (Ce) | 26 | 0.130 | 0.610 | 1.580 | 0.118 | 0.215 | 1.888 | 21.53 | 51.85 | 348.1 |
| Praseodymium (Pr) | 26 | 0.020 | 0.100 | 0.260 | 0.224 | 0.361 | 2.840 | 7.42 | 40.48 | 52.7 |
| Neodymium (Nd) | 26 | 0.090 | 0.390 | 0.980 | 1.302 | 1.798 | 13.43 | 33.97 | 174.2 | 239.7 |
| Samarium (Sm) | 26 | 0.050 | 0.160 | 0.390 | 0.511 | 0.662 | 3.851 | 8.12 | 38.76 | 53.1 |
| Europium (Eu) | 21 | 0.020 | 0.050 | 0.130 | 0.065 | 0.076 | 1.172 | 2.416 | 10.42 | 13.1 |
| Gadolinium (Gd) | 26 | 0.040 | 0.110 | 0.250 | 0.400 | 0.598 | 4.454 | 9.77 | 40.85 | 63.3 |
| Terbium (Tb) | 26 | 0.010 | 0.020 | 0.050 | 0.050 | 0.096 | 0.667 | 1.426 | 6.53 | 8.40 |
| Dysprosium (Dy) | 26 | 0.040 | 0.110 | 0.270 | 0.528 | 0.711 | 4.648 | 8.94 | 39.73 | 51.8 |
| Holmium (Ho) | 26 | 0.010 | 0.030 | 0.070 | 0.173 | 0.177 | 1.232 | 2.116 | 8.88 | 11.8 |
| Erbium (Er) | 26 | 0.030 | 0.080 | 0.180 | 0.430 | 0.612 | 3.490 | 6.167 | 24.73 | 34.7 |
| Thulium (Tm) | 26 | 0.010 | 0.020 | 0.040 | 0.073 | 0.079 | 0.482 | 0.894 | 3.61 | 5.1 |
| Ytterbium (Yb) | 26 | 0.030 | 0.070 | 0.170 | 0.449 | 0.534 | 3.055 | 5.783 | 22.87 | 33.4 |
| Lutetium (Lu) | 26 | 0.010 | 0.030 | 0.060 | 0.069 | 0.095 | 0.509 | 0.972 | 3.63 | 5.5 |

Table C.9 Summary descriptive statistics for lanthanide rare earth elements for the **pure limestone** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 35 | 0.080 | 0.340 | 0.880 | 1.699 | 2.318 | 9.100 | 21.05 | 66.33 | 153.6 |
| Cerium (Ce) | 34 | 0.130 | 0.610 | 1.580 | 0.054 | 0.242 | 4.165 | 17.72 | 40.66 | 364.3 |
| Praseodymium (Pr) | 35 | 0.020 | 0.100 | 0.260 | 0.294 | 0.678 | 2.199 | 5.040 | 14.00 | 52.0 |
| Neodymium (Nd) | 35 | 0.090 | 0.390 | 0.980 | 1.572 | 3.289 | 10.26 | 22.35 | 58.13 | 228.0 |
| Samarium (Sm) | 35 | 0.050 | 0.160 | 0.390 | 0.498 | 0.855 | 2.394 | 4.972 | 12.21 | 52.3 |
| Europium (Eu) | 32 | 0.020 | 0.050 | 0.130 | 0.126 | 0.192 | 0.659 | 1.296 | 3.01 | 12.5 |
| Gadolinium (Gd) | 35 | 0.040 | 0.110 | 0.250 | 0.632 | 0.950 | 3.722 | 6.050 | 15.55 | 48.1 |
| Terbium (Tb) | 35 | 0.010 | 0.020 | 0.050 | 0.121 | 0.149 | 0.507 | 0.888 | 2.47 | 6.8 |
| Dysprosium (Dy) | 35 | 0.040 | 0.110 | 0.270 | 0.916 | 1.132 | 3.746 | 5.977 | 16.79 | 37.7 |
| Holmium (Ho) | 35 | 0.010 | 0.030 | 0.070 | 0.285 | 0.291 | 1.017 | 1.530 | 4.33 | 7.6 |
| Erbium (Er) | 35 | 0.030 | 0.080 | 0.180 | 0.791 | 1.101 | 3.169 | 4.717 | 13.59 | 20.8 |
| Thulium (Tm) | 35 | 0.010 | 0.020 | 0.040 | 0.105 | 0.179 | 0.546 | 0.710 | 2.10 | 3.0 |
| Ytterbium (Yb) | 35 | 0.030 | 0.070 | 0.170 | 0.788 | 1.194 | 3.613 | 4.652 | 14.05 | 18.5 |
| Lutetium (Lu) | 35 | 0.010 | 0.030 | 0.060 | 0.152 | 0.210 | 0.607 | 0.789 | 2.35 | 2.8 |

Table C.10 Summary descriptive statistics for lanthanide rare earth elements for the **non-calcareous sedimentary** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 33 | 0.080 | 0.340 | 0.880 | 1.440 | 3.049 | 23.55 | 154.1 | 674.6 | 2647 |
| Cerium (Ce) | 33 | 0.130 | 0.610 | 1.580 | 0.305 | 0.452 | 8.882 | 240.0 | 929.4 | 5121 |
| Praseodymium (Pr) | 33 | 0.020 | 0.100 | 0.260 | 0.925 | 1.135 | 6.689 | 67.40 | 318.1 | 1131 |
| Neodymium (Nd) | 33 | 0.090 | 0.390 | 0.980 | 4.799 | 7.562 | 30.44 | 349.5 | 1234.9 | 6818 |
| Samarium (Sm) | 33 | 0.050 | 0.160 | 0.390 | 1.608 | 2.104 | 7.849 | 108.6 | 254.6 | 2495 |
| Europium (Eu) | 31 | 0.020 | 0.050 | 0.130 | 0.291 | 0.425 | 2.434 | 28.41 | 57.1 | 636.7 |
| Gadolinium (Gd) | 33 | 0.040 | 0.110 | 0.250 | 2.128 | 2.200 | 11.16 | 125.4 | 251.5 | 2902 |
| Terbium (Tb) | 33 | 0.010 | 0.020 | 0.050 | 0.220 | 0.277 | 1.537 | 13.88 | 31.9 | 300.6 |
| Dysprosium (Dy) | 33 | 0.040 | 0.110 | 0.270 | 1.129 | 1.362 | 8.476 | 65.57 | 175.6 | 1303 |
| Holmium (Ho) | 33 | 0.010 | 0.030 | 0.070 | 0.241 | 0.320 | 2.098 | 12.53 | 35.4 | 230.2 |
| Erbium (Er) | 33 | 0.030 | 0.080 | 0.180 | 0.681 | 0.834 | 6.278 | 31.97 | 93.3 | 554.8 |
| Thulium (Tm) | 33 | 0.010 | 0.020 | 0.040 | 0.104 | 0.138 | 0.879 | 4.298 | 12.2 | 71.7 |
| Ytterbium (Yb) | 33 | 0.030 | 0.070 | 0.170 | 0.572 | 0.896 | 5.743 | 25.44 | 64.9 | 420.2 |
| Lutetium (Lu) | 33 | 0.010 | 0.030 | 0.060 | 0.127 | 0.149 | 0.997 | 4.11 | 9.41 | 66.5 |

Table C.11 Summary descriptive statistics for lanthanide rare earth elements for the **igneous** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 14 | 0.080 | 0.340 | 0.880 | 1.501 | 4.818 | 17.97 | 76.0 | 310.6 | 325.2 |
| Cerium (Ce) | 13 | 0.130 | 0.610 | 1.580 | 0.441 | 0.671 | 11.21 | 84.0 | 377.4 | 578.5 |
| Praseodymium (Pr) | 14 | 0.020 | 0.100 | 0.260 | 0.357 | 1.159 | 10.98 | 18.7 | 62.3 | 67.3 |
| Neodymium (Nd) | 14 | 0.090 | 0.390 | 0.980 | 2.540 | 5.277 | 59.36 | 82.7 | 228.5 | 238.2 |
| Samarium (Sm) | 14 | 0.050 | 0.160 | 0.390 | 1.515 | 1.604 | 14.85 | 20.3 | 54.3 | 71.4 |
| Europium (Eu) | 13 | 0.020 | 0.050 | 0.130 | 0.402 | 0.440 | 2.68 | 4.34 | 12.5 | 14.8 |
| Gadolinium (Gd) | 14 | 0.040 | 0.110 | 0.250 | 1.893 | 2.277 | 20.73 | 25.9 | 80.0 | 100.7 |
| Terbium (Tb) | 14 | 0.010 | 0.020 | 0.050 | 0.279 | 0.350 | 3.00 | 3.50 | 10.9 | 12.7 |
| Dysprosium (Dy) | 14 | 0.040 | 0.110 | 0.270 | 1.825 | 2.310 | 17.83 | 21.6 | 67.7 | 74.7 |
| Holmium (Ho) | 14 | 0.010 | 0.030 | 0.070 | 0.463 | 0.498 | 3.92 | 5.1 | 16.8 | 17.9 |
| Erbium (Er) | 14 | 0.030 | 0.080 | 0.180 | 1.356 | 1.558 | 11.40 | 15.5 | 52.1 | 55.5 |
| Thulium (Tm) | 14 | 0.010 | 0.020 | 0.040 | 0.250 | 0.263 | 1.675 | 2.35 | 7.8 | 8.2 |
| Ytterbium (Yb) | 14 | 0.030 | 0.070 | 0.170 | 1.452 | 1.601 | 10.65 | 14.8 | 48.7 | 49.4 |
| Lutetium (Lu) | 14 | 0.010 | 0.030 | 0.060 | 0.220 | 0.228 | 1.855 | 2.48 | 8.2 | 8.4 |

Table C.12 Summary descriptive statistics for lanthanide rare earth elements for the **metamorphic** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 33 | 0.080 | 0.340 | 0.880 | 1.040 | 2.843 | 29.50 | 278.0 | 954.7 | 3704 |
| Cerium (Ce) | 33 | 0.130 | 0.610 | 1.580 | 0.011 | 0.547 | 7.582 | 195.5 | 1440.6 | 2088 |
| Praseodymium (Pr) | 33 | 0.020 | 0.100 | 0.260 | 0.468 | 0.817 | 11.81 | 65.14 | 294.1 | 466.9 |
| Neodymium (Nd) | 33 | 0.090 | 0.390 | 0.980 | 2.644 | 4.798 | 51.54 | 278.9 | 1258.6 | 1512 |
| Samarium (Sm) | 33 | 0.050 | 0.160 | 0.390 | 0.572 | 1.381 | 12.94 | 61.98 | 219.9 | 464.2 |
| Europium (Eu) | 31 | 0.020 | 0.050 | 0.130 | 0.074 | 0.247 | 3.293 | 15.19 | 43.7 | 120.7 |
| Gadolinium (Gd) | 33 | 0.040 | 0.110 | 0.250 | 0.773 | 1.720 | 13.61 | 63.61 | 197.2 | 512.3 |
| Terbium (Tb) | 33 | 0.010 | 0.020 | 0.050 | 0.098 | 0.291 | 2.091 | 8.91 | 27.55 | 83.5 |
| Dysprosium (Dy) | 33 | 0.040 | 0.110 | 0.270 | 0.640 | 1.606 | 12.38 | 50.84 | 147.9 | 511.7 |
| Holmium (Ho) | 33 | 0.010 | 0.030 | 0.070 | 0.150 | 0.384 | 2.909 | 11.25 | 30.8 | 120.8 |
| Erbium (Er) | 33 | 0.030 | 0.080 | 0.180 | 0.393 | 1.066 | 8.784 | 31.31 | 90.0 | 349.1 |
| Thulium (Tm) | 33 | 0.010 | 0.020 | 0.040 | 0.046 | 0.167 | 1.352 | 4.94 | 13.3 | 51.9 |
| Ytterbium (Yb) | 33 | 0.030 | 0.070 | 0.170 | 0.257 | 1.026 | 8.540 | 28.30 | 87.1 | 329.6 |
| Lutetium (Lu) | 33 | 0.010 | 0.030 | 0.060 | 0.053 | 0.155 | 1.516 | 4.55 | 14.99 | 50.9 |

Table C.13 Summary descriptive statistics for lanthanide rare earth elements for the **sand and gravel** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 6 | 0.080 | 0.340 | 0.880 | 1.818 | 2.135 | 4.226 | 4.27 | 6.57 | 6.99 |
| Cerium (Ce) | 6 | 0.130 | 0.610 | 1.580 | 0.097 | 0.219 | 0.731 | 1.39 | 3.89 | 4.70 |
| Praseodymium (Pr) | 6 | 0.020 | 0.100 | 0.260 | 0.179 | 0.286 | 0.851 | 0.85 | 1.31 | 1.32 |
| Neodymium (Nd) | 6 | 0.090 | 0.390 | 0.980 | 0.934 | 1.453 | 4.042 | 4.06 | 6.29 | 6.42 |
| Samarium (Sm) | 6 | 0.050 | 0.160 | 0.390 | 0.490 | 0.574 | 1.236 | 1.11 | 1.53 | 1.61 |
| Europium (Eu) | 3 | 0.020 | 0.050 | 0.130 | 0.024 | 0.064 | 0.429 | 0.31 | 0.48 | 0.48 |
| Gadolinium (Gd) | 6 | 0.040 | 0.110 | 0.250 | 0.721 | 0.742 | 1.484 | 1.60 | 2.74 | 2.95 |
| Terbium (Tb) | 6 | 0.010 | 0.020 | 0.050 | 0.104 | 0.107 | 0.211 | 0.22 | 0.37 | 0.40 |
| Dysprosium (Dy) | 6 | 0.040 | 0.110 | 0.270 | 0.800 | 0.825 | 1.899 | 1.82 | 2.97 | 3.22 |
| Holmium (Ho) | 6 | 0.010 | 0.030 | 0.070 | 0.253 | 0.260 | 0.595 | 0.58 | 0.95 | 1.02 |
| Erbium (Er) | 6 | 0.030 | 0.080 | 0.180 | 0.938 | 0.941 | 1.951 | 2.11 | 3.52 | 3.60 |
| Thulium (Tm) | 6 | 0.010 | 0.020 | 0.040 | 0.143 | 0.159 | 0.322 | 0.37 | 0.70 | 0.77 |
| Ytterbium (Yb) | 6 | 0.030 | 0.070 | 0.170 | 1.022 | 1.179 | 2.316 | 3.01 | 6.61 | 7.83 |
| Lutetium (Lu) | 6 | 0.010 | 0.030 | 0.060 | 0.180 | 0.219 | 0.386 | 0.64 | 1.67 | 2.06 |

Table C.14 Summary descriptive statistics for lanthanide rare earth elements for the **mixed bedrock and gravel** lithological group. All values are in ng $l^{-1}$

| | Nr | BEC | LoD | LoQ | Min | 5%ile | Med | Mean | 95%ile | Max |
|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanum (La) | 9 | 0.080 | 0.340 | 0.880 | 2.162 | 2.216 | 5.019 | 5.67 | 12.84 | 15.2 |
| Cerium (Ce) | 9 | 0.130 | 0.610 | 1.580 | 0.215 | 0.352 | 1.361 | 3.07 | 11.03 | 15.7 |
| Praseodymium (Pr) | 9 | 0.020 | 0.100 | 0.260 | 0.482 | 0.504 | 0.639 | 1.07 | 2.51 | 2.7 |
| Neodymium (Nd) | 9 | 0.090 | 0.390 | 0.980 | 2.215 | 2.292 | 3.079 | 4.78 | 11.04 | 12.0 |
| Samarium (Sm) | 9 | 0.050 | 0.160 | 0.390 | 0.648 | 0.666 | 0.977 | 1.32 | 2.61 | 2.7 |
| Europium (Eu) | 6 | 0.020 | 0.050 | 0.130 | 0.152 | 0.159 | 0.247 | 0.25 | 0.33 | 0.34 |
| Gadolinium (Gd) | 9 | 0.040 | 0.110 | 0.250 | 0.677 | 0.753 | 1.234 | 1.60 | 3.23 | 3.4 |
| Terbium (Tb) | 9 | 0.010 | 0.020 | 0.050 | 0.125 | 0.138 | 0.211 | 0.236 | 0.43 | 0.48 |
| Dysprosium (Dy) | 9 | 0.040 | 0.110 | 0.270 | 0.843 | 0.897 | 1.775 | 1.78 | 3.04 | 3.5 |
| Holmium (Ho) | 9 | 0.010 | 0.030 | 0.070 | 0.209 | 0.238 | 0.500 | 0.52 | 0.88 | 1.0 |
| Erbium (Er) | 9 | 0.030 | 0.080 | 0.180 | 0.737 | 0.906 | 1.857 | 1.97 | 3.37 | 3.5 |
| Thulium (Tm) | 9 | 0.010 | 0.020 | 0.040 | 0.087 | 0.122 | 0.295 | 0.35 | 0.65 | 0.65 |
| Ytterbium (Yb) | 9 | 0.030 | 0.070 | 0.170 | 0.621 | 0.910 | 2.319 | 2.86 | 5.78 | 6.3 |
| Lutetium (Lu) | 9 | 0.010 | 0.030 | 0.060 | 0.059 | 0.100 | 0.528 | 0.59 | 1.31 | 1.6 |

# Appendix D Chemical monitoring data

This appendix contains plots of the minor ion and trace element data for the four monitoring wells: St Kieran's well Castlekeeran (Co Meath), Bride's well Calgath (Co Meath), St Moling's well St Mullins (Co Carlow) and St Brigid's well Tully (Co Kildare). Results are presented for each well in turn, with separate graphs for alkali and alkali earth elements; non-metals and metalloids; transition elements, etc.

## St Kieran's well Castlekeeran, Co Meath

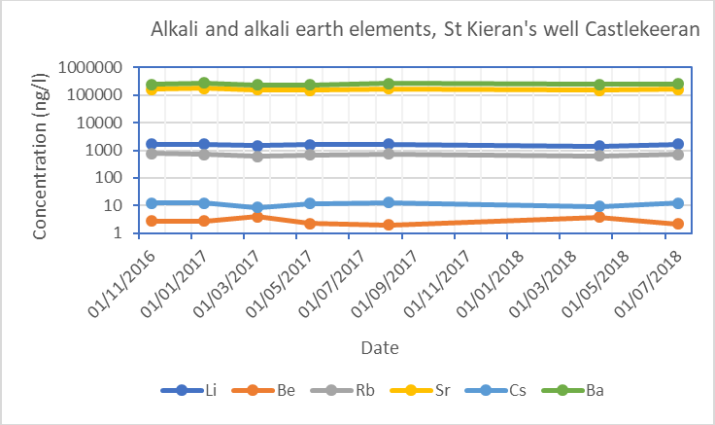



Figure D.1 Monitoring results, St Kieran's well Castlekeeran: alkali and alkali earth elements

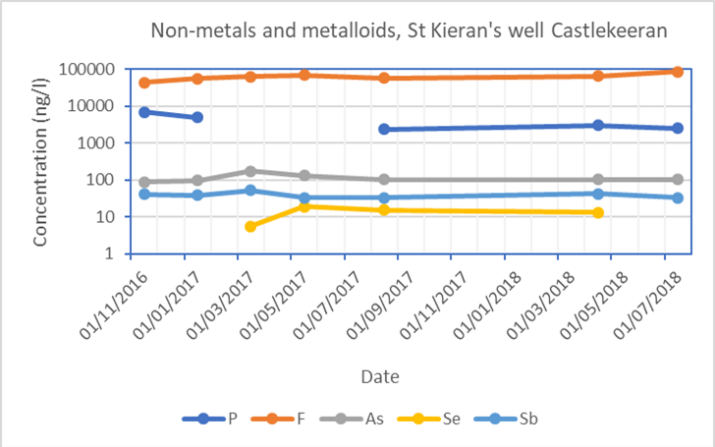



Figure D.2 Monitoring results, St Kieran's well Castlekeeran: non-metals and metalloids

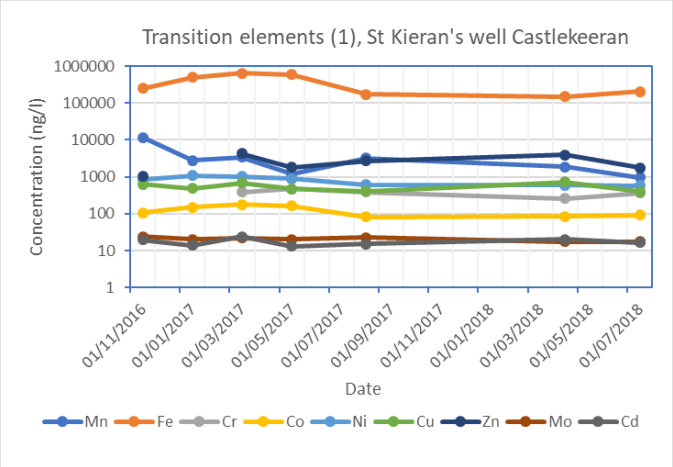



Figure D.3 Monitoring results, St Kieran's well Castlekeeran: transition elements (1)

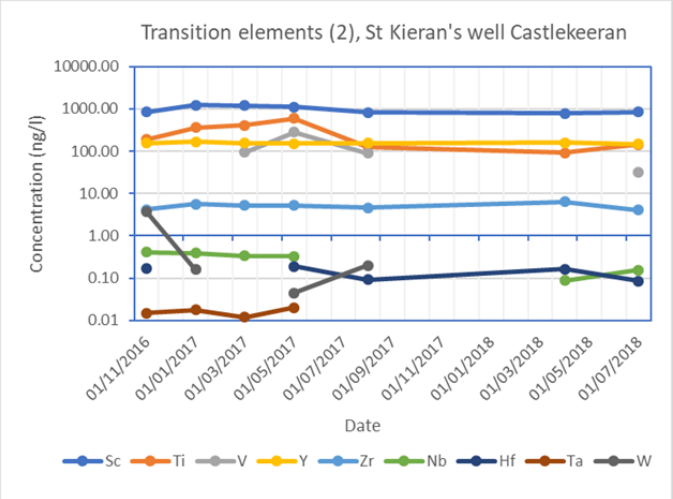



Figure D.4 Monitoring results, St Kieran's well Castlekeeran: transition elements (2)

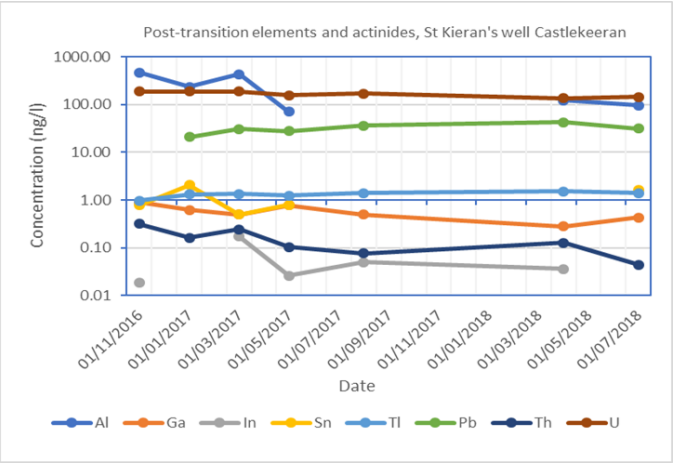



Figure D.5 Monitoring results, St Kieran's well Castlekeeran: post-transition elements and actinides

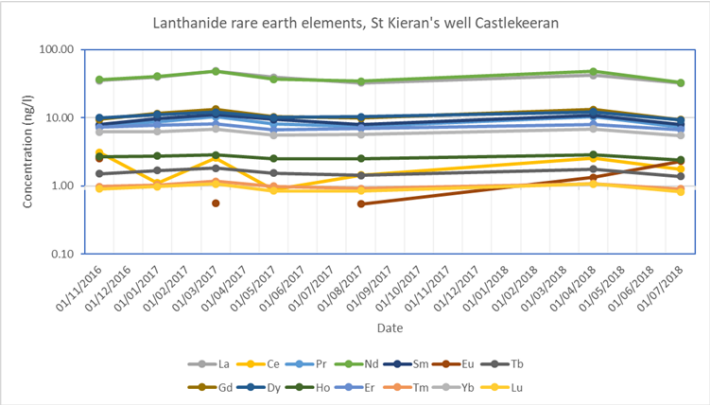



Figure D.6 Monitoring results, St Kieran's well Castlekeeran: lanthanide REEs

## Bride's well Calgath, Co Meath

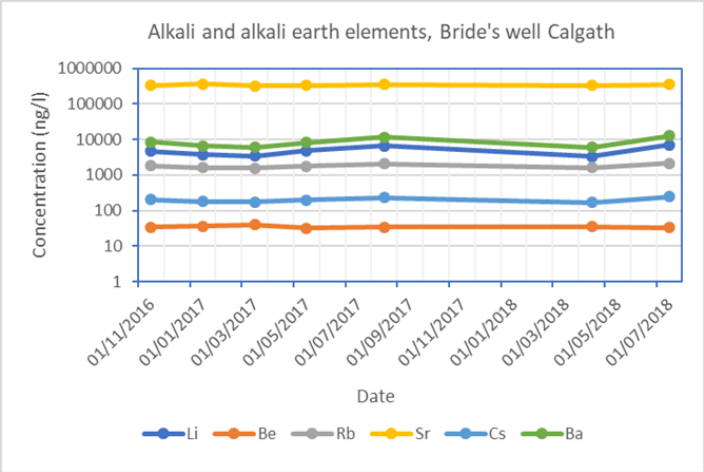



Figure D.7 Monitoring results, Bride's well Calgath: alkali and alkali earth elements

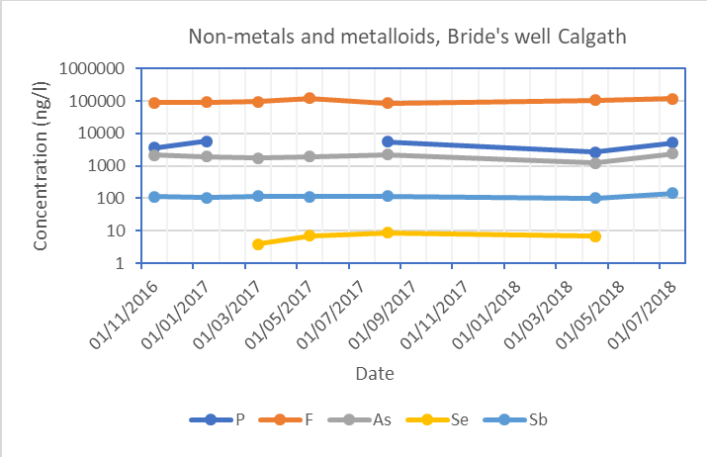



Figure D.8 Monitoring results, Bride's well Calgath: non-metals and metalloids

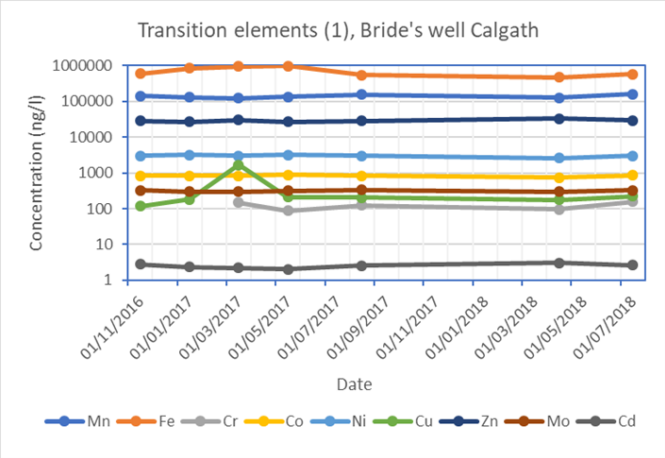



Figure D.9 Monitoring results, Bride's well Calgath: transition elements (1)

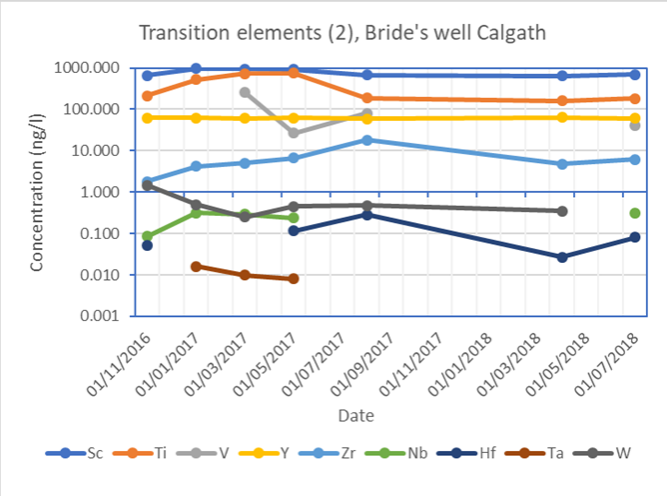



Figure D.10 Monitoring results, Bride's well Calgath: transition elements (2)

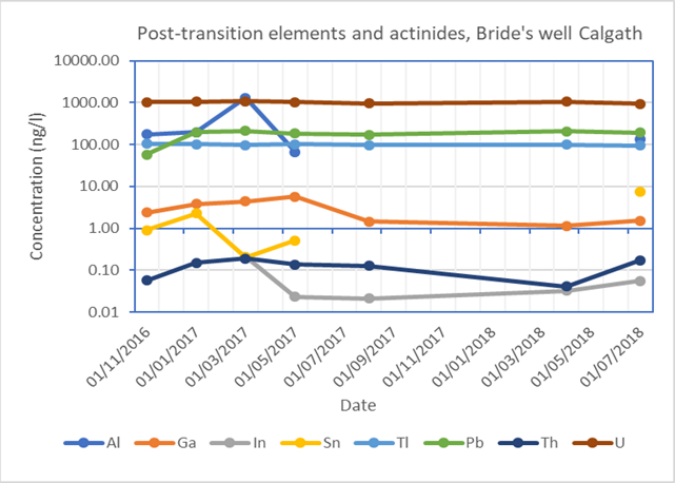



Figure D.11 Monitoring results, Bride's well Calgath: post-transition elements and actinides

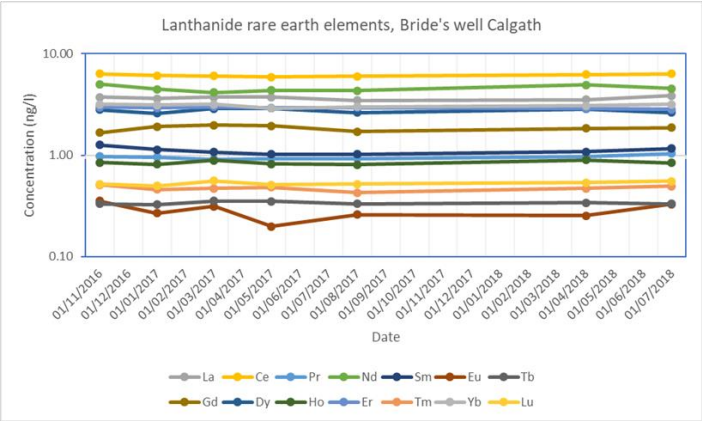



Figure D.12 Monitoring results, Bride's well Calgath: lanthanide REEs

## St Moling's well St Mullins, Co Carlow

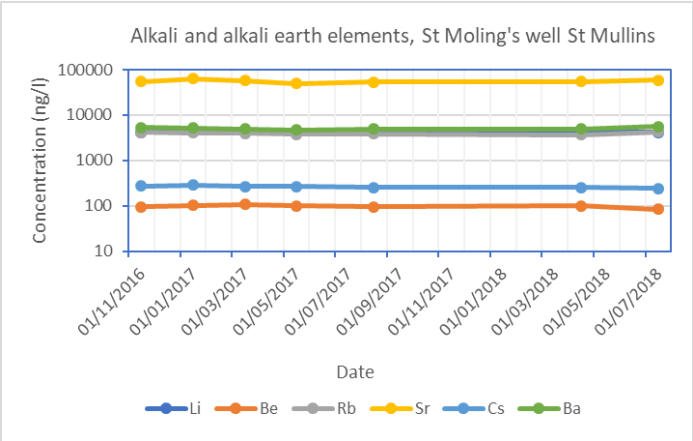



Figure D.13 Monitoring results, St Moling's well St Mullins: alkali and alkali earth elements

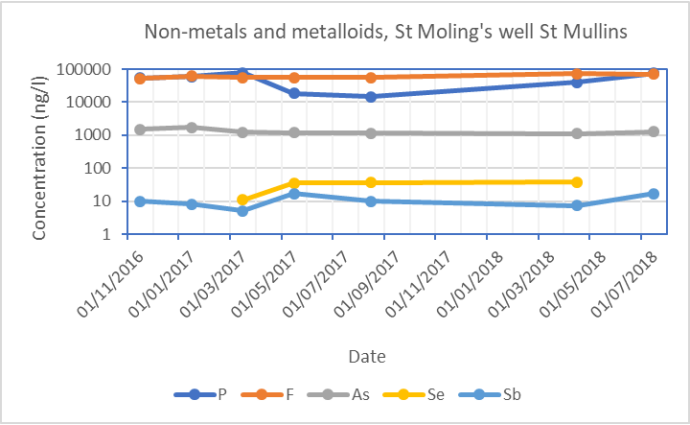



Figure D.14 Monitoring results, St Moling's well St Mullins: non-metals and metalloids

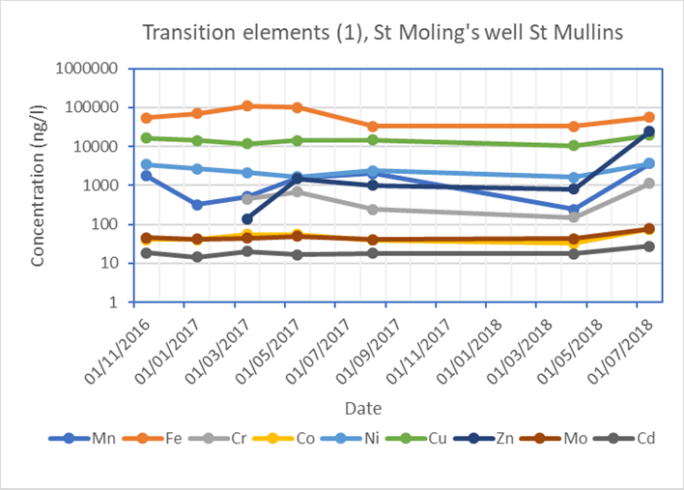



Figure D.15 Monitoring results, St Moling's well St Mullins: transition elements (1)

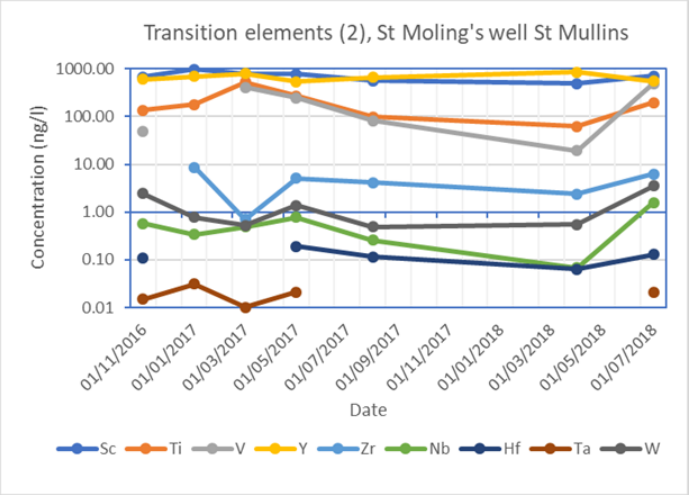



Figure D.16 Monitoring results, St Moling's well St Mullins: transition elements (2)

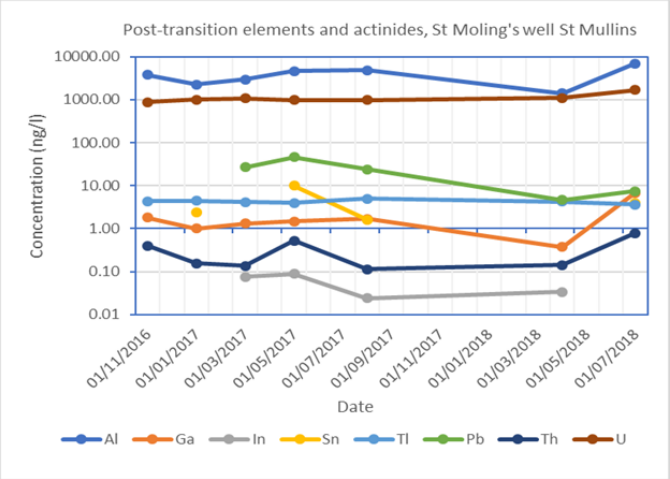



Figure D.17 Monitoring results, St Moling's well St Mullins: post-transition elements and actinides

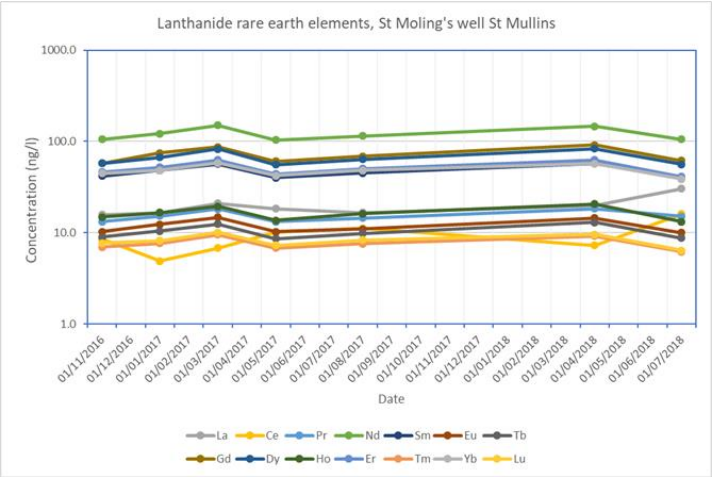



Figure D.18 Monitoring results, St Moling's well St Mullins: lanthanide REEs

## St Brigid's well Tully, Co Kildare

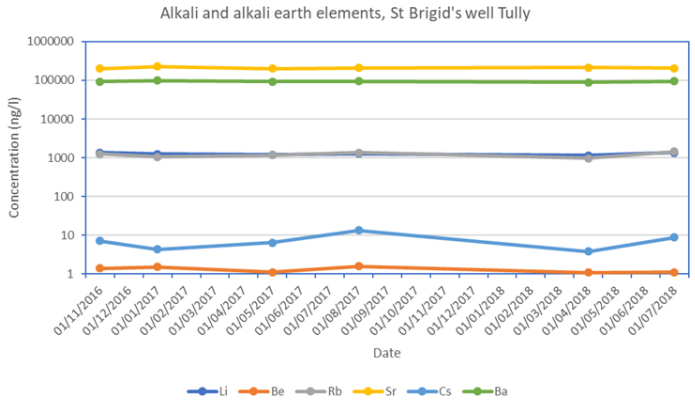



Figure D.19 Monitoring results, St Brigid's well Tully: alkali and alkali earth elements

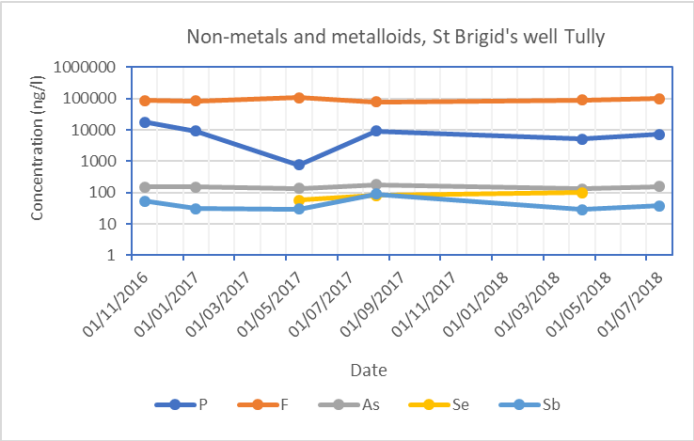



Figure D.20 Monitoring results, St Brigid's well Tully: non-metals and metalloids

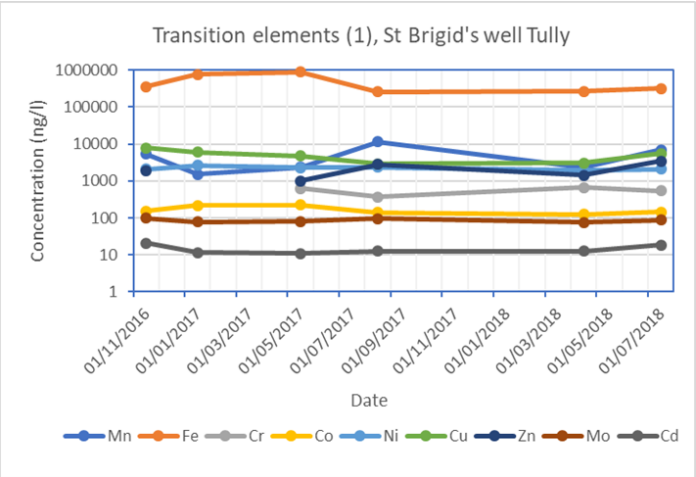



Figure D.21 Monitoring results, St Brigid's well Tully: transition elements (1)

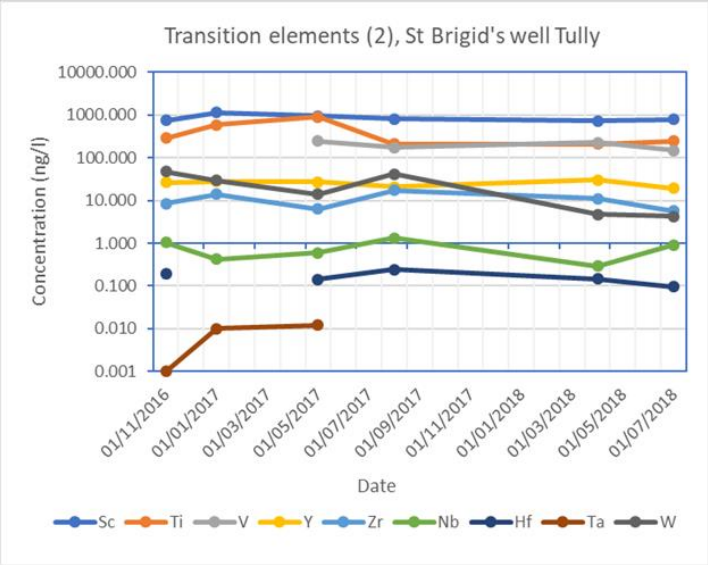



Figure D.22 Monitoring results, St Brigid's well Tully: transition elements (2)

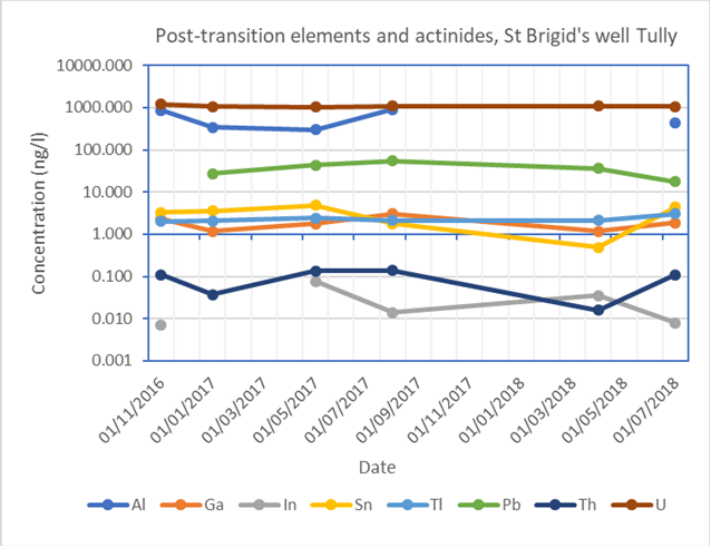



Figure D.23 Monitoring results, St Brigid's well Tully: post-transition elements and actinides

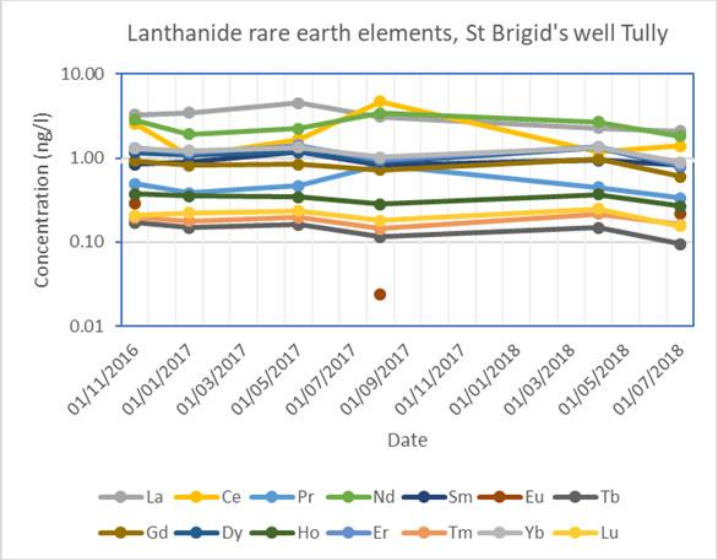



Figure D.24 Monitoring results, St Brigid's well Tully: lanthanide REEs