Investigation of Particulate Phosphorus Mobilised by Run-off in Small Agricultural Catchments

A Dissertation to Fulfil the Requirements to the Degree of Research Master of Science

Submission year of 2022

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Summary

The present investigation on the impact of particle-bound phosphorus (PP), associated with fluvial suspended sediment, in small agricultural catchments was conducted using conventional and advanced solid phase analytical techniques. The former included Konelab, a photometric equipment that relies on colorimetric measurements to determine nutrient concentration on aqueous samples; as well as phosphorus fractionation methods that allowed for the separation, via sequential chemical extraction, of the different types of phosphorus compounds based on their relative reactivity, and solubility in different extraction solutions. The latter were performed in collaboration with the Canadian Light Source, in Saskatoon, making use of the available synchrotron facilities and equipment to perform X-Ray Absorption Near Edge Structure, X-Ray Fluorescence and topochemical mapping of sediment surface structure. Modelling techniques were also employed in this research, namely a run-off (SMARTpy) and a sediment dynamics model (SimplyP), in order to have a better understanding of the particulate phosphorus loads (and, consequently, its chemical fractions) being mobilised by the monitored Irish streams during a continuous period.

Field research was carried out within three geologically and hydrologically contrasting agricultural catchment streams in Ireland: Bunoke (BE, County Limerick), Ballyboughal (BB, County Dublin), and Tintern Abbey (TTA, County Wexford). Three sampling sites were monitored over, at least, 12 months. The sampling sites layout consisted of an outflow location and two other sites further upstream where water and sediment samples were collected periodically.
This investigation concluded that seasonal variations for in-stream soluble reactive P concentrations ranged between 0.05 and 0.2 mg/L at BE, and between 0.015 and 0.2 mg/L at BB and TTA. Dissolved P load transported was calculated to be, approximately, 23.6 tonnes km\(^{-2}\) (from April to November 2019), and 20.4 tonnes km\(^{-2}\) year\(^{-1}\), for BE and BB catchments, respectively. Particulate sediment concentration ranged from 0.9-8.1, 0.4-0.7 and 1.6-11.2 mg L\(^{-1}\) at BE1, BE2 and BE3 respectively; 0.6-0.9, 0.3 and 1.7-3.2 mg L\(^{-1}\) at BB1, BB2 and BB3 respectively; and 0.4-1.1 mg L\(^{-1}\) at TTA1. Particulate P daily concentrations varied at each catchment, with BE having the highest measured PP concentration (BE1: 0.9-2.3 mg g\(^{-1}\); BE2: 1.2-2.5 mg g\(^{-1}\); BE3: 2.1-2.2 mg g\(^{-1}\)), followed by TTA (TTA1: 0.16-1.8 mg g\(^{-1}\); TTA2: 0.3-1.2 mg g\(^{-1}\); TTA3: 0.3-1.5 mg g\(^{-1}\)) and BB (BB1: 0.5-1.5 mg g\(^{-1}\); BB2: 0.3-0.4 mg g\(^{-1}\)). Sequential sediment extractions showed a decrease in residual P, loosely sorbed P, and organic P fractions when comparing a winter period (December 2017) to samples taken in the summer (June 2018) in TTA and BB, while BE saw a decrease in Fe/Mn bound P and non reducible P fractions from January to June 2019. In addition, at BB outflow, the dynamics of the PP fraction within fluvial suspended solids revealed that P fraction composition in the sediment significantly changed throughout storm events: during a summer storm, before the event, the major detected fraction was composed of organic P and inorganic P afterwards; during a winter storm the inverse was observed. Finally, the hydrology and P transport in the rivers monitored catchments were simulated using computer models of which were then used to extrapolate the findings to longer periods. These simulations suggested that BE had the highest yearly in stream sediment load and that PP is the main contributor to total P found in stream water, largely surpassing total dissolved P.
Acknowledgement

I would like to express my utmost gratitude towards Dr. David O’Connell, for he was the person directly involved in accommodating me in Dublin and allowing me to become a Trinity College student for the past 2 years. I am truly thankful to him for allowing me to experience this privileged work and educational opportunity that I otherwise would have certainly missed. Besides that, his supportive and passionate approach to research along with his inspiring guidance made my first years abroad a fulfilling and enriching experience, both at an academic and personal level. Along with his own expertise and knowledge on the research at task that was shared with me along the way, David also instilled confidence in my own ideas and work ethic within the research and laboratory environments.

I am also extremely grateful to Prof. Laurence Gill for taking the time out of his own work and busy schedule to help me with the computational modelling and reviewing of this dissertation. Additionally, without his and David’s huge assistance, motivation and sense of direction given on our periodic meetings, writing would have been an exceptionally agonising process.

The rest of the Watts Building Environmental Laboratory group, Shi, Li, and Luka whose knowledge and experiences guided me through the challenges faced in the laboratory and motivated me to keep moving forward with timely advice and honest smiles. A special word of appreciation to Luka that was always available for anything and everything, even if all that I needed was a simple good-humoured conversation that inevitably lead to genuine laughs. These special friendships made the late working nights and early mornings, and even weekends much easier.
I wish to extend these acknowledgements to all the technical staff for their continued assistance throughout the years, including Mary, Patrick, Eoin, Robert, and Dave. A special thanks to Mary and Eoin for they were the ones I worked more closely with.

An importance acknowledgement must be made for Cindy and our collaborators at the Canadian Light Source, Dr. Yongfeng Hu, Dr. Qunfeng Xiao and Dr. Mohsen Shakouri. They welcomed me to Canada and received me very well. Their expertise in advanced spectroscopic techniques and patience to educate me in it, in just a few days, was much appreciated.

Finally, a heartfelt Thank You to my parents. They endured through really tough emotional and financial few months at the start of my degree to give me the chance to keep going. And, last but not least, a strong, warm hug to all the special friends I have made along the way, from Niko to Olga, from Cristina to Eduardo. Circumstances made so that we cannot stay in touch as regularly as we did, but their warmthness, support, availability, openness, and friendship along these years were fundamental in keeping a clear head during these extraordinary times.

Acknowledgements are rarely fair to make. The probability that someone that helped me along the way and is left out of this formal acknowledgement is not null. Thus, let this final remark thank those I haven’t specifically stated but, in one way or another, contributed to the conclusion of this dissertation.
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Abstract

Research carried out in this work has contributed valuable insights and new findings into the impact of particulate phosphorus (PP) associated with fluvial suspended sediments, in terms of its sources and speciation dynamics within geologically and hydrologically contrasting agricultural catchment streams. Various conventional and advanced solid phase analytical techniques were used, in order to provide a detailed analysis of the phosphorus (P) fractions associated with fluvial suspended sediments. Three agricultural catchments were monitored which showed seasonal dynamics in nutrient concentrations and export: Bunoke (BE), Ballyboughal (BB), and Tintern Abbey (TTA). Seasonal variations for in-stream soluble reactive P concentrations ranged between 0.05 and 0.2 mg/L at BE, and between 0.015 and 0.2 mg/L at BB and TTA. Dissolved P load transported was calculated to be, approximately, 23.6 tonnes km\(^{-2}\) (from April to November 2019), and 20.4 tonnes km\(^{-2}\) year\(^{-1}\), for BE and BB catchments, respectively. Sediment concentration ranged from 0.9-8.1, 0.4-0.7 and 1.6-11.2 mg L\(^{-1}\) at BE1, BE2 and BE3 respectively; 0.6-0.9, 0.3 and 1.7-3.2 2 mg L\(^{-1}\) at BB1, BB2 and BB3 respectively; and 0.4-1.1 mg L\(^{-1}\) at TTA1. Particulate P daily concentrations varied at the each catchment, with BE having the highest measured PP concentration (BE1: 0.9-2.3 mg g\(^{-1}\); BE2: 1.2-2.5 mg g\(^{-1}\); BE3: 2.1-2.2 mg g\(^{-1}\)), followed by TTA (TTA1: 0.16-1.8 mg g\(^{-1}\); TTA2: 0.3-1.2 mg g\(^{-1}\); TTA3: 0.3-1.5 mg g\(^{-1}\)) and BB (BB1: 0.5-1.5 mg g\(^{-1}\); BB2: 0.3-0.4 mg g\(^{-1}\)). Sequential sediment extractions showed a decrease in residual P, loosely sorbed P, and organic P fractions when comparing a winter period (December 2017) to samples taken in the summer (June 2018) in TTA and BB, while BE saw a decrease in Fe/Mn-bound P and non-reducible P fractions from January to June 2019. In addition, at BB outflow, the dynamics of the PP fraction within fluvial suspended solids revealed that P fraction composition in the sediment significantly changed throughout storm events: during a summer
storm, before the event, the major detected fraction was composed of organic P and inorganic P afterwards; during a winter storm the inverse was observed. $P_{\text{Res}}$ fraction predominated at BB1 and TTA1 and BE2 (1.1, 1.3 and 1.0 mg g$^{-1}$, respectively); $P_{\text{HCl}}$ and $P_{\text{Org}}$ were measured the highest at BE1 (0.4 mg g$^{-1}$) and BE3 (0.3 mg g$^{-1}$), respectively; PNR was the second most common P pool detected, with BE3 having the highest concentration (0.6 mg g$^{-1}$); PRedox was the least dominant PP extracted fraction, with BB1 having highest measured PRedox concentration (0.3 mg g$^{-1}$); PH2O fraction varied greatly with catchment location, with the highest concentrations found at BE2 (0.5 mg g$^{-1}$), BB1 (0.4 mg g$^{-1}$), and TTA2 (0.3 mg g$^{-1}$). Finally, the hydrology and P transport in the rivers monitored catchments were simulated using computer models of which were then used to extrapolate the findings to longer periods. These simulations suggested that BE had the highest yearly in-stream sediment load and that PP is the main contributor to total P found in stream water, largely surpassing total dissolved P.

*Keywords*: water quality; environmental chemistry; sediment sequential P fractionation; synchrotron analysis; surface runoff model; sediment dynamics model; agriculture catchment; particulate phosphorus
1. Introduction

This research focused on quantifying and characterising various forms of phosphorous-bound compounds associated with suspended sediments in surface waters, from three agricultural catchments.

Globally the discharge of excess bioavailable phosphorous compounds from agricultural catchments to associated aquatic ecosystems is a significant water pollutant. The accumulation of such phosphorus compounds accelerate eutrophication leading to degradation of water quality (Charlton et al. 2018). Eutrophication is the term given to the gradual increase in plant nutrient concentration in an aging aquatic ecosystem (Richardson and Jørgensen, 1996).

In intensive agricultural catchments excessive use of artificial fertilizers and/or manure which is not utilized by crops often form enriched runoff which finds its way to surface waters. Consequently, the aquatic ecosystem becomes enriched with phosphorus from such anthropogenic activities. This increase of nutrients to the system promotes the growth of algae and other microscopic organisms, and, in more dire cases, a dense aquatic population of microscopic photosynthetic organisms – known as a algal bloom – completely covers the surface of lakes and slow-flowing rivers/streams. The overgrowth of algae and other microscopic organisms has a detrimental effect on both the quality of water (discoloured water, and the possibility to irritate skin and respiratory tract of humans) and on the aquatic ecosystem (by preventing light to penetrate the surface, the consequent depletion of dissolved oxygen buy microorganisms feeding off the increased organic matter being produced as a result of the algae, the organisms or the toxic substances excreted by them poison aquatic animals and waterfowl) (Brooks et al., 2015).
Nitrogen (N) and phosphorus (P) are the main nutrients that algae and other microscopic organisms need to proliferate and cause the system to become eutrophic (Schindler et al., 2016), however, of the two, only P is the limiting nutrient for plankton growth in fresh water ecosystems (Ma et al., 2019), making the control and ongoing monitoring of its concentration in high-risk catchments a necessity.

There are several possible sources of artificially added nutrients that make their way either indirectly from land into water bodies – agricultural activities via over fertilisation using chemical additives or animal manure, and stormwater runoff from roads – or that are directly transported to the fresh water bodies – discharge from industrial sources, municipal wastewater effluent, and septic tank contamination (Lennox et al., 1998).

This study involves monitoring geologically contrasting agricultural catchments to assess the level of P inputs into the rivers associated with sediment transport. This can enable the discussion to take place to establish a neutral ground between farmers expected agricultural yield and maintaining good water quality and a balanced aquatic ecosystem. Moreover, the world’s P supply is finite and non-renewable (Jordan-Meille et al., 2012) and so the usage of fertilisers needs to be as efficient as possible in order to extend P availability for the future. It should be noted that inconsistencies between advised and reported P fertiliser consumption on an EU level have been found and published (Tóth et al., 2014), reflecting the generally poor nutrient-use efficiency.
Historically, crop yield was only dependant on the natural P availability on a given soil complemented by organic manure input from farmers. However, with the increase in population and a more accessible and wider market, food demands have surged dramatically. With this steady growth followed improvements in agrotechnology, and fertilizer P application became a significant source of soil P (Cordell et al., 2009).

Soil P is one of the essential nutrients for plant development and growth, yet it is often found sorbed to soil clay surfaces, aluminium (Al) and iron (Fe) oxides, carbonates and organic matter which, in turn, slows down the chemical processes that render it bioavailable, within the soil environment (Tóth et al., 2014). In fact, the sorption potential of P by most soils and sediments is several orders of magnitude higher than the corresponding dissolved P concentration (Frossard et al., 2000). In a recent study, Pavinato et al. analysed soils subject to artificial addition of P in the form of fertilisers and found that over 70% of the excess P added to the soil remained in the soil, and most of it was present in chemical forms that aren’t easily accessible to crops (Pavinato et al, 2020).

The recurrent practice of overusing artificial nutrients by farmers leads to the formation of large reservoirs of residual P that accumulate in the soil over the years, also known as legacy P. This form of residual P can be transported to surface water bodies physically, through what is called a “cascade”, or chemically via a collection of processes known as “spiralling” (Sharpley et al., 2013). A cascade is a term used to describe the transfer of nutrients from areas of runoff and sediment erosion, utilizing transport pathways and intermediate stores, to the watershed outlet (Burt and Allison, 2010), while spiralling refers to a myriad of biogeochemical processes
such as mineral precipitation and dissolution (House, 2003; Pierzynski et al., 2005), sorption and desorption (Froelich, 1988; House et al., 1998; Reddy et al., 1999), organic P mineralisation (Condron et al., 2005; Jakobsen et al., 2005) and molecular diffusion (Frossard et al., 2000; Moore and Reddy, 1994).

Research on this pollution source has been growing and an increased awareness on the need to gather more information related to nutrient transport mediated by fluvial suspended sediments has also been shown in recent publications (Zhang et al. 2020, Huang et al. 2020). It is now understood that, from the total load of phosphorous transported in rivers, a significant proportion of it is in the form of particulate phosphorus (PP) (Ballantine et al. 2008) – a definition that encompasses all non-dissolved phosphorus compounds that can be removed from a water sample by filtration. Furthermore, the rate of which fluvial solids deposit on the channel bed or floodplains can alter P long-term storage and, in a parallel way, remobilization of channel bed sediments along with erosion of the embankment can increase its short-term availability by reintroducing PP, in the form of sediments, to the river. This hazard evaluation was achieved by studying potential agricultural catchments at risk owing the high levels of suspended solids during high flow periods; evaluating the rivers’ water quality and sampling suspended sediments at different points along the catchments; and performing several chemical and instrumental analysis on both water and sediment samples to further improve and complete the sampled information.
2. Literature review

2.1. Introduction

Water quality improvement is an emphasized goal of national management efforts focused on watersheds / catchments, particularly in Ireland, due to the increased pressure exerted by agricultural activities, and land use, on small catchments (EPA, 2020). Under the EU Water Framework Directive [WFD] (2000/60/EC), groundwater and surface water should be considered as components integrated in the overall water balance of a river basin. The WFD seeks all water bodies to reach a standard deemed “good”, however (and despite the a significant impact on water quality that fluvial suspended sediment concentrations can have), currently there are no legal limits in place to keep fluvial suspended sediment concentrations under potentially nefarious levels. A suspended sediment annual mean threshold of 25 mg L$^{-1}$ was introduced for rivers through the EU Freshwater Fish Directive (FFD – OJEU, 2006) but was subsequently removed.

Surface water quality can be defined by hydrological and biogeochemical mechanisms such as land cover, use, and management, geology and soil type, climate, topography, catchment hydrology (Lintern et al., 2018); these are mechanisms that control the source, mobilisation, and
supply of nutrients and other chemical species to surface waters (Hanrahan et al., 2021), all of which are significantly influenced by agrarian activities (Blann et al., 2009).

Among its other uses, P plays a fundamental role in terms of global food production (Némery and Garnier, 2016) and its impact in water bodies, primarily due to losses from agricultural soils, can lead to ecological issues caused by eutrophication (Andersen et al., 2017). To date, it is widely known that excessive in-stream P concentrations is one of the most common cause of eutrophication and degradation of surface water quality (Crocker et al., 2021).

![Figure 2.2. Typical summer scenario at the Bunoke catchment, where tall aquatic vegetation bloom in low flow conditions and high dissolved P concentrations.](image)

Under high concentrations of P compounds, surface water systems tend to be dominated by algae or duckweed, which leads to more surface shading and, potentially, anoxic conditions and
therefore deterioration of aquatic ecosystems (Zhang et al., 2017). Additionally, more extensive surface coverage and subsequent biodegradation of abundant organic matter, produced by algal and duckweed blooms, leads to the eventual exhaustion of dissolved oxygen levels, which, consequently, is responsible for the depletion of aquatic fauna diversity, as well as the development of bad odours (Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

### 2.2. Phosphorus forms

Naturally occurring P species are diverse but can be classified in terms of their origin and chemical bond to other elements. Total P (TP) generally encompasses all P forms of dissolved and particulate P; dissolved P could contain orthophosphates (pH dependent forms of phosphoric acid), organic (adenosine triphosphate, for example) and inorganic (pyrophosphate, or trimetaphosphate) condensed phosphates, organically bound phosphates (such as phospholipids, phosphoamides or phosphoproteins); particulate P (PP) might also contain some organically bound P, but also mineral P (as P is covalently bound to metal complexes such as hydroxyapatite, fluorapatite, or brushite) and is typically associated with sediment particles (Maher et al., 1998). Studies have shown that a significant amount of TP loads transported in streams and rivers are mostly in the form of PP (Ballantine et al. 2008, Tang et al., 2018). Subsequently, in the past few years, there has been increasingly more awareness to the importance of fluvial suspended sediments in the transport of nutrients, such as P, in agricultural catchments (Pulley et al. 2016, Sandström et al., 2020).
Most of dissolved P sources are anthropogenic, reaching the streams via surface runoff (Wang et al., 2020) – typically organic phosphate forms of P – or through domestic or industrial wastewater discharges (Wu et al., 2020) – normally condensed inorganic phosphates used in detergents, for example. Dissolved orthophosphate sources derive from fertilisers and manure applied to agrarian or residential cultivated land, while dissolved organic compounds containing esters of phosphoric acid and phosphonates originate from the microbiological breakdown of organic material, or from excreted metabolic side-products (Maher et al., 1998). PP may be found incorporated in minerals, adsorbed to particle surfaces, and associated with organic matter (Maher et al., 1998). Naturally occurring PP originates from weathering and erosion products,
authigenic mineral formation by precipitation of inorganic phosphorus, and plant, animal and bacterial cellular material (Broberg and Persson, 1988).

### 2.3. Phosphorus cycle

The natural phosphorus cycle starts with the weathering of P-containing minerals into the soil and streams in the form of PP; when released from PP from P can then taken up by microbes and plants, and subsequently by herbivorous animals that eat the plants; P returns to the soil via animal excretions, and by decomposition of dead fauna and flora, restarting the cycle (Jupp et al., 2021). The main mechanisms responsible for the release of P from PP are the reduction of phosphate complexes, typically under conditions when available oxygen concentrations are very low or non-existent, ligand-exchange reactions in alkaline conditions, and mineralization of organic P via natural biogeochemical reactions (Zhang et al., 2012).

With time, some phosphorus is inevitably and naturally lost to the sea, where over an extended (geological) time period it is reincorporated in sedimentary rock, however, the increased amount of phosphate in the soil, resulting from decades of fertiliser and animal excrement use in agriculture, also leads to an inevitable increase in the loss of phosphates into waterways, as a result of the anthropogenic cycle of P (Jupp et al., 2021).

The anthropogenic cycle starts with the mining of phosphate rock (PR) and respective mineral extraction. Global food needs require extensive mining of PR, which poses a serious problem for the not-so-distant future, since PR is a finite geological resource and keeps dwindling the more it is mined. Refined P compounds are then used for crop cultivation, where a portion of
the available P is consumed, and the excess P is unavoidably mobilised to the nearest waterway, leading to anthropogenic eutrophication of the aquatic ecosystem. Part of the soil excess P can be recovered and recycled at wastewater treatment plants, lessening the scarcity of PR and completing the artificial cycle (Jupp et al., 2021). Thus, today P is a double-edged problem: unsustainable P insufficiency, with the dwindling supply of accessible PR (potentially causing economic volatility and political tensions worldwide) (Cordell and White, 2011), and an excess of P in surface waters that raise serious environmental concerns.

2.4. Run-off: Soil P Pathways and Sources

Agriculture is responsible for more than 50% of the poor water quality cases in Irish catchments (EPA, 2015). Legislation is currently in place to protect water quality at an European level, mostly through the instrumentation of both EU Nitrates (Council Directive 91/676/EEC,
1991) and Water Framework (Directive 2000/60/EC, 2000) directives. These legislative directives ultimately aim to reduce the input of agriculturally-derived nutrients into headwaters, while promoting good farming practices via mandatory or incentivised programmes at a European level. However, despite these regulatory frameworks being in place for over two decades, agriculturally-derived nutrient mobilisation to freshwaters remains a threat to water quality (Kleinman et al., 2015; Murphy et al., 2015; Buckley et al., 2016; Barry and Foy, 2016; Melland et al., 2018).

The major concerns around water quality in Ireland are related to the impacts of cattle faecal waste (EPA, 2010), which is a problem aggravated by a steady expansion of agricultural activities in the country: the area of agricultural land farmed organically in Ireland increased by 267% between 1997 and 2017 and, to boot, in 2019, Ireland had the fourth largest cattle herd in the EU28 (Central Statistics Office, 2019). Balancing the plates of the environmental scale implies reconciling the Agriculture Department goals (Food Harvest 2020 and Food Wise 2025, for example) to increase food production and generate revenue, with the increasing pressure to monitor and improve water quality. Adding to the current land management hardships, there are also knowledge gaps concerning dissolved and particulate nutrients’ diffuse and point agricultural pollution sources (Harrison et al., 2018).

Diffuse agricultural pollution sources refer to certain catchment locations where nutrients normally mobilise towards receiving waters, typically via storm-generated surface run-off (Edwards and Withers, 2008). Point sources, on the other hand, are easier to identify as they consist of areas where nutrients and other pollutants enter water channels through direct discharge
and are, therefore, routinely monitored (Palmer-Felgate et al., 2009). Point sources in farmyards are easily identifiable but can nonetheless greatly contribute to high nutrient concentrations and poor water quality. It is argued that management practices that are currently in place to control diffuse P inputs from farmland and the surrounding landscape to aquatic systems, may be ineffective in bettering stream water quality (Harrison et al., 2019).

Furthermore, occasional small-sized, discrete, areas within the catchment that are unusually rich in nutrients, can, in turn, contaminate waterways via drainage ditches, as heavy rainfall events generate surface run-off from impermeable surfaces such as farm roadways, farmyards and cattle drinking areas (Heathwaite et al., 2003; Edwards and Withers, 2008). Within nutrient-rich parts of a watershed, typically fields where cattle is being raised, areas more susceptible to soil saturation, including streams, disproportionately feed more nutrients to streams than other parts of the catchment (Archibald et al., 2014; Lerch et al., 2015; Peukert et al., 2016). Surveying, identifying and dealing with many such small intermediate eutrophic sources, that potentially may discharge elevated quantities of nutrients into the stream network, is a difficult and time consuming challenge to tackle on-site due to the complexity and diverse variety of potential pollution sources and the seasonal dynamics of these endangered geo-hydrological systems. Moreover, discharge from such intermediate sources make up a major, and largely unaccounted for, source of excess nutrients, for which not enough data exist (Heathwaite et al., 2003). Thus, further research is required in order to better understand, and rapidly detect and manage multiple intermediate pollution source inputs in agricultural catchments.
Run-off samples of polluted water containing dissolved and particulate P from agricultural catchments, especially dense in dairy farmyards, have been proven to contain a high load of soluble reactive P (SRP), as well as ammonium and OM, typically traced back to large quantities of manure, silage effluent and other dairy waste that could easily be found in close proximity to farmyards (Hatch et al., 2004; Edwards et al., 2008; Edwards and Hooda, 2008). Moreover, cattle behaviour appears to have significant impacts on site hydrology (Georgakakos et al., 2018). If allowed, while seeking water or simply the comfort of shade, cattle can compact the soil near streams and, consequently, increase the risk of run-off (Trimble and Mendel, 1995).

Practices like avoiding fertilisation, spreading manure, or faecal deposition in areas at risk of generating run-off have been proven to mitigate diffuse source pollution in agricultural catchments (Thodsen et al., 2015; Winchell et al., 2015; Knighton et al., 2017). Additionally, uncultivated borders to streams, also known as riparian buffers, are sometimes applied strategically to mitigate nutrient pollution in agricultural catchments because 1) they reduce the mobility of pollutants within the buffer area, 2) they slow surface run-off flow and allow for deposition and degradation of nutrients, and 3) unbuffered waterways and their respective riparian zones generate disproportionate amounts of run-off due to increased levels of soil moisture (Georgakakos et al., 2018).

2.4.1. Particulate-P

Determining and characterising P sources is especially important in agricultural watersheds, where diffuse pollution sources may endure despite efforts to reduce P input, often due to the mobilization of legacy P pools (Powers et al., 2016). In addition to dissolved P, particulate P (PP)
is also an important fraction in river water, as PP may account for over 40% of the P load in rivers (Jarvie et al., 2006). For example, sediments and PP, derived from erosion of arable land that eventually mobilise into surface waters, have been shown to contribute substantially to pollution of waterways in agricultural catchments, from an extensive study in the Swiss Midlands over 20 years (Remund et al., 2021). According to the authors, of the total amount of soil lost to erosion, 21% of it reached water bodies, on average. Furthermore, 88% of the total sediments and PP found its way to surface waters indirectly, being transported through drainage pipes with inlet shafts from farm roadways.

Nonetheless, the contribution of mobilised P, via subsurface pathways such as tile drains, is still downplayed in the scientific community (Jiang et al., 2021). Subsurface transport of P during heavy rainfall periods (typically associated with storm events) has been shown to be responsible for major P losses in agricultural systems (Sims et al., 1998; Heathwaite and Dils, 2000; McDowell and Sharpley, 2001; Uusitalo et al., 2001), and mechanisms linked to subsurface P loss have been suggested to be preferential flow and artificial drainages, which include both ditches and tiles (King et al., 2015; Laubel et al., 1999).

Published in 2021, an in-depth study on the P fractionation of PP, performed on suspended sediments collected from areas dominated by row crop production, reported that on a Spring storm event, the SRP concentration in tile waters was already near or above the eutrophication inducible P level: approximately 0.02 mg L$^{-1}$, however, disconcertingly, the PP concentration in tile lines was more than double that amount (Jiang et al., 2021). The authors found that phosphate enriched particulates can be transported for long distances in agricultural networks, especially if associated
with colloidal particles. P speciation lead the researchers to conclude that silt and colloidal size particles were responsible for effectively transporting both inorganic and organic P, and that, by adsorbing to clays and clay minerals, ortho-P and organic P are more easily mobilised through tile lines. Linked to the impact of clay soils in the transport of PP, a study conducted in Sweden demonstrated that, in agricultural catchments, both clay content in the soil, and fraction of agricultural land in the catchment have the highest potential to influence the concentration of in-stream suspended sediments (Sandström et al., 2020). Additionally, it was shown that Organic P is transported through water channels, it could potentially mineralise and further contribute to the concentration of legacy P in the Mississippi River, where the research was conducted (Jiang et al., 2021).

Filling knowledge gaps in P cycling is of great importance for land management and water quality control, especially as we move forward towards a world where extreme weather conditions will become increasingly more prevalent. Extreme events derived from climacteric changes has been proven to be linked with increased mobilisation of highly reactive PP and dissolved P species to surface waters (Mavrocordatos et al., 2000; Kilroy and Coxon, 2005), as well as with the mobilisation of these P species from diffuse sources in agricultural catchments (Wu et al., 2012; Mellander et al., 2015; Bol et al., 2018).

2.4.2. Legacy P

Of all the P in manure and artificial fertilisers used in agricultural cultivation, less than 50% of it is utilized by the growing harvest crops, with less than 30% of such P input being converted into food for human consumption (Van Dijk et al., 2016). Because artificial P inputs
surpass agronomic requirements, the surplus P tends to accumulate in the soil, over time. This accumulated P is named legacy soil phosphorus, or legacy P for short (Kleinman et al., 2015). A recent study estimated that mobile P fractions in the soil could have a residence time of approximately 30 years (McCrackin et al., 2018).

Legacy P may be washed off critical source areas within the agricultural catchment into rivers, streams, or lakes in different particulate mineral and/or organic forms (Zhang et al., 2020). Legacy P slowly releasing into surface waters can cover water quality improvements, rendering the task of distinguish the effects of current conservation measures from historical land mismanagement more difficult (Hamilton, 2012; Jarvie et al., 2013). Thus, it is critical to manage fertiliser and manure usage so as to strike a balance between a worldwide economic demand for large scale food production, and a sustainable use of the already depleting P reserves.

2.5. Chemical P fractionation of particulate-bound phosphorus

Sediments play a major role in P cycling because they can act as P sinks, or as P sources, with PP functioning as an interface between aquatic systems and sediment layers (Jarvie et al., 2005). The amount of P released from PP is called internal P loading and the fractionation of PP associated with fluvial sediment can be beneficial to achieve a better understanding of P cycling in the aquatic ecosystem (Fytianos K. and Kotzakioti A., 2005).

Depending on the chemical bond type to other molecules or metals, or on the type of electrostatic interactions with the sediment matrix, PP can be chemically extracted into different
fractions/pools. These fractions are often named after the extractant solution or the chemical properties of P in that specific fraction. A commonly used nomenclature for the different fractions is as follows:

- labile P, referring to loosely bound or adsorbed P and serves as an estimation of the immediately available P;
- reducing P, the biodegradable P fraction within PP that is easily oxidised and typically found on iron hydroxide surfaces;
- metal-bound P, generally adsorbed to metal oxide agglomerates such as Al₂O₃;
- calcium-bound P, a fraction where P is commonly found bound to carbonates, but also in apatite and other acid soluble oxides; and

Depending upon soil redox conditions, partial release, and consequential mobilisation of P in these fractions from PP may occur (Rydin, 2000). P mobilisation from sediments may depend on the quantity and spatial distribution of P fractions within the sediments, the degree of saturation of exchangeable adsorbed P and of hydrological conditions (Ruttenberg, 1992; Balchand et al., 1994). For example, loosely sorbed P not only can be readily consumed by organisms (Zohar et al., 2010; Jaisi et al., 2011), but also easily transported into agricultural surface waters (Vitousek et al. 2009). In addition to different P pools having distinct and variable reactivity, P fractions also can be interconverted with each other (Ruttenberg, 1992; Lin et al., 2018). Thus, a better understanding of the source and transformation of different P pools
in PP associated with sediments is essential for better land management, resource sustainability and more environmentally aware agricultural practices.

Over the years, sequential chemical extraction methods have been established (Cross and Schlesinger, 1995; Likkari et al., 2007) and improved so as to better elucidate the chemical nature of different types of sediment associated PP (Hupfer et al., 1995; Kaiserli et al., 2002; Cavalcante et al., 2018; Kumar et al., 2018). Chemical P fractionation involving sequential extraction methods is based on differences in reactivity of the various P fractions to different extractant solutions conditions such as pH, redox potential, and temperature (Hietltjes et al., 1980).

Currently, different variations of already published methods are being applied to chemical P fractionation of PP associated with sediments of different geological origin. Examples of these chemical extraction methods are the modified Hedley’s P fractionation procedure (Zhang and MacKenzie, 1997); the SEDEX wet chemical sequential extraction (Ruttenberg, 1992); and the standard measures technology (SMT) procedure (Ruban et al., 1999), which, in turn, is a modified Williams method (Williams et al., 1967).

Wang et al. (2021) used a modified Hedley’s chemical extraction to characterise sedimentary P in Lake Erie, at the border between Canada and the USA. In this method sedimentary P was fractioned into eight pools: H$_2$O-P$_{\text{inorganic}}$, H$_2$O-P$_{\text{Organic}}$, NaHCO$_3$-P$_{\text{inorganic}}$, NaHCO$_3$-P$_{\text{Organic}}$, NaOH-P$_{\text{inorganic}}$, NaOH-P$_{\text{Organic}}$, HCl-P$_{\text{inorganic}}$, and residue P. To achieve this, a 0.5 g sediment sample was sequentially extracted using 30 mL of four different extraction
solutions: deionized water, 0.5 M NaHCO$_3$, 0.1 M NaOH, and 1.0 M HCl. The samples were kept in suspension by shaking for 16 h. Afterwards, sediment was centrifuged for 10 min at 16000 rpm, and the supernatant was filtered through a 0.45 μm filter for each extraction step. TP content was determined after digesting a portion of the H$_2$O, NaHCO$_3$ and NaOH extracts (103.4 kPa, 121°C for 1.0 h, using acidified ammonium persulfate as oxidising agent). Labile P and Ca-bound P extracted fractions were analysed directly, while a portion of NaHCO$_3$ and NaOH extracts were acidified first, in order to precipitate extracted organic matter, and the supernatant posteriorly analysed to determine the respective inorganic P fractions’ concentration. Remaining residues after sequential extraction were digested with concentrated sulfuric acid and hydrogen peroxide and analysed for P concentration. This method estimates organic P portion as the difference between TP and inorganic P.

Kumar et al. (2018) were interested in studying P fractionation in sediments of an industrially polluted freshwater reservoir in India. They opted for a SEDEX wet sequential extraction scheme and categorised extracted PP into five sedimentary P pools: loosely sorbed P, Fe(III)-bound-P, authigenic carbonatefluorapatite (CFAP) and biogenic apatite plus CaCO$_3$-bound P, detrital inorganic P, and organic P. Sequential extraction began with a 0.5 g surface sediment sample being extracted using 50 mL of a 1 M MgCl$_2$ solution (pH 8). Samples were kept in suspension by shaking for 2 h. This extraction step was repeated using the same MgCl$_2$ solution on the solid residue, followed by two repetitions using deionised water. Supernatants were collected and analysed as a whole. Following this, 45 mL of an extraction solution comprised of 1.125 g of Na$_2$S$_2$O$_4$ dissolved in solution of 0.30 M Na$_3$-citrate and 1.0 M NaHCO$_3$ (known as a CDB solution) was used as the second step on the extraction sequence. After 8 h shaking and in
suspension, supernatant was collected in a similar fashion to the previous step. The remaining residue was extracted twice more using 50 mL of 1 M MgCl₂ solution and 50 mL of deionised water, each shaking for 2 h and the supernatant was joined with CDB extracted supernatant. The third extraction step involved 50 mL of an acetate buffer solution (1 M Na-acetate solution buffered to pH 4 with acetic acid) being added to the sediment residue and let shake for 6 h. Afterwards, the remaining residue was extracted twice more using 50 mL of 1 M MgCl₂ solution and once more using 50 mL of deionised water, each shaking for 2 h and the supernatant was added to the buffer extracted supernatant. 50 mL of a 1 M HCl solution was then left shaking for 16 h at room temperature, with no further MgCl₂ or deionised water extractions. Finally, the residual sediment was ignited at 550 °C for 6 h and extracted with a 1 M HCl solution while shaking for 16 h. Supernatants were centrifuged at 5000 rpm for 15 min and subsequently filtered through a 0.45 μm GF/C filter membrane after every extraction step.

An attempt to harmonise P extraction methods has been taken by the European Commission through the Standards, Measurements and Testing (SMT) programme (Ruban et al., 2001). In 2018, Christophe Waterlot followed the SMT method and managed to differentiate five P pools: non apatite inorganic P (NAIP, containing P bound to Al, Fe and Mn-oxyhydroxides); organic apatite P (AP, containing P bound to Ca and associated with carbonates); inorganic P (IP); organic P (OP); and total P (TP) (Waterlot, 2018). Unlike what was shown previously, this fractionation method combines three separate chemical extractions and uses three batches of the same sediment sample. Firstly, a sample of 200 mg of soil was extracted using 20 mL of 1 M NaOH as extraction solution, for 16 h. After 20 min centrifugation at 4530 rpm, 10 mL of the supernatant were treated for a further 16 h with 4 mL of a 3.5 M HCl solution. The
acidic treatment results in the complete fractionation of the NAIP pool. The ensuing residue from the first extraction was rinsed off with 20 ml of distilled water, with the supernatant being subsequently discarded, in order to prepare for the extraction of the AP fraction. To this residue, 20 mL of a 1 M HCl solution were added, and the AP pool was acquired after a 16-hour extraction period. Second, a fresh sample of 200 mg of soil was extracted with 20 mL of 1 M HCl for 16 h, with the supernatant/residue separation being done by centrifugation at 4530 rpm, for 20 min. The resulting supernatant contained the IP fraction. Leftover residue was calcined for 3 h at 450 °C and the OP fraction was obtained after a final 16 h extraction performed on the residue ashes with 20 mL of a 1 M HCl extraction solution. A third chemical extraction provided the TP fraction in three steps: 1) calcining 200 mg of a new soil sample in a furnace at 450 °C, for 3 h; 2) extracting sample ashes for 16 h, at room temperature, using 20 mL of a 3.5 M HCl extraction solution; and 3) centrifuging the residue for 20 min at 4530 rpm and collecting the supernatant.

These given examples demonstrate how varied sequential extraction schemes can be, with different extraction solutions used to extract the same P pool. It also showed that it is possible to achieve a higher or lower degree of P fractionation, depending on the extraction method chosen, leading to less or more individual P fractions. A visual comparison between the different methods is shown in Table 2.1.
<table>
<thead>
<tr>
<th>Extraction method (modified)</th>
<th>Number of P fractions</th>
<th>Extraction solutions used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hedley's</td>
<td>8</td>
<td>Di-H2O; 0.5 M NaHCO₃; 0.1 M NaOH; 1.0 M HCl</td>
</tr>
<tr>
<td>SEDEX</td>
<td>5</td>
<td>1 M MgCl₂; CDB solution; acetate buffer solution; 1 M HCl; (washing done with Di-H₂O and 1 M MgCl₂)</td>
</tr>
<tr>
<td>SMT</td>
<td>5</td>
<td>1 M NaOH; 3.5 M HCl; 1 M HCl</td>
</tr>
</tbody>
</table>

Sequential extraction methods have made serious contributions to the understanding of P cycling (Zhang et al., 2020). Nonetheless, due to the lack of evaluation between available schemes, the choice of extraction methods tends to be arbitrary, and comparisons between datasets are difficult (Levy and Schlesinger, 1999), thus, simply looking at P fractionation can be quite limiting and a broader set of analytical techniques is required, if a better understanding of P dynamics in the environment is to be achieved.

2.6. Agricultural Catchment Modelling

Hydrological flow is the foundation of aquatic ecosystems and its natural fluctuations are fundamental in keeping the ecological integrity of such ecosystems (Poff et al., 1997). Ever increasing threats on the quality of water in agricultural catchments, particularly due to intensive farming, have raised demands for the development of environmental models that are able to accurately simulate the movement of diffuse pollution sources, particularly in endangered catchments.

Computational models are a popular tool to study the potential effects of land management, land use change and climate change on water quality (Jackson-Black et al., 2017). Hydrological
models can be used, for example, to make educated backtracking predictions (by interpolating sparse monitoring data) and forecasts, and help design better environmentally aware strategies to combat water pollution, while simultaneously providing evidence to support higher level decision making by governance entities. Plenty of different simulation techniques regarding hydro-ecological systems have been developed and used in the past for both research and operational purposes, however, new conceptual models are still being formulated to incorporate a better understanding of specific catchment processes and places (Franks et al., 1999; Pinhati et al., 2020), and to facilitate the demands of new pressures on water resources, including nutrient enrichment (Futter et al., 2014).

As hydrological flows drive the transport, mobilisation and attenuation of nutrients and other potential pollutants, individual hydrological processes in models need to be represented in a meaningful manner (Medici et al., 2012). In particular, the relative contribution of groundwater and surface run-off to rivers is of interest (Futter et al., 2014), as PP is predominantly delivered via overland flow (Jordan et al., 2005). In Nature, surface landscapes and subsurface formations have an end-to-end hydrological flow continuum, however, to improve the practical transition from a natural, complex and real environment into a computer simulation, hydrological models try to consider just the dominant processes in a catchment, in order to improve conceptual implementation of the model and its development, data analysis, as well as to reduce computing time (Mockler et al., 2016).

Up to recently, the vast majority of nutrient modelling studies have been performed using five models: SWAT (Arnold and Fohrer, 2005) INCA-P (Wade et al., 2002), AnnAGNPS
(Young et al., 1989), HSPF (Bicknell et al., 2001), and HBV, now superseded by HYPE (Lindström et al., 2010), according to a review study published in 2015 (Wellen et al., 2015). All of these models differ in the way they are built, and each requires a plethora of user-supplied parameters in order to simulate catchment hydrology and sediment and P dynamics. Furthermore, many of the parameters needed to run these models cannot be directly measured and are highly uncertain, and, consequently, their values must be estimated by calibrating the model to observational data collected (Jackson-Black et al., 2017). Over-parameterised modelling approaches have inherent consequences, namely the fact that different parameter sets will fit the calibration data in a similar fashion (Beven and Binley, 1992), but might yield, however, very different extrapolative predictions of how the hydrological system would behave as conditions change; this can lead to poor validation performances when applied to other systems (Seibert, 2003).

Due to the complexity of these models used to simulate various hydrological conditions and nutrient dynamics, there is a growing interest in less detailed models that capture the relevant behaviour of the studied system at the appropriate scale of interest (Jackson-Black et al., 2015; Jackeman et al., 2006; Radcliffe et al., 2009). Model complexity, reflected in its over-parametrisation, often proves to be impractical (Perrin et al., 2001) and, moreover, the worth of less complex hydrological models for investigating the dominant pathways and processes in catchments have been widely discussed in the past (Refsgaard and Henriksen, 2004; Sivapalan et al., 2003).
The models used to interpolate data sets and predict discharge behaviour in the studied rural/agricultural catchments fall into the parametrically parsimonious category. On one hand, there is SMARTpy: an open-source hydrological catchment model in Python, which was developed with a focus on sub-surface flow paths (Mockler et al., 2016) and designed to simulate and output an in-stream discharge time series, using less than 10 total parameters. Alternatively, there is SimplyP: a parsimonious phosphorus model which incorporates a rainfall/run-off model and a biogeochemical model and is able to simulate daily streamflow, suspended sediment, as well as particulate and dissolved P dynamics (Jackson-Black et al., 2017). These two models work in concert and make up robust monitoring, research and management tools that additionally have the potential to be useful building blocks for future model development, or to be used as benchmarks against which more detailed models could be evaluated.

2.7. **Summary**

Eutrophication refers to a phenomenon where a water body is over enriched with nutrients, typically in an artificial fashion and often due to excessive use of artificial fertilisers and/or manure which ends up in the run-off from agricultural land as well from the uncontrolled discharge of municipal wastewaters. It is well established that elevated P compounds may promote eutrophication and degradation of surface water quality (Sharply et al. 2015), furthermore, studies have shown that a significant proportion of total P loads are transported in streams and rivers in the form of PP associated with fluvial suspended sediments in agricultural catchments (Ballantine et al. 2008). Less than half of all P applied to agricultural crops is utilised by the growing harvest crop, with less than 30% of such P input subsequently converted into food for human consumption (Van Djik et al., 2016). The remaining surplus P, which is beyond agronomic requirements,
accumulates in soils and is called legacy soil P or legacy P, for short (Kleinman et al., 2015). This legacy P may be washed off critical source areas within the agricultural catchment into rivers, streams, lakes largely in different particulate mineral and/or organic forms (Zhange et al. 2020; EPA 2020).

This is a global environmental problem that may result in harmful algal blooms, oxygen depletion, and fish mortality, all of which have subsequent negative impacts on humans in terms of reduced water quality, potential health risks to both humans and animals and increased management costs (Jennings et al., 2003). Under the EU Water Framework Directive [WFD] (2000/60/EC), the water cycle is to be viewed as an integrated system, i.e., groundwater and surface water should be taken as components in the overall water balance of a river basin. The WFD seeks all water bodies to reach a “good” standard, however currently there are no legal limits for fluvial suspended sediment concentrations which can have a significant impact on water quality. A suspended sediment annual mean threshold of 25 mg L$^{-1}$ was introduced for rivers through the EU Freshwater Fish Directive (FFD – OJEU, 2006) but was subsequently removed.

Figure 2.5. Photograph taken in June 2019 of the overgrowth in and around the outflow of Ballynamona river in County Limerick. A layer of algae floating above the river is also visible.
Hence, to achieve the goals set out in the WFD there is a research need for more detailed information on sedimentary P speciation fluxes, storage, mobilisation and bioavailability within agricultural streams on both a temporal and spatial scale for appropriate catchment scale management policies. Despite increased recognition of the importance of PP within freshwater systems (particularly lakes), relatively little attention has been given to P speciation dynamics in suspended and streambed sediments within agricultural catchments. Few studies have specifically characterised PP speciation dynamics (McDowell et al., 2005; Pan et al., 2013) and fewer still have examined their reactivity, especially in fluvial suspended sediments from small agricultural catchments.
3. Materials and Methods

3.1. Sites’ description

The selection of the specific field sites monitored in this work followed an initial screening process of several small agricultural catchments across Ireland. This screening process looked for certain characteristics such as the existence of a contrasting geology between sites, the presence of predominantly low subsoil permeability in the catchment and a high concentration of suspended solids present in surface water. This screening was performed utilizing GIS to compile information regarding the aquifer type, surrounding geology and land use. Field site visits were carried out afterwards to inspect these stream catchments in more detail and examine the suitability of the potential sampling spots. Factors like terrain accessibility and the possibility of it being monitored over different seasonal conditions were considered when deciding on sampling locations. The studied catchments were spread over the country and include Ballyboughal (BB), in county Dublin, Tintern Abbey (TTA), in county Wexford and Bunoke (BE), in county Limerick, as shown in Figure 3.1.

The land-use of the BE catchment consists predominantly of pasture grazing while the TTA and BB catchments have a mixture of pasture grazing and crop cultivation. In addition to farming activities, BB has a wastewater treatment plant within its catchment. In terms of water quality, all catchments have a medium to high level of eutrophication, according to the EPA’s 2015-2017 Water Quality map (EPA, 2018).
A breakdown of each site’s characteristics according to groundwater vulnerability, aquifer category, bedrock, soil and subsoil type, and land-use is listed in Table 3.1.

Table 3.1. Detailed information of Ballyboughal (BB), Tintern Abbey (TTA) and Benoke (BE) catchments.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Bedrock(^\ddagger)</th>
<th>Groundwater vulnerability</th>
<th>Aquifer category(^\ddagger)</th>
<th>Soil type</th>
<th>Subsoil</th>
<th>Land-use</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB 23 km²</td>
<td>LU, NA</td>
<td>Extreme X, Extreme E, High Vulnerability and Low Vulnerability</td>
<td>Lm, LI, PI</td>
<td>Mosaic of mineral poorly drained topsoil from basic and non-calcareous material</td>
<td>River alluvium, fine loamy drift with limestones, and siliceous stones</td>
<td>Considerable arable land for tillage and horticultural crops along with pasture-based agriculture</td>
</tr>
<tr>
<td>TTA 10 km²</td>
<td>CA</td>
<td>Extreme X and Extreme E, High and Medium Vulnerability</td>
<td>Rf, PI</td>
<td>Poorly drained shallow mineral topsoil (mainly non-calcareous)</td>
<td>River alluvium and fine loamy drift with siliceous stones</td>
<td>Mainly pasture-based agriculture with some tillage and woodland</td>
</tr>
<tr>
<td>BE 15 km²</td>
<td>VIS, CS, CF</td>
<td>Extreme X and Extreme E, Medium and Low Vulnerability</td>
<td>LI, PU</td>
<td>Poorly drained mineral soils from areas of both calcareous and non-calcareous soils</td>
<td>Till derived from sandstones, limestones, namurian sandstone and shales</td>
<td>Pasture-based agriculture and woodland</td>
</tr>
</tbody>
</table>

\(^\ddagger\) Aquifer categories: Lm = Bedrock which is Generally Moderately Productive; LI = Bedrock which is Moderately Productive only in Local Zones; PI = Bedrock which is Generally Unproductive except for Local Zones; PU = Bedrock which is Generally Unproductive; Rf = Fissured bedrock.

\(^\ddagger\) Bedrock categories: LU = Lucan Formation (dark limestone stone/shale); NA = Naul Formation (limestone, calcarenite, minor chert and occasional thin shale); CA = Campile Formation (felsic formation); VIS = Visean Limestone Formation; CS = Clare Shale Formation (mudstone, chert and black shales); CF = Cloone Flagstone Formation (greywacke, siltstone and silty shale).
For each of the three catchments, multiple sampling locations were located at the end of tributaries and the main catchment outlet in order to monitor periodically the surface water flow, water quality and suspended sediments. Given the importance of the catchment outflow location, more intense monitoring was carried out at these locations for each stream. Comprehensive catchment maps of the soil types for each stream catchment, including details on site sampling locations, can be seen on Figure 3.2 and Figure 3.3.

### 3.1.1. Ballyboughal Catchment

The Ballyboughal catchment (BB) is the catchment with the greatest surface area, rounding at 23 km$^2$. The soil type is predominantly derived from acidic parent materials, with the major soil constituent being a deep, poorly drained mineral soil (AminPD). Some deep, well drained mineral soil (AminDW) is present to the north of the catchment. A chunk of both deep well drained (BminDW) and poorly drained (BminPD) mineral soil derived from calcareous parent materials can be seen to the south and extending to the eastern part of the catchment. Other soil types are included in BB, such as fine loamy drift with limestones, siliceous stones, shales, sandstone, and limestone tills, as shown in Figure 3.2(a). This combination of soil types makes BB a poorly draining catchment, even though its soils are essentially very mineral.

### 3.1.2. Tintern Abbey Catchment

Tintern Abbey catchment (TTA) is smaller in size, with a catchment area of around 10 km$^2$, and contrasting to the moderately productive aquifer at BB, the TTA catchment is located over a poor aquifer. Additionally, TTA is a shallow catchment, comprised mostly of AminDW soil, with some AminPD and mainly acidic shallow well drained mineral soil (AminSW), with no particular
agglomerated area. Surrounding the rivers soils such as river alluvium and fine loamy drift with siliceous stones are present, which can be seen on Figure 3.2(b).

Figure 3.2. Catchment maps with detailed soil type and sampling locations on BB (a) and TTA (b).

AlluvMIN = Alluvial (mineral); AminDW = Deep Well Drained Mineral (mainly acidic); AminSW = Shallow Well Drained Mineral (mainly acidic); AminPD = Poorly Drained Mineral (mainly acidic); AminSP = Shallow Poorly Drained Mineral (mainly acidic); BminDW = Deep Well Drained Mineral (mainly alkaline); BminPD = Poorly Drained Mineral (mainly alkaline); BminSW = Shallow Well Drained Mineral (mainly alkaline); Made = Made ground; Lac = Lacustrine type soils

3.1.3. Benuke Catchment

The Benuke catchment (BE) is located in the mid-west of Ireland and extends for approximately 15 km². Similar to the TTA, it has shallow and poorly draining soil. BE is fairly layered, with big stretches of fine loamy soil over mudstone, shale or slate bedrock; fine loamy drift with limestones; and clayey drift with limestones (see
Figure 3.3). It is also composed of extensive patches of fine loamy drift with siliceous stones and a few, yet smaller areas consisting of peat, coarse loamy and clayey drift with siliceous stones, and river alluvium.

Figure 3.3. Map with detailed soil type and sampling locations on BE catchment.

3.2. Fieldwork

Most of the fieldwork involved sampling which consisted largely of collecting stream sediment and/or water samples from the different sampling positions (see Figure 3.4 for an example), and moving them to laboratory conditions as quickly as possible, while trying to preserve its biochemical characteristics as best as possible.
Sampling was carried out intermittently, at the BB and TTA sites, between June 2017 and July 2018, and on the BE catchment between January 2018 and November 2019.

3.2.1. Water Sampling Methodology

Water samples of 50 mL were collected from the streams regularly and in duplicate. These samples were filtered using 0.2 µm filters, transferred to clean 50 mL plastic vials and, while in the field, kept in a cooler until properly refrigerated at 4 °C in the lab. Water chemistry characteristics measured in the field included pH, conductivity, dissolved oxygen, TDS and temperature using a Hannah instruments 98194 Multi-parameter meter every time the surface water was gathered.
Besides regular *in loco* manual sampling, events such as high-resolution sampling of significant storms sweeping the catchment area were also carried out. To aid the storm events sampling process, ISCO™ 6712 autosamplers were installed at the primary discharge location, near one of the banks (see Figure 3.5). These samplers were locally activated the day prior to the storm peak and set to start collecting water samples once stage values reached a predetermined number, usually 3-4 cm above background levels. The samplers collected around 900 mL of water every hour, typically, up to a total of 24 hours.

3.2.2. **Sediment Sampling Methodology**

Additionally, sediment traps were put in place within the channel of the stream outflows. These fluvial sediment traps (shown schematically in Figure 6 and on location in Figure 3.9b), also named Philips samplers (Phillips *et al.*, 2000), consisted of a hollow PVC cylinder with a funnel placed over the inlet and an end cap with internal “O-rings” and a drilled hole on the outlet. They were submerged in the middle of the stream, fixed to two steel uprights using cable ties, at approximately 60% of the average water depth. When clear PVC cylinders were used to construct the traps, a nylon film was applied around the tube to cover its body in order to limit amount of sunlight reaching the inside of the trap and, consequently, discourage algae growth.
These Philips samplers collect suspended sediment particles via a precise relationship between the flow coming in the inlet and the flow velocity once water reaches the main cylinder (Phillips et al., 2000). By virtue of an increase in cross-sectional area, flow is substantially reduced past the inlet and sedimentation occurs as the water moves towards the outlet hole. Suspended sediment was left to settle inside the traps over a period of 10 weeks, yielding various quantities of solids that would fit through the inlet’s diameter.

After the sedimentation period was over, sediment traps were carefully removed from the uprights and the outlet cap was removed, emptying the contents to clean 10 L containers with the help of a funnel. Soon after collection, the containers were transported back to the lab and its contents filtered through a 63 µm stainless steel sieve. The < 63 µm portion was transferred to 250 mL plastic bottles and centrifuged at 3000 rpm in an Eppendorf 5804R. The supernatant was readily discarded, and the sediment sludge was transferred to 50 mL plastic vials and kept in a -20˚ freezer overnight. Once frozen, the vials were prepared for freeze-drying by uncapping and

Figure 3.6. Philips sampler schematic. Image adapted from Phillips et al., 2000.
covering the top with a layer of absorbing paper held in place by rubber bands. After drying for approximately 12h, sediment samples were capped and kept under dry conditions for further analysis.

3.2.3. **Discharge Computation Methodology**

Flow measurements were also performed in order to determine stage-discharge relationships. Discharge values were calculated using the same methodology used by the EPA on their stations ([EPA, 2021](https://www.epa.gov)). An in-depth description of the employed method can be found in the international standard [ISO 748:2007 Hydrometry - Measurement of liquid flow in open channels using current-meters or floats](https://www.iso.org). Broadly, this method consists of measuring width, either by means of steel tape or by some other surveying method, and depth at a number of points across the width (named verticals), determine the shape and area of the cross-section; gathering velocity observations using current-meters are made at each vertical, preferably at the same time as measurement of depth; and computing discharge results by summing the products of the velocity and corresponding area for a series of observations in a cross-section ([ISO 748:2007](https://www.iso.org)).

Field site visits often meant a 6-hour return drive which, coupled with sampling and water chemistry measurements, limited the amount of measurements that could be performed before sundown. Thusly, mean velocities in each vertical were determined using a combination of reduced point methods as opposed to a stricter velocity distribution method that, typically, requires a long period of time for taking measurements ([ISO 748:2007](https://www.iso.org)).
To determine stream length at the day of measurement, a tape measure was fixed at both ends and kept as straight as possible across the stream (Figure 3.7). Verticals were set at every 20 cm length and depth at each vertical was recorded using a long plastic ruler. Subsequently, wading velocity measurements were performed using one- (measured velocity represents the average velocity of the water column and is assumed to be representative of the respective vertical) and two-point methods (average velocity in the vertical is determined by calculating the arithmetic mean of the velocities taken at two different points): if measured depth at a given vertical was equal or below to 46 cm, measurements were taken at 60% depth, measured from the water surface to the river bottom, otherwise, observations were made at 20% and 80% depth (Clasing et al., 2018).

Wading velocity readings were carried out using an OTT ADC Flow-meter during periods of high and low flow in order to cover the widest range of flow conditions.
Discharge was then computed using the mid-section method. The assumption that river cross-section is regarded as being made up of several segments, each containing a vertical is underlined in this method. Discharge \( (q) \) in each segment was computed by multiplying the previously estimated velocity \( (\bar{v}) \), by the measured depth \( (d) \) and by the corresponding width \( (b) \) measured along the water-surface line (Figure 3.8). This width was taken as the sum of half the width from the previous vertical to the current vertical plus half the width from this vertical to the corresponding adjacent vertical on the other side. (ISO 748:2007).

![Figure 3.8. Illustration of the mid-section method (ISO 748:2007). Discharge at the n\(^{th}\) vertical is calculated by multiplying estimated velocity at that vertical by half the area of the previous (n-1\(^{th}\) to n\(^{th}\) vertical) and the following cross-section areas (n\(^{th}\) to n+1\(^{th}\) vertical).](image)

\[ q_n = \bar{v}_n \times d_n \times \left(\frac{b_{n-1} + b_{n+1}}{2}\right) \]

In each catchment, and on the different sites per catchment, a hollow metal tube was installed close to the margins of the stream (an example of this tube is shown in Figure 3.9 a). The tube was roughly 1.5 m tall and attached to it was a stage logger that recorded submergence (in cmH\textsubscript{2}O) every 15 min. The logger was set in such a way that it remained slightly above the stream bed. Submergence data was converted to depth of water by summing submergence readings and the height difference between the tube bottom and the logger head. During every field site visit the length of string not submerged in the stream was measured to help with logger calibration. A
Barodiver Pressure Transducer was also placed at each site to allow for proper compensation of water depth recorded by the logger against changes in atmospheric pressure.

Stage-Discharge rating curves were then plotted for each monitored site on all catchments. Calculated discharge, derived from discrete flow measurements done at the field, was graphed against the average daily depth recorded by the logger on the same day (Figure 3.10). A linear trendlines were initially fitted to 5 points, however, to achieve a better-quality coefficient of determination ($R^2$), up to 2 points that deviated from the trendline were removed. Rating curves linear regression was subsequently used to compute discharge from logged depth and build hydrographs.

Figure 3.9. Photo taken from a bridge that overlooks BE2, taken in July 2019. In this picture it’s visible the pole where a stage logger was attached to (a) and the sediment trap strapped to two steel rebars close to the stream’s bed (b).
3.3. Analytical methods

3.3.1. *Nutrient Photometric Quantification*

Collected water samples were analysed in Thermo Scientific Konelab 20 Clinical Chemistry Analyzer (Figure 3.11). Nutrient concentration was determined by the colorimetric method present in Konelab. Before use, this method was previously calibrated using Konelab’s user manual instructions and calibration solutions were prepared from Sigma-Aldrich certified reference solutions. Concentration ranges during calibration were suited to the deemed acceptable maximum and minimum values for agricultural catchments, in order to obtain a wide enough range of concentrations. This is an important step as a large range of concentrations allows the same calibration curve equation to be used on all
samples analysed, rather than using different ones which can introduce unnecessary sources of uncertainty to the determined nutrient concentration. A list of the nutrients analysed, the reagents used in each analysis as well as calibration parameters is laid on Table 3.2.

Table 3.2. Nutrients analysed in Konelab, reagents used and calibration parameters such as the calibration curve type and equation, the coefficient of determination of the given curves and calibration range of concentrations.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Calibration curve type</th>
<th>Calibration curve equation</th>
<th>Coefficient of determination ($R^2$)</th>
<th>Calibration range (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho-Phosphate (PO$_4^{3-}$)</td>
<td>Linear</td>
<td>$y = 0.094x$</td>
<td>0.999401</td>
<td>0 – 1</td>
</tr>
<tr>
<td>Ammonia (NH$_4^+$)</td>
<td>Linear</td>
<td>$y = 0.5384x$</td>
<td>0.999392</td>
<td>0 – 0.1</td>
</tr>
<tr>
<td>Sillica (SiO$_2$)</td>
<td>Linear</td>
<td>$y = 0.074x$</td>
<td>0.999571</td>
<td>0 – 10</td>
</tr>
<tr>
<td>Sulphate (SO$_4^{2-}$)</td>
<td>Linear</td>
<td>$y = 0.006x + 0.003$</td>
<td>0.999166</td>
<td>0 – 10</td>
</tr>
<tr>
<td>Cloride (Cl$^-$)</td>
<td>Linear</td>
<td>$y = 0.011x + 0.025$</td>
<td>0.997443</td>
<td>0 – 10</td>
</tr>
</tbody>
</table>

Konelab comes with an integrated autosampler, allowing for a set of up to 14 subsamples per tray to be prepared prior to analysis, totalling 84 subsamples total per uninterrupted run. From each batch analysis, approximately 1.5 mL of duplicate blanks, standard solutions, and subsamples of each site were pipetted into 2 mL plastic cups, placed on the sample tray and analysed. Analysis time varied between 5-30 min, depending on the number of tests issued.
3.3.2. **Determination of Total Phosphorus (TP)**

Determining the concentration of TP in an environmental water sample requires a digestion step prior to analysis. Such is the case because many of the P species aren’t present as ortho-P, but covalently bonded to other species by P–O–P, C–O–P and C–P type bonds that need to be broken down preceding analysis (Worsfold et al., 2005).

Coupled with various oxidising agents such as perchloric acid, hydrogen peroxide, sulphuric acid – nitric acid or peroxydisulfate, a great variety of digestion techniques can be employed to rupture these covalent bonds and release ortho-P into the solution, namely fusion, ignition, dry ashing, conventional heating using a hot plate, sand bath or aluminium block, UV-photo-oxidation, and autoclave or micro-wave heating (Maher et al., 1998). Autoclaving methods, however, tends to be preferred for their accuracy, precision, ease, and simplicity when compared to other available options (Jarvie et al., 2002).

A comprehensive review of acidic and alkaline autoclave digestion methods for different sample matrixes such as drainage water, estuarine waters, pond water and river water, to name few examples, was compiled by Worsfold et al., 2005. From the extensive list, the method presented by F. I. Ormaza-González and P. J. Statham was selected to digest BB, TTA and BE water samples (Ormaza-González et al., 1996). According to it, the acidic digestion solution should be prepared by diluting 5 mL of 4.5 M sulphuric acid (H₂SO₄) to 100 mL of distilled deionised water (DDW) and dissolving in this solution 5 g of potassium peroxosulfate (K₂S₂O₈, the oxidizing reagent); the solution resulting from the mixture of sample and digestion solution should be autoclaved for
30 min, at 120 °C (Ormaza-González et al., 1996). The ratio of sample volume to digestion solution used in BB, TTA and BE samples was 7:0.5.

After digestion, samples were left to cool to room temperature before its TP concentration was determined using the Konelab nutrient analyser, using the same method and calibration as for ortho-P analysis.

3.3.3. Chemical Sequential Extraction of P

Fluvial sediment samples collected from sediment traps along the catchment were sequentially extracted using a modified Psenner method (Psenner et al. 1984, Lei et al. 2020). Following the method’s principles, a bespoke extraction device was designed to sequentially extract up to eleven samples at a time with decreased extraction time per sample, reduced intermediary steps and, consequently, minimal sample losses. This newly developed vacuum manifold device is divided into three major components: a vacuum pump (Figure 3.12 b1), a vacuum chamber (Figure 3.12 a3), and the extraction lid (Figure 3.12 a4).

3.3.3.1. Extraction manifold description

The vacuum pump is connected to the vacuum chamber via a Teflon tube. The chamber is made of borosilicate glass which can sustain at least 72 kPa of pressure, the maximum pressure differential exerted by the pump. Inside, the extracted solution is collected in 15 mL plastic vials, held by an adjustable and removable support. Furthermore, the top of the chamber is covered by a thick polyurethane gasket so that, when the extraction lid’s grooves rest on top of it, the chamber becomes airtight and sealed.
The extraction lid is comprised of a mainframe with eleven taps that can be connected to 25 mL filtration tubes. These tubes have a main body that holds the sediment sample and extraction solution, and a filtration piece. The filtration piece is comprised of a funnel that easily attaches to the lid mainframe taps and a removable holed cap that evenly distributes suction power during filtration.

For extraction tubes assembly, the first step involves placing a rubber band and a filter with the desirable porosity on top of the holed cap. In doing so it ensures the rubber band does not come in contact with the sediment sample; the second step involves attaching the tube’s main body on top of the filtration piece; the third and final step involves connecting the tubes to the taps on the extraction lid. Once all tubes are assembled, 10 mL of distilled water (di-H₂O) is added to them, while taps are closed,
and, if no leaks are forming immediately after, test water is filtered and discarded, leaving the apparatus ready to start. The filter does not need to be dried since the first extraction uses di-H₂O as extraction solution.

Two square legs are attached to the mainframe of the lid at a 45° angle, keeping the samples vertically straight while filtering as well as at an angle during shaking process to stimulate an increased movement of sediment particles and increase contact area between sediment and extraction solution.

3.3.3.2. Sequential extraction procedure

Extraction procedure was adapted from several authors (Coelho et al., 2004; Hupfer et al., 2009; Psenner, 1984; Shilla et al., 2009). Sediment P pools fractionation via chemical extraction in this study yielded, sorted by sequence, the following fractions: loosely sorbed P (P_{H₂O}), easily released in aqueous media; iron/manganese-bound P (P_{Redox}), a redox sensitive fraction; non-reducible P and P bound to aluminium hydroxide complexes (P_{NR}); organophosphates (P_{Org}); acid-soluble P, including humic P complexes, calcium-bound (especially detrital apatite), and magnesium-bound P (P_{HCl}); and residual P (P_{Res}), composed of refractory organically bound P and non-extractable mineral P.

Extraction solutions were prepared beforehand and in bulk, except for digestion solution that, due to its shorter lasting quality, it was prepared often and in lower quantity. Precautions should always be taken when preparing considerable volumes of chemical solutions, this includes proper handling of glass reagent bottles and other glassware, working under a fume hood and
wearing adequate personal protection equipment (PPE). The buffered dithionite (BD) solution was prepared by dissolving 8.7 g of sodium dithionite (Na$_2$S$_2$O$_4$, 174.11 g/mol, flammable and irritant) and 4.6 g of sodium bicarbonate (NaHCO$_3$, 84.01 g/mol) in a 500 mL of di-H$_2$O. Similarly, 0.1 M and 2 M sodium hydroxide (NaOH, 40.00 g/mol, corrosive) solutions were prepared by dissolving 4 and 40 g of NaOH in 1000 and 500 mL of di-H$_2$O, respectively (care should be taken when dissolving NaOH, as dissolution in water is a very exothermic process and can cause chemical and physical burns; small portions of NaOH should be dissolved at a time and with constant stirring to disperse the heat). The digestion solution was obtained by dissolving 12.5 g of potassium peroxosulfate (K$_2$S$_2$O$_8$, 233.24 g/mol) in 250 mL of di-H$_2$O, stored in an amber glass bottle and kept away from light. Hydrochloric acid (HCl, 36.46 g/mol, corrosive and acute toxic) 0.5 M and 1 M solutions was prepared by diluting 40 mL of concentrated HCl into 1000 mL and 500 mL of di-H$_2$O, respectively, (caution is advised when handling concentrated acidic solutions; like NaOH dissolution in water, HCl dilutions too are an exothermic process; small volumes of acid should be diluted at a time followed by constant stirring).

The first fraction, P$_{H2O}$, was obtained by weighing five fluvial sediment samples between 100 and 150 mg, in duplicate, to 10 numbered filtration tubes and adding 10 mL of di-H$_2$O to each tube. The 11$^{th}$ tube was kept sediment free and functioned as a blank during every extraction sequence. After shaking for 2 hours, samples were vacuum filtered through 0.45 µm filters into 15 mL plastic vials, capped and stored at 4 °C until analysed. From this stage forward, sequential extraction steps were repeated only with slight changes to extraction solution composition and shaking duration.
Next, 10 mL of BD solution were added to each filtration tube and, after shaking for 1 hour. Following vacuum filtration, BD extracted solutions containing $P_{\text{Redox}}$ were left uncapped overnight to allow for oxidation before being stored in the fridge. Sequential extraction continued with the addition of 10 mL of 0.1 M NaOH to the filtration tubes that were left shaking for 14-18 hours (typically left shaking overnight). To prepare later analysis, two separate 1 mL aliquot of NaOH-extract solutions were diluted and slightly acidified up to a total volume of 5 mL, as shown in Figure 3.14. Analysis of the undigested and digested solutions yielded $P_{\text{NR}}$ fraction and TP concentrations, respectively, and the difference between digested TP and undigested $P_{\text{NR}}$ constitutes the organic fraction, $P_{\text{Org}}$, concentration (Reitzel et al. 2005).

![Diagram of extraction process](Figure 3.14. Preparation of NaOH-extracted samples for analysis. Undigested extract (top) yields the $P_{\text{NaOH}}$ fraction, while TP concentration can be determined from the digested extract (bottom).)

The fraction comprised of $P_{\text{HCl}}$ was differentiated by adding 10 mL of 0.5 M HCl to the filtration tubes and letting the samples shake for 16-24 hours. Like NaOH-extracts, an intermediate
dilution and neutralisation step was required to prepare HCl-extracts for later analysis. In this instance, 0.25 mL of 2 M NaOH is added to 1 mL of HCl-extract and the volume is topped up to 5 mL with di-H$_2$O.

After all extracts were collected, sediment residue deposited on top of the filter was dried at 105 °C overnight, ignited at 520 °C for 2 hours and cooled to room temperature (~25 °C) overnight. Following that, sediment and filter ashes were transferred to digestion tubes and 5 mL of 1 M HCl were added. The resulting sludge, containing the P$_{Res}$ fraction, was autoclaved at 120 °C for 30 min and left at rest until it reached room temperature.

It should be noted that combining filter and sediment ashes facilitated minimal losses of sample material and decreased time of analysis by avoiding having to scrape sediment residue off the filter, plus, the ignited filters had a negligible influence in P measurements.

Stored samples were analysed in Konelab using the ortho-P method and calibration previously discussed. Dilution factors were introduced whenever concentration values were higher than the previously established calibration range. A visual representation of the complete extraction scheme is presented in Figure 3.15.
After use, extraction tubes were soaked in a, roughly, 5% Decon 90 Surfactant solution (a biodegradable, phosphate and enzyme free, water rinsible surface active cleaning agent) overnight and thoroughly washed and dried before next use. Having two sets of extraction tubes allowed for continual use of the extraction manifold with P-free equipment.
3.3.4. Synchrotron Spectroscopy: XRF and XANES

Freeze dry sediment samples were shipped to the Soft X-Ray Micro-characterisation Beamline (SXRMB) at the Canadian Light Source (CLS), in Saskatchewan, Canada (Figure 3.16). There it was possible to use one of the very few synchrotron facilities in the world and gather information on sediment elemental composition, via X-Ray Fluorescence (XRF), and predominant types of inorganic P complexes and their relative concentration, correlation and distribution in the sediment using X-Ray Absorption Near-Edge Structure (XANES).

With a small spatula, small amounts of each fluvial sample were uniformly applied to double-sided carbon tape, attached onto a stainless-steel sample holder, which was loaded into the vacuum chamber for spectral collection. Inside this bulk sample chamber, optical images of the sample holder were being transmitted on a high-resolution CCD camera (image feedback example given on Figure 3.17) which allowed to better direct the beam’s positioning and alignment relative to the samples. A 7-element silicon drift detector (SDD) inside the vacuum chamber acquired XRF and XANES spectra. The former was done at 7200 eV of photon energy whereas the latter was centred around absorption edge energies of relevant elements like P, Ca and Fe: 2145.5, 4038.5, and 7112.0 eV, respectively.
Furthermore, XANES core scans were performed on select high interest samples, due to the long analysis time (approximately 2 hours per sample). A smooth and as uniform as possible 3 × 2 mm sample region was picked (Figure 3.18a) and simultaneous P, Fe, Ca, and TEY intensities were mapped with 40 µm step increment, first horizontally and then vertically (Figure 3.18b).

Figure 3.17. Leftmost image shows the SXRMB control panel interface. A zoomed image of the CCD camera feedback from inside the vacuum chamber, where the sample holder is loaded (a), is shown on the right. To keep track of the radiation beam, two sticky notes on the screen point to where the beam is currently aiming since last calibration (b). A fluorescent material is loaded at the top and bottom of the sample holder to help visualise the beam’s position at the start and end of the run (c).
Following a coarse resolution XANES analysis, specific areas of interest (referred to as hotspots) were identified based on elemental distribution and correlation. Another batch of samples was prepared onto a new sample holder, as described previously, and loaded in the microprobe chamber (Figure 3.19).

![Figure 3.18](image1)

Figure 3.18. a) Determining beam location and a suitable sample window to begin mapping; b) P, Fe, Ca and TEY core maps being acquired simultaneously on a BE outflow sample.

![Figure 3.19](image2)

Figure 3.19. Sample holder with 4 sediment samples for microprobe analysis is being prepared (left) and loaded (right) onto the sample holder device. a) Fluvial sediment sample attached to double-sided carbon tape; b) microprobe sample holder; c) fluorescent material attached to the sample holder that helps with calibrate beam’s position before mapping.
A pair of Kirkpatrick-Baez (KB) mirrors was used to reduce beam size and focus the microprobe spot to an area of 10 µm² with a photon flux of 10⁹ photons/100mA/s (Xiao et al., 2017). Making use of a 4-element SDD, fine-resolution µ-XRF spectra and P, Ca and Fe µ-XANES relative intensity maps were acquired on several hotspots (Zhang et al., 2020). Microprobe mapping of samples included a 1 mm² sample window range and 12 µm step size. Several microprobe intensities maps, at the time of acquisition, are shown in Figure 3.20.
4. Agricultural Catchments Hydrological Results

4.1. Discharge Analysis

Rating curves were plotted for each site at the surveyed catchments and are displayed in Figure 4.1, with catchments arranged by rows and sampling sites within each catchment organized by columns. Discharge was computed from flow and cross-sectional area measurements while stage values were recorded by level-loggers.

![Figure 4.1](image-url)

Figure 4.1. Stage-Discharge rating curves for the monitored catchments over periods of low and high stream flow. Rating curve of outflow locations is plotted on the leftmost column, while sites 2 and 3 are represented on the respective columns.
Comparing the slope of the linear regressions in each column, it becomes clear that the outflow site (represented in the 1st column) is much more sensitive to changes in stage than its respective upstream locations. Additionally, given a certain stage value, discharge is greater in the outflow than in each upstream site, as expected.

Making use of the depth continuously recorded by loggers in the stream at each gauging site and the respective rating curve regressions, discharge data for each site of all monitored catchments was calculated and plotted, as seen in Figure 4.2, Figure 4.3, and Figure 4.4.

Figure 4.2. Rated stream average daily discharge at TTA outflow (grey line) and TTA2 (dashed line), located directly upstream, from September 2017 to March 2018. Daily rainfall on each site is also depicted (in black).
Figure 4.2 shows that TTA1 and TTA2 display a very similar discharge pattern. It should be noted that the logger at TTA3 malfunctioned and reported very imprecise results that, consequently, were abandoned. One can also observe, in Figure 4.3, that all BB sites return to different baseflow values after peaking, with BB1 having the highest value, as expected s the downstream outflow of the catchment. The outflow location at BB had a slower response time to rain events as evidenced by the superimposed BB2 and BB3 peaks and the right-shift of BB1 peaks, evidencing the classic flood routing behaviour (Bormann et al., 1999).

Figure 4.3. Rated stream average daily discharge at BB outflow (grey line), BB2 (dashed line), and BB3 (dotted line), from September 2017 to September 2018. Daily rainfall on each site is also depicted (in black).

BE outflow had the highest computed discharge of all catchments and sites, with several peaks reaching, at least, 4 m$^3$/s, seen in Figure 4.4. Unlike TTA and BB, the recession time from rain events at BE was prolonged, meaning that stream flow remained elevated for a longer period after the event compared to the much flashier TTA and BB peaks which could be due to faster
runoff due to more impermeable soils and different land-use at BB and TTA (Kalantari et al., 2014). Another contrasting characteristic of BE comes from peak analysis of the constructed hydrographs. When compared to other catchments, peak discharge values on non-outflow locations (BE2 and BE3) are considerably lower in comparison to the outflow: BE1 resulting in peaks 1246% higher, on average, than the same peak values in BE2 and BE3 plots. This is a considerable disparity when compared to the 269% and 198% exhibited by TTA and BB, respectively.

![Figure 4.4. Rated stream average daily discharge at BE outflow (dotted line), BE2 (dashed line), and BB3 (grey line), from April to November 2019. Daily rainfall on each site is also depicted (in black).](image)

It should be noted that the discharge data for the BE3 site, however, was directly gathered from an EPA station situated at that site (EPA, 2021) and can be seen for the 12-month period on Figure 4.5.
All catchments exhibited two distinct seasonal behaviours: a dry season made of frequent and intense discharge peaking that lasted from around May to August; and a wet season from September to April, characterised by a flat discharge curve.

Another observation is how quickly these catchments responded to precipitation. Such a flashy response to rain events was expected due to the predominant cover of low-permeability subsoils in all catchments, meaning that the dominant hydraulic pathways are likely to be via shallow subsurface, interflow and artificial drainage networks. The small size of the catchments would also cause quick response times.

Differences in baseflow are also visible in all catchments and are accentuated when comparing BE with TTA or BB. BB and BE have a very stable baseflow during the warmer periods: from May to August 2019, however, baseflow is generally higher at TTA than at the other two, especially from September to March. The contrasting baseflow between these catchments is

Figure 4.5. Rated stream average daily discharge at BE3 for the full year of 2019.
potentially due to different variations in soil permeability that result in differences in infiltration and groundwater recharge.

4.2. Stream Water Chemistry

All catchments evidenced very distinct time variations in terms of P concentration on the outflow (Figure 4.6) from the spot samples taken. As observed previously in Figure 4.2, discharge values remained fairly constant at TTA, leading to unsurprisingly constant dissolved P concentrations over the 8-month period. BB, on the other hand, evidenced a decline in concentration with time, over the yearlong period, likely due to the heavier rainfall having a diluting factor on P concentrations during the measured period; BE saw a drastic increase during the summer period and a steep decrease from July 2019 to September 2019, which contrasted with the BE1 hydrograph in Figure 4.4. BE and BB outflows have considerably higher concentrations than other reported sites (Bernal et al., 2015, p.; Nguyen and Sukias, 2002; Wojciechowska et al.,
2018), placing an environment risk (Cassidy et al., 2019) and aggravating the need for a better water quality and land management.

Figure 4.6. Dissolved PO$_4$-P concentration over time different sampling periods.
Dissolved PO$_4$-P concentration is shown to vary from within each catchment in Figure 4.7. In the case of BB, the site which was furthest from the outflow had significantly higher concentration than at the outflow, during wet and dry seasons. The decrease over time of dissolved PO$_4$-P concentration, as noted previously in Figure 4.6, is here visibly affecting all sites on the BB catchment.

At TTA, as observed before, dissolved PO$_4$-P concentration did not show significant alterations during wet or dry periods. The intermediate TTA2 location showed a greater amount of dissolved PO$_4$-P per volume unit than the outflow in two sampling months.

Sampling at BE was assisted by the Limerick County Council which, in turn, provided with a greater sampling range on the three catchment locations. At the three sites, dissolved PO$_4$-P concentrations remained relatively low during the first months of the year and significantly increased from June to August 2019, especially in BE3, located at about 3 km upstream from the outflow. It should be noted that, particularly at
BE3, a very intense growth of tall fluvial vegetation was experienced after August, which could have been aided by the surge in dissolved PO$_4$-P concentration at this site.

Other chemical species present in water were also analysed, namely the concentration of silica (SiO$_2$), sulphate cations (SO$_4^{2-}$) and chloride anions (Cl$^-$).

Comparing the three sampling sites, located about 1 km from each other, there do not appear to be significant differences in concentration within the BE catchment, with the exception of one or two occasions. Some of those instances are shown in Figure 4.8, particularly the significantly lower concentration of silica in BE2 and BE3 for the months of April and May, respectively, and the drastically higher concentration of chloride in BE2 and BE1 during June and September, respectively.

![Figure 4.8. Comparison of dissolved silica, sulphate, and chloride concentration, respectively, at the outflow and the other two sites upstream for BE.](image-url)
At all three BE sites, silica and sulphate concentrations remained between 4-6 mg/L and 5-10 mg/L, respectively, during most of 2019. The highest concentration of these two species was observed in the month of September 2019. Contrasting this spike in concentration, silica was barely detected in all sites during November 2019 sampling.

Apart from sporadic spiking in concentration in some sampling sites within the catchment, chloride concentrations remained below 20 mg/L during months characterised by frequent and more intense rainfall periods and increased to approximately 25 mg/L during the summer of 2019, mirroring the behaviour of ortho-P seen in Figure 4.7.

Regarding the TTA catchment (left column, Figure 4.9), silica concentrations were lower during a drier period (June 2018). Curiously, during that period, silica concentration decreased as sampling was done closer to the outflow. Inversely to silica, sulphate and chloride had higher concentration values during the same dry period, with sulphate concentration at the outflow being, approximately, twice as high as the other upstream sampling locations.

Water chemistry analysis at BB (right column, Figure 4.9) revealed silica and chloride concentration during wet and dry periods behaved similarly to what was observed in TTA samples. Nonetheless, BB water samples showed a constant silica concentration along the different sites in the catchment. Sulphate concentrations at BB3 remained constant during wet and dry months, with BB1 and BB2 having a fairly wide range of concentrations during the sampled period.
Given the parameters of water quality published by the EPA, all monitored catchments fall under mandatory limit values for silica, sulphate, and chloride (EPA, 2001).

4.3. Dissolved Concentration of Ortho-P

Another aspect studied was a temporal analysis on how dissolved PO$_4$-P concentration was changing over time. To plot this data, a relationship between dissolved PO$_4$-P concentration measured at different discharge conditions needed to be defined.
Measured dissolved PO$_4$-P concentrations were assumed to represent that month’s average and so, these were compared to monthly average discharge values. To determine monthly discharge, daily values were normalised and averaged to its respective month. After plotting the results, a linear trendline was fitted to the results of each catchment, as shown in Figure 4.10, with, at least, two degrees of freedom. For the gauged discharge period, unlike BB and BE, TTA had a poor relationship with ortho-P measured concentrations. Hence, TTA outflow concentrations will be discussed on a later section (Section 6). BE1 concentrations are positively correlated with discharge, while BB1’s were negatively correlated. The more scarce data points for BB1 could explain the negative correlation since it is known that dissolved PO$_4$-P concentrations aren’t always positively correlated to discharge (Stamm et al., 1998).

All catchments displayed interesting behaviour when looking at concentration change at the outflow (Figure 4.11). Compared to BE, BB outflow has a completely different behaviour to changes in discharge and, consequently, rain events. In response to a discharge spike, the dissolved PO$_4$-P concentration decreases abruptly and but then rises back up to the previous value shortly afterwards. BB was also the catchment where the highest concentration of dissolved ortho-P could be seen consistently. Additionally, a plateau is established during the driest months, with
concentrations remaining high at, approximately, 0.16 mg L$^{-1}$ and relatively constant from mid-May until the start of September 2018.

BE shows an equally dramatic response to discharge spikes, however, unlike BB where sharp reductions in concentration arise within a short time period, the overall behaviour seen at BE shows sharp increases in PO$_4$-P concentration in direct response to discharge spikes following rain events. The overall highest concentration was reached during September to November 2019 rain events, with dissolved ortho-P surpassing 0.2 mg L$^{-1}$, likely due to antecedent drier conditions over the summer months (Pérez-Gutiérrez et al., 2017); in contrast to BB, at BE concentrations were at the lowest during the summer months.

Both catchments have visible differences when it comes to rain events response due to the different correlation types. More data points are needed for a more concrete assessment of Figure 4.11. Comparison charts of dissolved PO$_4$-P concentration (dashed line) and discharge during the same period for the outflow site of BE and BB, respectively.
4.11, nonetheless, assuming that the current correlation stands, the PO$_4$-P concentration increase at BE with heavy rain events might come predominantly from runoff and topsoil, whereas the PO$_4$-P dilution at BB during similar rain events could be explained by a lesser contribution of runoff in comparison to the river’s base flow.

The magnitude of the dissolved PO$_4$-P results at BB and BE are of concern with respect to the threshold values for High and Good ecological status in Ireland set at less than 0.025 g m$^{-3}$ and less than 0.035 g m$^{-3}$, respectively (EPA, 2020). According to the results, BB and BE streams should be categorised as “seriously polluted” in terms of Molybdate-Reactive Phosphate (MRP) due to the estimated annual median values of 0.24 g m$^{-3}$ and 0.12 g m$^{-3}$, respectively (EPA, 2001).

### 4.4. Dissolved Load of Ortho-P

Estimates of P loads ($L$, kg day$^{-1}$) were determined out on each stream through Eq. 4.1: the product of daily discharge values ($Q$, m$^3$ s$^{-1}$) and the respective estimates of PO$_4$-P concentration ($c$, g m$^{-3}$), multiplied by a unit conversion factor ($F$).

$$L = Q \times c \times F, \quad F = 86.4 \quad \text{(Eq. 4.1)}$$

The dissolved P load data for each catchment is plotted against precipitation on Figure 4.12. Analysis of load estimates for BB and BE outflow sites indicate that, despite having different concentration responses to changes in discharge, load plots closely mimic discharge plots, where peak load values are achieved during peak discharge.
At BB, a constant rise in baseload until January 2018 is shown in Figure 4.12, followed then by a steady decrease of load down to under 2 kg of suspended ortho-P transported per day, exhibited during the much drier May-September summer period. It should be noted that despite the higher frequency of rain events up until May 2018, the maximum transported load barely surpassed 8 kg/day.

The BE catchment P load graph shows two interesting phenomena, which are absent in BB. The first is the considerably higher spikes in load that occurred during September and November 2019. Comparing to BB across a similar period, with relatively equal rainfall intensities and volume, loads were 10 times higher in BE than in BB. Due to the positive slope linear relationship between concentration and discharge (Figure 4.10) and the overall higher discharge
values (Figure 4.4), this shows that BE transports most of its dissolved P load over short periods associated with

In total, the estimated load transported by each stream was calculated to be, approximately, 23.6 tonnes km\(^2\) (from April to November 2019), and 20.4 tonnes km\(^{-2}\) year\(^{-1}\), for BE and BB catchments, respectively.
5. Fluvial Suspended Sediment Analysis Results

Fluvial suspended sediments were gathered from the sediment traps after 10-week accumulation periods at monitored catchments, at different times. The first installation of sediment traps was in the TTA and BB catchments and after an initial implementation, a seasonal approach to the collection of sediments was followed. In contrast the BE catchment, being monitored one year after the TTA and BB catchments), had, in turn, an intra-catchment strategy where upstream sites were analysed in comparison to the outflow during the same sampling period.

5.1. Accumulated Sediment in Traps

Fluvial suspended sediment samples gathered at each trap, at different collection periods, were freeze-dried and weighed. Figure 5.1 facilitates the visualisation of the cumulative amount of sediment gathered at each site, as well as how much sediment yield occurred across each sampling period.

![Mass of fluvial suspended sediment under 63 μm collected at each catchment.](image)

TTA yielded a total of approximately 60 g if suspended sediment at the outflow location, of which more than 50% was gathered from the October 2017 sub-sample. At TTA2, the site
located directly upstream from the outflow, a single sample yielded almost as much as TTA1 yielded from a sum of three samples. At the outflow of BB catchment, a total of approximately 70 g of less than 63 µm suspended sediment was collected from two separate sampling periods. However, the upstream BB3 site yielded a higher mass of sediment, reaching close to 85 g, with close to 75% being collected from the February 2018 sample. BB2 was sampled in October 2017 and yielded the least amount of sediment of all three sites during the same collection period.

Comparing TTA1 samples from different seasons, wetter seasons indicate a larger amount of sediment collected which could be related to a higher transported load of sediments due to the increased runoff that carries more sediment to the stream. Additionally, BB1 and BB3 showed that more suspended sediment (particle size less than 63 µm) was collected in February 2018 than in October 2017. This also points towards a lower amount of sediment being suspended in the stream during months after summer, possibly due to the increase in evapotranspiration and therefore decreased effective rainfall and consequent decrease in runoff volume and discharge values.

Sampled the same number of times, the BE outflow sampler (BE1) yielded 170% more sediment than BE2, located roughly 1 km upstream, having been gathered from March to October 2019, approximately, 105 g and 62 g, at BE1 and BE2, respectively. At BE3, unfortunately the trap set to gather sediments between August and October 2019 ended up being destroyed and had to be replaced. Nonetheless, this site yielded a little over 85 g of sediment from only three samples, with most of it being collected from the June 2019 sample. This shows that suspended sediment concentration does not necessarily increase as sampling moves closer to the outflow location. It should also be noted that BE1 also shows a clear sequential decrease in sediment
sampled from March to October 2019, which is aligned with the findings at TTA1 and BB1 previously discussed.

5.2. Stream Suspended Sediment - Concentrations and Loads

In order to compute the effective net sediment concentration for each sampling period on the various streams, the volume (V, in m$^3$) of water that flowed through the traps needed to be assessed. This was achieved by calculating the product of daily discharge ($q_{trap}$, in m$^3$ s$^{-1}$) that flowed into the trap’s inlet area, by a day’s equivalent in seconds ($t$) – Eq. 5.1 $V = q_{trap} \times t$, $t = 86400$ s/day (Eq. 5.1).

$$V = q_{trap} \times t, \ t = 86400 \text{ s/day} \quad \text{(Eq. 5.1)}$$

Assuming an uniform flow and sediment concentration across the cross-sectional area of the river, discharge through the trap was derived from the product of the ratio between the constant cross-sectional area of the trap’s circular inlet ($A_T$) and the computed daily average cross-sectional area of the stream ($A_S$), by the stream rated discharge ($q$, in m$^3$ s$^{-1}$) – Eq. 5.2, Eq. 5.3 and Eq. 5.4.

$$A_T = \pi r^2, r = 0.004 \text{ m} \quad \text{(Eq. 5.2)}$$

$$\text{Ratio} = \frac{A_S}{A_T} \quad \text{(Eq. 5.3)}$$

$$q_{trap} = \frac{A_S}{A_T} \times q \quad \text{(Eq. 5.4)}$$
In order to obtain $A_s$ values, the relationship between measured river cross-sectional area ($A$, in $m^2$) and respective logger recorded depths ($D$, in $m$), from data collected at each field visit, were plotted for each sampling location on the catchments. These plots are shown in Figure 5.2.

Figure 5.2. Measured river cross-sectional area and logger recorded depth linear relationship for each monitored catchment.
Using the regression parameters (slope, $\frac{\delta D}{\delta A}$, and intercept, c), $A_S$ can be simply computed from the respective depth value – Eq. 5.5. Respective depth (d, in m), in turn, could be calculated from discharge (q) via the catchment corresponding rating curve regression parameters (slope, $\frac{\delta Q}{\delta D}$, and intercept, k) found in Figure 4.2, Figure 4.3, and Figure 4.4 – Eq. 5.6.

$$A_S = \frac{\delta D}{\delta A} \times d + c \quad \text{(Eq. 5.5)}$$

$$d = \frac{\delta Q}{\delta D} \times q + k \quad \text{(Eq. 5.6)}$$

The final derived average 10-week suspended sediment concentration results are plotted and shown on Figure 5.3. Each concentration value is related to the net amount of deposited sediment (under 63 µm) and the estimated discharge in each site during the 10-week collection period. It should be noted that not all concentration values could have been determined due to unavoidable field occurrences such as logger equipment failure to record or the destruction of samplers during the sediment settling period.

At BE a consistent decrease in concentration can be observed from June to October 2019 in all sites, except BE2, which remained constant throughout. BB1 and BB3 both show an increase in concentration from October 2017 to February 2018, whereas sediment concentration at TTA1 was more than halved from October to November 2017.

Sediment concentration is, by definition, a ratio which is heavily dependent on volume, specifically, the volume of water that passed through the sediment trap’s inlet. Hence, in order to
have a wider view of how sediment is transported within the catchment and over extended periods of time, sediment loads were estimated from concentration values previously calculated.

Figure 5.3. Suspended sediment concentration in each surveyed catchment.

To achieve load estimates, plots of suspended sediment concentration as a function of average 10-week discharge were fitted to a second degree polynomial trendline, shown in Figure 5.4. Discharge was previously normalised to the average discharge of the entire time series; this allowed the inclusion of concentration values related to all sites in a catchment and increase
trendline’s degrees of freedom. Daily sediment concentration values were derived from normalised discharge via the respective trendline equation.

Sediment recovered from, as well as discharge data recorded at TTA resulted in a trendline with unsatisfactory degrees of freedom and, because of this, load estimates will be discussed later in later chapters where a modelled approach to load estimates was used.

![Figure 5.4. Suspended sediment concentration as a function of normalised discharge, averaged to a 10-week period.](image)

Although, in theory, the second degree polynomial trendline best fits the data available in both cases, it should be noted that its application on BB data indicates the possibility of below zero concentrations, which are absurd. In practice, this should be taken as an approximation. Thus, due to the parabolic shape of the trendline, limit boundaries were established in case concentration values had to be extrapolated from the derived polynomial relationship equations, which might otherwise result in negative values in BB’s case. Making use of the respective trendline equation, sediment concentrations were calculated using normalised discharge values between the lower and
upper boundary conditions. If a normalised discharge value was calculated to be outside these
established boundaries, its respective concentration was assumed to be equal to a fixed value,
shown in Table 5.1.

Table 5.1. Lower and upper boundary conditions set on discharge and sediment concentration for BE and BB catchments.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Lower Boundary</th>
<th>Upper Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Discharge/ m³ s⁻¹</td>
<td>Concentration/ mg L⁻¹</td>
</tr>
<tr>
<td>BE</td>
<td>1.08</td>
<td>4.00</td>
</tr>
<tr>
<td>BB</td>
<td>0.95</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>0</td>
</tr>
</tbody>
</table>

Subsequently, daily load (L, in kg day⁻¹) estimates were determined by the product of the
respective discharge (q, in m³ s⁻¹) and sediment concentration (c, in mg L⁻¹), calculated as
previously described, by a unit conversion factor (f) (Eq. 5.7). Following this, area normalised
loads (L_A, in kg day⁻¹ km⁻²) were computed for each site in BB and BE catchments by dividing
load values by the estimated upstream catchment area (A, in km², shown in Table 5.2), of each
sampling site, in order to provide more direct comparisons between the catchments (Eq. 5.8).

Table 5.2. Estimated upstream catchment area for BB and BE sampling sites.

<table>
<thead>
<tr>
<th>Location</th>
<th>BB/ km²</th>
<th>BE/ km²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Outflow)</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

\[
L = c \times q \times f, \quad f = 86.4 \quad \text{(Eq. 5.7)}
\]

\[
L_A = \frac{L}{A} \quad \text{(Eq. 5.8)}
\]
Fluvial suspended sediment load, as well as daily precipitation plots are drawn below, in Figure 5.5.
Figure 5.5. Estimated suspended sediment load per day, for each of the three monitored locations at BE (on the left) and BB (on the right). Daily precipitation at each location is depicted in blue.
From these plots, at both BE and BB, it is apparent that most of the sediment load tends to be transported past September, once the stormiest weather conditions settle in. In terms of absolute load, of the monitored sampling sites, the outflow at BE was the one where estimated transported load was the highest: up to 5 tonnes/day during a storm event in September 2019); while BB3 had the lowest maximum load value of just under 150 kg/day during a storm event in November 2017.

Interestingly, for the same period, estimated baseload at BE2 is much higher than at BE3, especially during summer months. However, analysing the total load displayed in Figure 5.6, compared to the roughly 87 tonnes of sediment transported at the outflow, both sites have similar cumulative load over the entire monitored period: 32 and 23 tonnes of suspended sediment are estimated to have been transported at BE2 and BE3, respectively. Looking at the plots for BE2 and BE3, one could conclude that BE3 has a behaviour similar to the outflow with load spikes past September 2019 making up most of the total load transported at this site, whereas load peaks at BE2 are less intense but a higher baseload compensates for it.

![Figure 5.6. Estimated total load for each BE (top) and BB (bottom) sites, during 208 and 368 monitored days, respectively.](image)
Total load at both outflows varies significantly between each other and between the outflow and the other respective upstream locations: at BB, upstream load sums up to the total load found at the outflow (just shy of 25 tonnes, roughly), while at BE, the sum of load transported through BE2 and BE3 is 64% smaller than the load transported through the outflow. Given the difference in discharge between the sum of BE2 and BE3 to BE1, already commented when discussing hydrographs, this observation suggests that sediment found suspended at the BE outflow location has additional sources other than what is carried from upstream, possibly due to an additional tributary stream.

Load values at BB1 are substantially lower than those estimated for BE1. This could be due to the heavier storm events commonly present in the west of Ireland. Intense rainfall generates more runoff that, in turn, drags more sediment particles into the stream, or causes significant erosion, especially on the stream banks, which potentially results in a greater load of suspended solids.

Regarding catchment area relative load, areal normalised load plots are presented in Figure 5.7 for BE and BB monitored locations. These plots show load peaks with larger maximum values as winter comes closer, shown as a clear increase in the amount of transported sediment; and, as summertime approaches, a distinct decrease in both load peak intensity and frequency. This pattern is well represented in BB load plots.
Figure 5.7. Estimated suspended sediment load per day, per area, for each of the three monitored locations at BE (on the left) and BB (on the right). Daily precipitation at each location is depicted in blue.
BE1 and BE3 showed similar loads of suspended sediment per unit catchment area during the same storm events. Interestingly, however, BE2 showed a lower load value per unit area compared to BE3 and the outflow, which are roughly 1 km upstream and downstream, respectively. This suggests the load found at the outflow is mostly being generated by the catchment upstream of BE3 instead of BE2. Field surveys performed in the area around and upstream of BE3 found drainage ditches being deepened, consequently causing exposure and mobilisation of additional band sediments. Sedimentation occurring along the watercourse from BE3 to BE2 might be the reason as to why a portion of suspended sediment found at BE3 is not being collected at BE2.

The majority of the transported load from April to November 2019, at BE1, occurred in the last three months of that period and in the form of very intense and relatively short load spikes that reached maximum values of over 400 kg/day/km$^2$.

Results from the BB catchment are very interesting, especially the difference in load transported at the outflow compared with the sampling sites upstream. Load values at BB1 are roughly half of what is estimated for BB2 or BB3. Such an observation might be due to sediment settlement closer to the outflow site. The maximum transported load at was observed during a very intense storm event in the month of November, reaching up to 35, 30 and 17 kg/day/km$^2$, roughly, at BB2, BB3 and BB1 respectively. A steady decline in load can be seen after the month of May 2018 in all three sampling sites.
5.3. Chemical Fractionation of P

5.3.1. \textit{P fractions variation within a catchment}

The comparison of the sequential extraction results relative to the three monitoring sites at TTA catchment (shown in Figure 5.8), reveal some interesting differences with respect to extracted P fractions. At TTA, $P_{\text{Res}}$ was the predominant fraction found in all locations. However, when comparing the extraction results from sediment collected, at the outflow (TTA1) and at the other two locations upstream (TTA2 and TTA3), in February 2018, a decrease in $P_{\text{Redox}}$ and in $P_{\text{H}_2\text{O}}$ is observable, with the latter fraction almost becoming a negligible fraction of the total extracted P at the outflow. In contrast, a higher percentage of extracted P in the $P_{\text{Res}}$ form was seen at the outflow.

![Figure 5.8. Relative percentages of each extracted P fractions of TTA sediment collected in February (at the top) and in December 2018 (at the bottom).](image)
Interestingly, in December 2018, a significant shift occurred between the outflow and the other two locations upstream: the TP, P_{NR}, and P_{HCl} fractions increased to more than 10% of total extracted P, at the outflow. Given that all sediments were collected on the same date, microbiological processes should not be considered relevant to such a significant difference. Thus, this shift might suggest that the sediment composition was altered closer to the outflow. This suggested difference in composition could have been caused, for example, by human activity in the area close to the outflow such as some sort of excavation, which allowed new sediment to be transported to the stream, mediated by runoff during storm events.

5.3.2. *P fractions variation between outflow locations*

When comparing the outflow locations between the catchments some interesting observations arise. Firstly, from Figure 5.9, a very high (51%) fraction percentage of P_{H\text{\textregistered}O} was found in BB1, compared to TTA1 and BE1 (only roughly 1% each) which may indicate that while in stream, a lower amount of P is desorbed from the sediment. This might be due to a shorter desorption reaction time, caused by a shorter time spent suspended, meaning that the sediment found at BB1 was more recently transported to the stream than the ones at TTA1 and BE1.

P_{\text{Redox}} was found to be relatively consistent between all catchments, but with TTA1 having slightly higher and BE slightly lower fractions. On the other hand, BE was found to be the catchment with the highest P_{NR}, TP, and P_{HCl} percentage fractions. This indicates that sediment found in BE could have higher content of aluminium hydroxides, as well as Mg and Ca in its composition. Additionally, P_{\text{Org}} was found to be 243% and 213% higher at BE1 than at TTA1 and
BB1, respectively, indicating a sediment composition at least twice as concentrated in organophosphates at BE1. This significant discrepancy might be caused by a rapid runoff time at BE, this way, organic P species formed on land or spread in the form of animal manure have only a short time to mineralise.

![Bar chart showing percentages of each fraction.]  

Figure 5.9. Percentages of each fraction, relative to the sum of all fractions at each catchment, of extracted sediment collected in February 2018 (TTA and BB) and in March 2019 (BE).

The residual fraction at TTA dominated over the others, making up 63% of the extracted P at that catchment: it was more than 3 and 8 times higher than what was found at BE and BB, respectively. Such a disparity might suggest that sediments at TTA have a higher mineral P composition, possibly due to prolonged microbiological activity.

5.3.3. *Seasonal P fractions variation*

Looking at differences between typical wetter versus warmer seasons, shown in Figure 5.10, Figure 5.11, and Figure 5.12, a common pattern arises. The $P_{\text{Res}}$ fraction decreases in all
monitored sites when comparing sediments collected during a warmer period (typically June and July) to sediments collected during wetter periods (such as September and March).

At TTA, significant shifts in the percentage contribution of each fraction to the total extracted P can readily be observed in Figure 5.10. From July to September 2017, TTA1 saw an increase in the PNR, TP and P_HCl fractions from 4% to 29%, 6% to 51% and 1% to 9%, respectively. This shift in percentage contribution was balanced by the sharp decrease of PRes from around 80% in July 2017 to 9% and approximately 0% in September 2017, in TTA1 and TTA3, respectively.

Figure 5.10 Relative percentages of each extracted fraction of TTA sediment collected in February (at the top) and in December 2018 (at the bottom).
Coupled with the increase in $P_{H_2O}$ fraction, this could indicate a higher amount of newly suspended sediment is to be found in wetter periods.

TTA3 also had a significant increase in $P_{Redox}$ fraction in September 2017, up to a total of 39% of extracted P, an interesting increase, considering the decrease of this same fraction in TTA1 to about 0% over the same time period. From a field survey done in 2018, ditch deepening was being performed close to the TTA3 sampling location, which caused a surfacing of new layers of soil and all the while making it more susceptible to erosion loss. The reactivity of loosely sorbed P contained in the exposed sediment with various Fe and Ca mineral phases would have been increased and might explain the significant increase in $P_{Redox}$. During the same field survey, there were some evidences of bank erosion towards TTA1, however, the natural runoff barrier provided by vegetation visible at the site could have stopped some of these sediments from being carried by the stream.

Unlike what was observed before, BB2 barely changed its relative fraction composition between September 2017 to June 2018, with only a slight increase in $P_{Redox}$ coupled with a decrease in $P_{Res}$. 
The outflow location at BB, on the other hand, shows a similar shift in fraction percentages to those seen in TTA, with a steep decrease in $P_{\text{Res}}$ and considerable relative increases in $P_{\text{H}_2\text{O}}$, $P_{\text{Redox}}$, $P_{\text{NR}}$, and TP fractions.
Contrasting to the obvious seasonal differences seen, for example at BB1 or TTA1, the coming of summer at BE produced only a slight shift in some fractions’ relative weight. Figure 5.12 shows the relative percentage of each extracted fraction from all three sites at BE.

From March to June 2019, BE3 saw a slight decrease in $P_{NR}$ and $P_{HCl}$ balanced by an equally slight increase in $P_{Res}$ and TP. On the other hand, at BE2, the $P_{H2O}$ fraction practically doubled, possibly associated with an increase in microbial mineralisation of less bioavailable P.
fractions to more bioavailable ones, such as $P_{\text{H}2\text{O}}$. All the while $P_{\text{Res}}$ decreased about 8%, potentially due to increased runoff, which carried with it more of the recalcitrant fraction from land soil. The outflow site showed a 14% increase in the $P_{\text{H}2\text{O}}$ fraction, however TP and $P_{\text{NR}}$ were reduced by approximately 10%; the residual fraction did not suffer any alteration, much different of what TTA and BB showed.

5.4. Spectroscopy Analysis of Solids

5.4.1. XRF

The XRF spectra for the sediment samples collected in BE catchment are displayed in Figure 5.13. XRF spectra were normalised to the intensity of 7200 eV. Several important observations may be made from analysing XRF spectra which include the wide variation of elemental distribution among the samples, not only between seasons, but also between sampling locations within the catchment.

![Normalised XRF spectra of seasonal sediment samples collected from each sampling location in the BE catchment. Typical fluorescence energy of Potassium (K), Calcium (Ca), Titanium (Ti), Manganese (Mn) and Iron (Fe) are also displayed above its respective signal peak.](image)
The above graph shows the significant presence of Fe (with its peak at 6390 eV, approximately) in BE’s sediment composition. From January through March to June 2019, the outflow location demonstrated a continual increase in Fe. The BE2 sediment, however, showed very little change in the detected Fe signal from March to June 2019, whilst sediment from BE3 exhibited a very significant decrease in signal intensity from March to June 2019. Mn (peaking at 5890 eV, approximately) showed a similar pattern to Fe results in all sampling locations.

Comparing the results from sequentially extracting P from BE sediment, the fraction directly related to Fe and Mn species – the P_{Redox} fraction – remained constant going from March to June 2019 in all sampling locations, suggesting a couple of conclusions: either the presence of Fe and Mn is naturally very high, and so P association with that fraction is not limited by the amount of Fe and Mn in the river; or that the presence of higher Fe- and Mn-bound P species are not a directly correlated with Fe or Mn concentration in the sediment.

On the other hand, Ca (at approximately 3690 eV) showed higher signal intensity on samples collected during the wet season, than during a warmer period. Sequential extraction data on BE1 and BE2 also showed a relatively constant P_{HCl} fraction, which contains Ca-bound P complexes, when comparing sediment collected in March to sediment collected in June 2019.

When compared to Fe and Ca, K, Ti and Mn had lower peak intensities, indicating that BE sediments tend to be very rich in Fe. Ca content in the sediment tends to fluctuate seasonally, apparently increasing in the sediment mobilised during periods of frequent rain events.
For the BB catchment, only one set of sediment samples were analysed from a sampling period in October 2018. This shows that the BB sediment composition is much higher in Ca than TTA, as seen in Figure 5.14. This is in line with the sequential extraction data presented in Figure 5.10 and Figure 5.11, where the $P_{HCl}$ fraction in BB’s extracts has a greater percentual contribution to the total P extracted from sediments during the wetter periods.

![Figure 5.14. Normalised XRF spectra of sediment samples collected from the outflow locations of TTA (dotted red line) and BB (green continuous line) catchments, in October 2018. Typical fluorescence energy of Silicon (Si), Calcium (Ca), Manganese (Mn) and Iron (Fe) are also displayed above its respective signal peak.](image)

### 5.4.2. XANES

Analysing the sediment samples using XANES spectra provided an important additional confirmation that P species in the sediment tend to change depending on factors such as seasonal discharge and intense storm events.

Collected spectra relative to BE sediment samples can be seen in Figure 5.15 and Figure 5.17. Analysing the pre- and post-edge peak shape allows for a boolean assessment of the type of
P species present in each sample. Comparing bulk spectra of outflow samples collected during contrasting discharge conditions, a clear change in the predominant type of P species can be observed.

This observation suggests a high likelihood of seasonal differences in the sediment composition. The BE1 sediment collected during the summer of 2019 provided a spectra dominated by a featureless post-edge peak, similar to that of phytic acid, indicating a significant presence of $P_{\text{Org}}$. In contrast, the bulk spectra relative to the sediment sample taken in October 2019 displays a post-edge peak shoulder that is absent on the other two samples. This shoulder could be due to a higher presence of inorganic P complexes such as $\text{Mg}(\text{HPO}_4)\cdot 3\text{H}_2\text{O}$, for example, which suggests that the $P_{\text{Redox}}$ fraction determined by sequential extractions might be underestimated.

Reference spectra relative to dimagnesium phosphate tryhydrate and phytic acid can be seen in Figure 5.16 (ESRF, 2021). Reference spectra agree with the above observations, correlation
with phytic acid spectra indicates the existence of significant P\textsubscript{Org} fraction in the sediment during the summer months, while the correlation of BE1 October sample with dimagnesium phosphate trihydrate spectra might indicate a surge of inorganic P complexes in addition to the existante P\textsubscript{Org}. Similar findings were published in recent years, where TTA and BB sediment P K-edge XANES spectra were compared to reference compounds such as apatite, phytic acid and iron(III) phosphate dihydrate (Zhang et al., 2020).

Looking at the three sampling locations within BE catchment no obvious differences can be determined from P K-edge spectra, shown in Figure 5.17, with only slight differences in each peak intensity. This might suggest that whilst P concentration in the sediment varies within the catchment, the dominant P species stay constant. Due to the similarities with phytic acid referred above, P\textsubscript{Org} is the dominant fraction in the present case.
Storm event sediment samples were also investigated using XANES spectroscopy. BB and TTA sediment samples collected relatively soon after the storm started and ended, for high and low discharge periods are shown on Figure 5.18 and Figure 5.19. Interestingly, during a storm event, not only does the relative concentration of P species in sediment change, as seen by the change in maximum peak intensity, but the predominant P species in the bulk tends to change as well. Different pre- and post-edge peak features, evident when looking at storm events recorded at BB, suggest that different types of sediment are being mobilised in the stream at different times during the storm.

BB sediment collected during a storm event, under a typically high discharge period, showed that P species were more concentrated in the sediment before the storm, as expected. However, pre- and post-edge peak shoulders evidenced on Figure 5.18(bottom) indicate that the
$P_{\text{Org}}$ fraction, characterised by a similar spectrum to that of phytic acid, was replaced as a predominant fraction of sediment collected after the storm.

A parallel change in the sediment’s composition of P species can be seen when analysing the July 2018 storm event, shown in Figure 5.18(top). As discussed before, pre- and post-edge peak features change when looking at sediment collected at different periods in relation to the storm, however, during low flow, these changes are inverted: a higher dominance of the $P_{\text{Org}}$ fraction seems to be evident towards the end of the storm. This could be due to surface agricultural sediment becoming freshly suspended, after being carried by surface runoff, and being collected at a later period. Additionally, the relatively small difference in maximum peak intensity indicates that during a low flow storm event, P species concentration in the sediment do not change drastically, as seen in high flow events.
TTA showed very constant XANES spectra before and after a storm event that occurred in January 2018. However, during a July 2018 storm, it is very clear that different predominant

Figure 5.18. P K-edge XANES spectra of bulk BB1 sediment samples from January (bottom) and July (top) 2018. The blue line refers to a sediment sample collected a couple of hours after the storm event started and the red line refers to a sediment sample collected a couple of hours after the event ceased.

Dotted red arrows are pointing to the pre-edge shoulder on after storm sediment, which is not present earlier on. Solid blue and red arrows are pointing to the post-edge shoulder, which were not detected before and after the respective storm event.

TTA showed very constant XANES spectra before and after a storm event that occurred in January 2018. However, during a July 2018 storm, it is very clear that different predominant
P species are present in the outflow sediment before and after the storm, likely due to the preceding biogeochemical conditions of the sediments due to the low flow regime – sediment could have partially or fully dried out due to the combination of low flow and increased sunlight exposure and air temperature, which would affect P speciation in the sediment. Additionally, in the months leading up to the July 2018 storm, microbial activity would be higher which would likely affect P speciation and P microbiological cycling.

Figure 5.19. P K-edge XANES spectra of bulk TTA1 sediment samples from January (bottom) and July (top) 2018. The blue line refers to a sediment sample collected a couple of hours after the storm event started and the red line refers to a sediment sample collected a couple of hours after the event ceased.
Sixteen hours after the storm event began, XANES spectra show a very keen similarity to that of phytic acid, suggesting that organically rich sediment entered the stream at a later stage ($P_{\text{org}}$ likely became mobilised later because of the different timings of sediment export coming from various landscape sections), while more inorganic P species would have been more commonly found in suspended sediment, in the moments before an event. Possibly, inorganic P which is flushed at the start of the storm was initially closer to the stream or riparian zones while organic P comes from more infrequently saturated areas.

5.4.3. µ-XANES

From the initial bulk XANES spectra, a core-scan analysis was performed on BE samples. This allowed for the detection of points of interest – hotspots. Four different hotspots, shown in Figure 5.20, were selected for a more refined surface scan.
Hotspot 1 was chosen as an example, however, all four hotspots pointed towards the same conclusion. Iron has a higher correlation to phosphorous, than calcium to phosphorous, meaning that P species are much more likely to be Fe-bound, than Ca-bound, at BE outflow.

Figure 5.20. Surface core-scan of BE1 samples collected in August 2019. Four hotspots selected and shown.
Micro-scans performed on Hotspots 2, 3 and 4 (as well as a higher resolution scan of Hotspot 1) can be found in the Appendix (see Section 9.1).
Comparing sequential extraction data to what can be observed in these micro-scans, the $P_{\text{HCl}}$ fraction, containing Ca-bound P and other acid soluble compounds, contributes 6% more to the total extracted P than $P_{\text{Redox}}$, containing Fe-bound P. These opposing pieces of data could differ due to the presence of humic P, confirming the significance of the humic fraction, as well as the likely high presence of P-Ca-humic complexes in the sediment.

In general, this section has shown that the complementary approach of applying detailed spectroscopic analysis has enabled a better understanding of how P species differ within the catchment, seasonal differences in sediment composition, as well as how storm events impact on P transport within suspended solids.
6. Modelling

In the environmental sector, field sampling can be challenging, especially when the monitored system is naturally complex and subject to unplanned disturbances that might originate from an untimely storm event or the unfortunate destruction of field equipment. These occurrences lead to the undesired loss of data that, if not for the existence of computer models, would be unrecoverable.

In questions regarding complex natural systems that require a prolonged period of data collection and multi-site sampling such as those tackled by this multi-disciplinary study, the use of computational tools is often required. These are pieces of computer software that take in input data (namely catchment area, discharge, rainfall, and potential evapotranspiration, for example) and, using a set of parameters that vary depending on the type of software used, allow the construction of numerical models with an elevated degree of certainty for hydrological data, allowing for the expansion of knowledge in both time and space. The modelled data provided by these tools can be used to recover lost information and even simulate data that was not sampled in the past, as well as make predictions into the future or under different land use / management scenarios with a certain level of statistical confidence.

The goal of tackling these simulated models using previously acquired field data was to expand our research in the behaviour of P loads across the different surveyed catchments. Thus, to begin with, a model focused on the hydrological component was worked on first. This allowed to achieve a significantly longer discharge time series to later apply a more comprehensive P model which was focused on outputting different P loads.
6.1. Hydrological model (smartPy)

In this study SMARTpy model was used to simulate a year’s worth of discharge data and, using the previously gathered information on fluvial sediments and their associated phosphorous concentrations, calculate phosphorous loads in three different catchments.

The Soil Moisture Accounting and Routing for Transport model, or SMARTpy for short, is an open-source hydrological catchment model using the programming language called Python. It is a command-line software that requires aereal rainfall and potential evapotranspiration time series to build a top-down rainfall-runoff model composed of a soil moisture accounting component and linear routing components.

SMARTpy uses 10 parameters to estimate and output a discharge time series, namely rainfall aerial correction coefficient (T), evaporation decay parameter (C), quick runoff coefficient (H), fraction of saturation excess diverted to drain flow (D), soil outflow coefficient (S), effective soil depth (Z), surface routing parameter (SK), inter-flow routing parameter (FK), groundwater routing parameter (GK), and river channel routing parameter (RK). This specific model requires the user to be knowledgeable in Python and GNU-Linux command-line to build and debug the script used to run the calculations as it does not provide a graphic user interface. Developed by Thibault Hallouin, Eva Mockler and Michael Bruen in 2019, SMARTpy: Conceptual Rainfall-Runoff Model was implemented in this study by at its version v0.2.1.
6.1.1. **Methodology**

To run the model, a python script was constructed using freely and publicly available source code (Thibault Hallouin, et al., 2019). Every catchment was modelled using the same script. This python script required three support files, one with the input data (discharge, rainfall and potential evapotranspiration), a second containing the catchment specific parameters (T, C, H, D, S, Z, SK, FK, GK and RK), and a third which defined model settings (catchment area, simulation start and end points, output timestep and warm-up days).

Firstly, measured discharge data, allied with rainfall and potential evapotranspiration data collected from Met Éireann weather stations nearest to the sampling locations were used to calibrate the model. Then, catchment and simulation specific characteristics such as catchment area, simulation start and end periods, were changed inside the settings file.

After running the script, an output file containing a discharge time series was created. To analyse the quality of the results, simulated and measured values were compared visually by plotting the corresponding hydrograph and rainfall, and by calculating the Nash Sutcliffe model efficiency coefficient (%NSE). An iterative calibration approach was then followed in order to improve the model fit, whereby one or more of the 10 model parameters were altered each simulation run to introduce the desired change to the hydrograph. Iterations continued until simulated discharge across the measured period would match as closely as possible to experimental results. The number of optimisation iterations required naturally depended on the quantity and quality of the measured data used for calibration.
Due to it being a relatively newly developed model, running optimisation steps while simultaneously achieving a high efficiency value resulted in a very time consuming and demanding manual optimisation.

6.1.2. **Simulated yearlong hydrographs and sediment loads**

Five total sampling locations were modelled, Bunoke including the outflow (BE1) and two upstream sites (BE2 and BE3), as well as Ballyboughal (BB1) and Tintern Abbey (TTA1) outflows.

Model parameters and settings used for each simulation, including %NSE values, are displayed in Table 6.1.

<table>
<thead>
<tr>
<th>Catchment site</th>
<th>Catchment area (km$^2$)</th>
<th>Modelled period</th>
<th>T</th>
<th>C</th>
<th>H</th>
<th>D</th>
<th>S</th>
<th>Z</th>
<th>SK (h)</th>
<th>FK (h)</th>
<th>GK (h)</th>
<th>RK (h)</th>
<th>%NSE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BE1</strong></td>
<td>10</td>
<td>2010 - 2019</td>
<td>0.65</td>
<td>6.5</td>
<td>6.5</td>
<td>1</td>
<td>0.05</td>
<td>2000</td>
<td>0.02</td>
<td>0.2</td>
<td>20000</td>
<td>65</td>
<td>60</td>
</tr>
<tr>
<td><strong>BE2</strong></td>
<td>6</td>
<td>Jan-2019 - Dec-2019</td>
<td>1.3</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>0.01</td>
<td>550</td>
<td>700</td>
<td>0.2</td>
<td>5000</td>
<td>60</td>
<td>74</td>
</tr>
<tr>
<td><strong>BE3</strong></td>
<td>3</td>
<td>Jan-2019 - Dec-2019</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
<td>1</td>
<td>0.01</td>
<td>20</td>
<td>10</td>
<td>0.1</td>
<td>2000</td>
<td>36</td>
<td>50</td>
</tr>
<tr>
<td><strong>BB1</strong></td>
<td>23</td>
<td>2017 - 2018</td>
<td>1.55</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>1.95</td>
<td>0.001</td>
<td>0.7</td>
<td>1500</td>
<td>2000</td>
<td>40</td>
<td>31</td>
</tr>
<tr>
<td><strong>TTA1</strong></td>
<td>10</td>
<td>2017 - 2018</td>
<td>1.5</td>
<td>0.4</td>
<td>0.15</td>
<td>0.005</td>
<td>10</td>
<td>0.5</td>
<td>0.5</td>
<td>1550</td>
<td>2500</td>
<td>25</td>
<td>55</td>
</tr>
</tbody>
</table>

Comparison graphs between modelled and measured discharge can be seen in Figure 6.1, Figure 6.3, and Figure 6.3, for BE, BB and TTA catchments, respectively.
Despite having the most available data for calibration, BE3 had the lowest %NSE value out of all BE locations. However, it’s the site where visual comparison indicates the highest match between simulated and measured discharge values, reinforcing the need for visual comparison as a complement to the goodness of fit provided by %NSE.
Figure 6.1. Comparison graphs between measured (dashed line) and modelled (blue line) discharge relative to each sampling location at BE. Daily precipitation also included.
Modelled hydrographs for a continual 1-year (BE catchment), 2-year (BB and TTA outflows) and 10-year (BE outflow) period are displayed on Figure 6.4 to Figure 6.7, below.
Figure 6.4. Modelled hydrographs of BE1, BE2 and BE3 sampling sites for the full 2019 calendar year.
Past extrapolative hydrograph shown in Figure 6.5 indicates a tendency for the outflow to consistently peak at, at least, 4 m³ s⁻¹ during heavy discharge periods and dip back down to very low values during summertime. Additionally, it is also visible two exceptional years when discharge reached up to 8 m³ s⁻¹, in 2014 and 2016, coinciding with intense rainfall during a longer period. Contrastingly, an atypical short burst of rainfall was recorded in 2012 during a predictably
low flow period, which resulted in sharp spike in modelled discharge values that surpassed high flow peak discharge seen on previous years.

Figure 6.7. Modelled hydrographs of TTA1, the outflow location, with simulated discharge over a 2-year period.

Figure 6.7. Modelled hydrographs of BB1, the outflow location, with simulated discharge over a 2-year period.
Modelled TTA1 and BB1, despite the different peak discharge values, do seem to have the same relative behaviour pattern: a slow rise in baseflow during the winter period and a smooth sloped, featureless descent during the summer. The disparity between TTA/BB and BE could be due to the different catchment soil, giving BE a flashier discharge pattern than what’s predicted for TTA or BB; another contribution to these observable differences could lie in the fact that BB and TTA measured discharge data were acquired by a different technician, possibly introducing user measurement bias.

Simulated discharge data was used to construct suspended sediment load graphs, using the methodology used and discussed on previous chapters. Sediment concentration as a function of normalised simulated discharge plots were graphed in order to determine sediment load at each modelled catchment. These graphs are shown in Figure 6.8. TTA’s graph has less degrees of freedom than advisable for a second-degree polynomial fit, nonetheless, it is the only fitting trendline to the available data.

**Figure 6.8.** Suspended sediment concentration as a function of normalised simulated discharge for BE, BB and TTA catchments (from left to right).
Sediment load per catchment area graphs is displayed below, in Figure 6.9 and Figure 6.10.

All BE sites demonstrate an estimated load spike during an intense rain event happening in April 2019. At BE2, the prediction derived from simulated discharge values indicates a constant high load being transported during the summer months, unlike the July spike seen at the other two.

Figure 6.9. Estimated suspended sediment load, per catchment area, at all sampling locations of the BE catchment.
locations. This phenomenon could be the result of the rigid boundary conditions put in place to avoid sediment concentration extrapolation, which are more noticeable during very high or very low flow conditions.

TTA outflow displayed a higher estimated baseload than BB outflow. However, caution should be taken when deriving concrete conclusions from estimated TTA load due to the short number of degrees of freedom used in the intermediary concentration calculations. Simulated sediment load results for a full year are shown in Figure 6.11.

![Figure 6.10. Estimated suspended sediment load, per catchment area, at BB (left) and TTA (right) catchment outflows.](image)

![Figure 6.11. Estimated sediment loads, per year, per catchment area.](image)
Nonetheless, in order to get a grasp of how exact the model affected load estimations were, a comparison graph of how total load differed between the measured and model estimations, during the same sampling period, was constructed and is shown in Figure 6.12. A period of 208 and 385 days was used to compare measured and simulated loads at BE and BB, respectively.

It followed that the sediment load derived from modelled discharge was being heavily underestimated (almost up to 70% of what was observed) in the cases of BE sampling locations and overestimated – by roughly 20% of what was measured in the same period – in the case of BB1. After adjusting BB1, BE1, BE2 and BE3 sediment load estimates provided by the model, annual estimated suspended sediment loads, per catchment area, are as follows:

![Figure 6.12. Percentage difference of estimated load relative to the measured load for BB1, BE1, BE2 and BE3.](image)

![Figure 6.13. Adjusted estimated sediment loads, per year, per catchment area.](image)
From Figure 6.13 one can conclude that, of all the outflows surveyed, BE1 had the highest suspended sediment being carried by the stream, over a year. Anthropogenic factors, such as the deepening of ditches near and around the stream (which displaced soil that could easily be carried by surface runoff during storm events, as well as subsequently increasing surface soil erosion, helping the breakdown of larger sediment and contributing to more potential suspended sediment near the stream) that was detected during field site surveying, allied to the already proved higher discharge values associated with storm events at BE (which aid the transport of a larger volume of suspended sediment over the) could play an important role in explaining as to why the outflow load at BE1 is roughly 20 times greater than TTA1 and BB1.

6.2. Sediment model (simplyP)

SimplyP is a dynamic water quality model, developed in 2015 at the James Hutton Institute (Scotland), which simulates hydrology, phosphorus, and sediment dynamics in catchments.

According to the developers, the main aim of SimplyP was “to minimize the process representation to only those processes that appear to control the catchment response, whilst maintaining the flexibility and functionality required for the model to be useful in hypothesis and scenario testing” (Jackson-Blake, et al., 2017), allowing for simple parameter values to be constrained using available observational field data.

As with SMARTpy, running SimplyP requires a Python installation and its model code is open source (SimplyP, 2021).
6.2.1. **Methodology**

Firstly, an Excel spreadsheet containing the model parameters, including model setup, reach structure, land use, sub-catchment reach and constants used in the underlying calculations. Secondly, model input was divided into three separate input files: chemical observations, namely of soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total phosphorus (TP) particulate phosphorus (PP) and suspended solids (SS); a time series of daily mean discharge values; and a metrological time series of precipitation and potential evapotranspiration data.

A python script was used to run the model and access the required three support files. The model, however, was accessed using a browser graphical interface. Every catchment modelled used the same script.

As with SMARTpy, rainfall and potential evapotranspiration data was collected from Met Éireann weather stations nearest to the sampling locations. Yet, discharge data used as input to SimpleP had been previously simulated using SMARTpy and optimised to a satisfactory level. Catchment and simulation specific characteristics such as catchment area, reach type, land use, simulation start and end periods, and many others were changed in the parameters file.

After running the script, an output file containing time series of SRP, TDP, TP, PP and SS concentrations and loads was created. SimplyP model efficiency was, however, not tested in this study.
6.2.2. *Simulated yearlong P loads*

Load simulated values were plotted as a time series and comparatively to SMARTpy simulated discharge during the same period as shown in Figure 6.14 and Figure 6.16.

Simulated loads at BE show a very featureless period coming from a steady decline in PP and TP and remaining at a constant, very low load value up until November 2019, a couple of months after the first rain events since the summer period. After November, once the soil is starting to remain more saturated due to the more frequent rain events, there seems to be a general increase in simulated load, particularly in PP and TP load. The peak of PP load, shown to be in April, might suggest that P is being stored in in the catchment during high flow periods, since similar duration rain periods, producing roughly the same discharge, have increasingly higher peak values.
According to Figure 6.14, PP makes up almost the totality of TP present in the stream at any point, reaching up to 40 kg/day around March and 15 kg/day in December 2019.

TTA demonstrated a modelled behaviour very similar to BE (Figure 6.15). Particulate P comprised the majority of the Total P, while SRP and TDP remained in the same order of magnitude. The 2-year simulation showed a drastic increase in TP when approaching the end of September, which overlapped with a more active rain (and consequently discharge) period. The predicted maximum TP load peaks, at TTA, were approximately 45 and 30 kg day$^{-1}$.

Figure 6.14. BE catchment modelled PP, TDP, SRP and TP load, over a 1-year period. Simulated discharge is also depicted at the top.
Figure 6.15. TTA catchment modelled PP, TDP, SRP and TP load, over a 2-year period. Simulated discharge is also depicted at the top.

BB catchment was also modelled using the 2-year discharge simulated data. Modelled data for BB seems to behave similarly as with BE, with estimated TP at its highest load value during high flow periods. However, BB has a much more active summer period than BE, with TP values spiking much more frequently. This could be due to model optimisation, which requires further development in complex agricultural catchments.
TDP load peak values are similar between BB and BE, much unlike PP loads which are almost 3 times higher at BE. This indicates that P content comes predominantly from sediment originated P, especially at the BE catchment where TP contains almost exclusively PP.

When comparing TDP observed load with simulated load, however, modelled estimations underestimate TDP load by as much as 4 and 14 times less than observed TDP load during the same interval period, for BB and BE respectively. Unlike what was done regarding sediment load values calculated from SMARTpy simulated discharge, adjustments to simulated SimpleP P load values were avoided due to the relatively lower amount of input information being provided to SimpleP simulations, justifying future model research and further data improvement.
According to the findings explicated above, PP is expected to have a major contribution to in-stream TP.

All three simulated load plots start with what seems to be an exponential decline of simulated load. This might be due to an initial model “warm-up” period. Although the discharge data was considered very satisfactory, a deeper valuation of this model, with more data points on the different P concentrations across a year-long period should be taken into consideration in future projects.
7. Conclusions

The three agricultural catchment streams studied showed seasonal dynamics in nutrient concentrations and export. All catchments were selected based on known historical issues related to fluvial suspended sediments, as well as the presence of areas with heavy soils, and flashy hydrological characteristics which promote runoff and sediment transport from land to aquatic systems.

Monitored BB and TTA outflows, located in the East and Southeast of Ireland, indicated a more moderate response to rain events in comparison to the BE catchment outflow, located in the mid-West of Ireland, which exhibited a flashy hydrological response to rain events. For the BE catchment, seasonal variations were quite evident for in-stream SRP concentrations, varying between 0.05 and 0.2 mg/L, from mid-summer to late autumn. In contrast, SRP concentrations in TTA and BB catchments were elevated between late summer and mid-winter with concentrations ranging between 0.015 and 0.2 mg/L. Dissolved P load transported was calculated to be, approximately, 23.6 tonnes km\(^{-2}\) (from April to November 2019), and 20.4 tonnes km\(^{-2}\) year\(^{-1}\), for BE and BB catchments, respectively.

Particulate sediment concentration ranged from 0.9-8.1, 0.4-0.7 and 1.6-11.2 mg L\(^{-1}\) at BE1, BE2 and BE3 respectively; 0.6-0.9, 0.3 and 1.7-3.2 2 mg L\(^{-1}\) at BB1, BB2 and BB3 respectively; and 0.4-1.1 mg L\(^{-1}\) at TTA1. Particulate P daily concentrations varied at the each catchment, with BE having the highest measured PP concentration (BE1: 0.9-2.3 mg g\(^{-1}\); BE2: 1.2-2.5 mg g\(^{-1}\); BE3: 2.1-2.2 mg g\(^{-1}\)), followed by TTA (TTA1: 0.16-1.8 mg g\(^{-1}\); TTA2: 0.3-1.2 mg g\(^{-1}\); TTA3: 0.3-1.5 mg g\(^{-1}\)) and BB (BB1: 0.5-1.5 mg g\(^{-1}\); BB2: 0.3-0.4 mg g\(^{-1}\)). Sequential sediment
extractions, that fractionated P into different pools, revealed spatial and temporal dynamics in PP fractions of suspended fluvial sediments collected from agricultural catchment streams. TTA and BB catchments, from December 2017 to June 2018, show residual P (P_{Res}), loosely sorbed P (P_{H2O}) and organic P (P_{Org}) fractions decreased while the Fe/Mn-bound P (P_{Redox}) and Al-P/OH⁻ anionic exchangeable P (P_{NR}) increased. Fluvial sediments collected in the BE stream, from January 2019 to June 2019 show a contrasting pattern in P fraction dynamics, with an overall decrease in P_{Redox} and P_{NR}. Site-specific factors, such as soil geochemistry, play a role in the forms and characteristics of the PP fractions present within suspended fluvial sediments.

A training period of a week at the synchrotron facilities was undertaken and allowed for a practical understanding of the concepts and mechanisms behind the spectra acquisition. Investigation into PP fraction dynamics within fluvial suspended solids from samples collected at various time periods during a storm event generally revealed that there were significant changes in the P fraction composition of the fine particles. XANES spectra of samples collected from the BB catchment showed a fluctuating dominance of organic and inorganic form of P as the storm progressed, depending on the time of the year of each storm event: the analysed summer storm event showed predominant inorganic forms of P at earlier stages and organic forms of P at later stages of the storm, however, a winter storm event displayed the exact opposite pattern. The increase in P_{Redox} during the storm event suggests that fine clays could influence P export during heavy rain events. This would also indicate that the source of sediments changes during a storm event as there is more hydrological connectivity between sources through overland flow pathways.
All modelled agricultural catchment had their sediment load determined from daily sediment concentrations and discharge fluxes. The BB catchment had the least sediment load per catchment area in a year, while BE had the highest sediment load. Additionally, BE and TTA catchments have similar areas, approximately 10 km², however, it is estimated that sediment load at BE is, at least, four times higher than at TTA. In terms of seasonal load variations, BE is expected to have a few major load peaks during winter, with a generally high baseload level, while BB is the estimated to have more intense and more frequent load peaks during winter comparatively to the featureless baseload estimated for the summer to late autumn. TTA’s estimated load displayed a considerably high and constant load level throughout the modelled 2-year period, however, more input data is required to achieve a satisfying number of degrees of freedom in TTA’s suspended sediment concentration as a function of discharge trendline. Simulated TP load indicated that PP fraction outperforms TDP fraction in BE and BB, which coupled with seasonal changes in P fractions seen in all sampling locations suggests that most of the P content in the stream was likely originated from sediment bound P and was most probably cycled to dissolved P via biogeochemical processes.

This research, as a whole, provided valuable insights and divulged new research into the impact of PP associated with fluvial suspended sediments, in terms of its sources and speciation dynamics within geologically and hydrologically contrasting agricultural catchment streams. Various conventional and advanced solid phase analytical techniques were used, summing up to a more detailed P composition of the fluvial suspended sediments, from the combined analysis of their results. All this knowledge can contribute to fluvial suspended sediment associated P assessment for different catchments and temporal targeted land-use and mitigation strategies.
8. References


field study of soil erosion. CATENA 203, 105290.
https://doi.org/10.1016/j.catena.2021.105290


9. Appendix

9.1. µ-XANES

9.1.1. Hotspot 1

Figure 9.1. Hotspot 1 micro-scan of Calcium in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.2. Hotspot 1 micro-scan of Iron in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.3. Hotspot 1 micro-scan of Phosphorus in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
9.1.2. *Hotspot 2*

Figure 9.4. Hotspot 2 micro-scan of Calcium in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.5. Hotspot 2 micro-scan of Iron in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.6. Hotspot 2 micro-scan of Phosphorus in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
9.1.3. **Hotspot 3**

Figure 9.7. Hotspot 3 micro-scan of Calcium in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.8. Hotspot 3 micro-scan of Iron in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.9. Hotspot 3 micro-scan of Phosphorus in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.10. Hotspot 4 micro-scan of Calcium in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.11. Hotspot 4 micro-scan of Iron in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.
Figure 9.12. Hotspot 4 micro-scan of Phosphorus in an August 2019 BE1. Relative intensities are colour-schemed: warmer colours indicate a higher signal count.

9.2. SmartPy

GENERAL INFORMATION:

SMARTpy

Documentation:

https://pypi.org/project/smartpy/0.2.1/

https://github.com/ThibHlln/smartpy
9.2.1. *Installing and running the model*

Python packages installed:

- numpy
- scipy
- future
- smartpy
- netCDF4
- hydroeval

**INSTRUCTIONS:**

0. Install the necessary software and dependencies. Copy and paste the following command (without the quotation marks):

```
$"python3 -m pip install numpy scipy future smartpy"
```
1. Name the input files found in root/in/CATCHMENT_NAME/ as:

"CATCHMENT_NAME".rain
"CATCHMENT_NAME".peva
"CATCHMENT_NAME".flow
"CATCHMENT_NAME".sttngs
"CATCHMENT_NAME".parameters

2. Edit ".sttngs" file in the root/in/CATCHMENT_NAME/ directory. This file should contain the same structure as the template found in TEMPLATES/template.sttngs file. Each variable should be typed line by line following the order in the template file. If gauged area is available, input the value at the end of the file, otherwise, the file should end with the warm up days.

3. Edit the ".parameters" file in the root/in/CATCHMENT_NAME/ directory. This file should contain the same structure as the template found in TEMPLATES/template.parameters file. Edit out the "VALUE" and insert the desired parameter value.

The parameters detailed below:

- T  rainfall aerial correction coefficient
- C  evaporation decay parameter
- H  quick runoff coefficient
- D  drain flow parameter - fraction of saturation excess diverted to drain flow
- S  soil outflow coefficient
• Z effective soil depth
• SK surface routing parameter
• FK inter flow routing parameter
• GK groundwater routing parameter
• RK river channel routing parameter

4. Go to the parent directory "SmartPy-Modelling/" and run the script "smart-py". You can run this script by entering the following command in the terminal (without the quotation marks):

```bash
"python3 smart.py CATCHMENT_NAME"
```

replacing the "CATCHMENT_NAME" with the actual catchment name you have in the root/in/CATCHMENT_NAME (e.g. python3 smart.py BA)

5. The generated observed and modelled output files are kept in the root/out/CATCHMENT_NAME/ directory and saved as "CATCHMENT_NAME.obs.flow" and "CATCHMENT_NAME.mod.flow", respectively.

6. If you want to save the output of this script you can do so by entering the command (without the quotation marks):

```bash
"python3 smart.py CATCHMENT_NAME > NAME_OF_FILE.txt"
```
This will make the script silently write the output in the file as it runs, freeing the terminal once it's complete. If you want to write the output to a file but also free the terminal and make the script run silently in the background, enter the following command:

```
"python3 smart.py CATCHMENT_NAME > NAME_OF_FILE.txt &"
```

9.2.2. *smart.py script source code, folders and files*

This script presupposes a file structure such as:

- `smart.py`
- `root/`
  - `in/CATCHMENT/
    - CATCHMENT.flow`
  - `CATCHMENT.peva`
  - `CATCHMENT.rain`
  - `CATCHMENT.settings`
  - `CATCHMENT.parameters`
- `out/CATCHMENT`

Below are images to serve as reference to the file structure needed.

Figure 9.13. Main folder containing a root folder and the smart.py script.
Figure 9.14. Both “in” and “out” folders are present inside the “root” folder. Outputted files are going to be created inside the `out/` folder, in the respective catchment name folder.

Figure 9.15. Content of “in” folder. Different folders of various modelled sites.
Figure 9.16. Content of one of the catchment folders containing the input (.flow; .rain; .peva), parameters and settings files.

Figure 9.17. Example of a .flow file.
Figure 9.18. Example of a .peva file.

Figure 9.19. Example of a .rain file.

Figure 9.20. Example of a .parameters file.
The script used to run the model presupposes that input data is given at an hourly timestep and the source code is available below:

```
# SMARTpy Modelling Script

import smartpy
import sys
import pathlib
from datetime import datetime, timedelta
import numpy as np
from hydroeval import evaluator, nse, kge

# defining a verbose functions

step = 0  # each step is a line of code being processed

def verbose(step, text):
    print("Step {}: {}...".format(step, text))
```
# step 1
step += 1
verbose(step, "importing smartpy")

# creating an instance of the class SMART for the desired catchment
# all input data will be collected from the input files
# located in the "root/in/catchment_name" directory
# all arguments are mandatory except gauged_area_m2
# if gauged_area_m2 is provided, discharge measurements are available
# and SMARTpy is expecting a .flow file in the input directory
# these measurements can be used later on in post-processing to evaluate
# simulation performance

# step 2
step += 1
verbose(step, "opening settings file")

# defining root,
# input settings file,
# & parameters file directories location

root = "root"

root_dir = "{{}}".format(
    pathlib.Path(__file__).parent.absolute(), root)

settings_f = "{{}}/{{}}.settings".format(
    root_dir, sys.argv[1], sys.argv[1])

parameters_f = "{{}}/{{}}.parameters".format(}
root_dir, sys.argv[1], sys.argv[1])

# accessing and reading the file containing the settings

with open(settings_f, "r") as f:
    catchment_f = f.readline().rstrip()
    catchment_area_m2_f = float(f.readline().rstrip())
    start_f = datetime.strptime(f.readline().rstrip(), '%Y-%m-%d %H:%M:%S')
    end_f = datetime.strptime(f.readline().rstrip(), '%Y-%m-%d %H:%M:%S')
    time_delta_simu_f = timedelta(hours=int(f.readline().rstrip()))
    time_delta_save_f = timedelta(days=int(f.readline().rstrip()))
    warm_up_days_f = int(f.readline().rstrip())
    gauged_area_m2_f = float(f.readline().rstrip())

# step 3
step += 1
verbose(step, "creating SMART instance for the catchment")

sm = smartpy.SMART(
    # catchment_name should have same name
    # as in dir root/in/catchment_name
    catchment=sys.argv[1],
    # catchment area in m2
    catchment_area_m2=catchment_area_m2_f,
    # beginning date
    start=start_f,
    # end date
    end=end_f,
    # simulated time interval in hours (REFER TO line 58)
    time_delta_simu=time_delta_simu_f,
    # output time interval in hours (REFER TO line 59)
time_delta_save=time_delta_save_f,
# warm up days
warm_up_days=warm_up_days_f,
# input files format
in_format='csv',
# output files format
out_format='csv',
# root folder
root=root,
# gauged area
gauged_area_m2=gauged_area_m2_f
)

print(""
    catchment name: {}
    area: {} m2
    start date: {}
    end date: {}
    warm up days: {}
    input directory: {}
    output directory: {}
    root directory: {}
\n")

print(""
    sm.catchment,
    sm.area,
    sm.start,
    sm.end,
    sm.warm_up,
    pathlib.Path(sm.in_f),
    pathlib.Path(sm.out_f),
    pathlib.Path(sm.root_f)
))
# step 4

step += 1

verbose(step, "feeding parameter values to the model")

# giving parameter values to the model
# using a file containing the parameter values
# accessible using the instance:
# sm.parameters.set_parameters_with_file("FILE_LOCATION/FILE.parameters")

sm.parameters.set_parameters_with_file(parameters_f)

# step 5

step += 1

verbose(step, "dealing with initial conditions")

# dealing with initial conditions
# if not initialised, the model states
# (i.e. soil moisture layers' levels, and linear reservoirs's levels)
# are set to zero
# use a warm-up period to initialise the model states (example: 365 days)
# if the user has some general information
# about the hydrology in their catchment
# SMARTpy will estimate the model states from this information
# to make an "educated guess" of the levels of the
# soil layers and the routing reservoirs:
# sm.extra = {'aar': 1200,
# 'r-o_ratio': 0.45,
# 'r-o_split': (0.10, 0.15, 0.15, 0.30, 0.30)}
# 'aar': an estimate of the annual average rainfall in millimetres,
# 'r-o_ratio': an estimate of the runoff ratio,
# 'r-o_split': an estimate of the runoff split between
# overland flow/drain,
# flow/interflow/shallow groundwater
# flow/deep groundwater flow
# if the user has access to accurate estimates for these values,
# they may prefer to use this option as
# initialisation method in place of a warm-up period,
# or in addition to the warm-up period

# sm.extra = {'aar': 1200,
#             'r-o_ratio': 0.45,
#             'r-o_split': (0.10, 0.15, 0.15, 0.30, 0.30)
#            }

# step 6
step += 1
verbose(step, "SIMULATING")

# simulating
sm.simulate(sm.parameters.values)

# getting the outputs
# the outputs are the simulated streamflow series
# and the observed streamflow series
# streamflow series is provided if and only if
# the gauged_area_m2 was provided in the SMART instance
# if so, the .flow file provided in the input folder
# has already been read and the data is directly
# available from the SMART instance
# in cases where catchment_area_m2 and gauged_area_m2
# are different, the observed streamflow
# series provided in the the .flow file is
# rescaled accordingly assuming proportionality

# step 7
step += 1
verbose(step, "writing the outputs in files")

# writing the outputs in files
# the format of the files used is the one provided in
# the out_format attribute of the SMART instance (either 'csv' or 'netcdf')
# outputing the file using the line:
# sm.write_output_files(which='both')
# the 'which' argument can take the value
# 'modelled' - writes the simulated streamflow series
# 'observed' - writes the observed streamflow series
# or 'both' - writes both series

sm.write_output_files(which='modelled')

#
#
# # FOR OUTPUT TIME STEPS LOWER THAN 1 DAY UNCOMENT SECTION BELOW
# #

# step 8
step += 1
verbose(step, "retrieving the outputs in numpy arrays")

# retrieving the outputs in numpy arrays
# directly getting the model outputs in the current Python session:
# evaluation_ = sm.get_evaluation_array()
# simulation_ = sm.get_simulation_array()

evaluation_ = sm.get_evaluation_array()
simulation_ = sm.get_simulation_array()

# step 9
step += 1
verbose(step, "post-processing the outputs with numpy and hydroeval modules")

# example of post-processing
# when comparing them using an objective function,
# only days with available observations can be used
# to deal with this use:

evaluation = evaluation_[~np.isnan(evaluation_)]
simulation = simulation_[~np.isnan(evaluation_)]

# now that the arrays have no missing value, but still the same length,
# they can be compared using any objective function
# use the hydroeval to get access to some
# of the most commonly used objective functions in hydrology:

# calculates the Nash-Sutcliffe efficiency
nse_ = 1 - evaluator(nse, simulation, evaluation)[0]

# calculates the bounded Nash-Sutcliffe efficiency
c2m = nse_ / (2 - nse_)

# calculates the original Kling-Gupta efficiency
kge_ = enumerate(evaluator(kge, simulation, evaluation), 1)
# step 10

```python
step += 1
verbose(step, "printing efficiency results")

print("\nНаш-Sutcliffe efficiency: NSE = {}\%.format(round(nse_ * 100, 2))")

print("\nБounded Nash-Sutcliffe efficiency: C2M = {}\%.format(round(c2m * 100, 2))")

for k, v in kge_:  
    print("\nOriginal Kling-Gupta efficiency {}: {}\%.format(k, round(v[0] * 100, 2))")
```

9.3. SimpleP

GENERAL INFORMATION:

SimplyP

SIMPLYP MODEL (github)

https://github.com/LeahJB/SimplyP
9.3.1. Installation

If you don't have an up-to-date Python installation, a good option is the Anaconda Python distribution. Model development was carried out using Python 2.7, but should now be run with Python 3.6 as Python 2.7 is being phased out.

0. From the Anaconda prompt, create a new clean conda environment for SimplyP (you can replace 'simplyp' with a name of your choice)

```
$conda create -n simplyp python=3.6
```

1. Activate the new environment

```
$activate simplyp
```

2. Install dependencies

```
$conda install jupyter=1.0.0 notebook=5.7.4 matplotlib=2.0.2 pandas=0.24.1 seaborn=0.9.0 numpy=1.15.4 scipy=1.2.0 xlrd=1.2.0
```

3. Download the SimplyP repository and unzip it to a location on your system. The folder Current_Release/vx-xx contains the main model code you will need to set up and run the model (vx-xx refers to the version number, which will change as development continues; e.g. v0-2A). The folder 'Example_Data' includes data to get you started with a model application using data from the Tarland catchment in Scotland.
4. From the Anaconda command prompt, change directories to the 'Current_Release/vx-xx' folder (which contains 'setup.py'), replacing the x-xx with the appropriate version number for the current release. To change directories, type cd followed by a space and then the filepath (e.g. cd C:\SimplyP\Current_Release\v0-2A). Then run

   ```
   python setup.py install
   ```

9.3.2. **Running the model**

   A simple example illustrating how the model can be used is here. To run this example:

0. From the Anaconda prompt, activate your SimplyP environment

   ```
   activate simplyp
   ```

1. Change to the directory containing 'Run_SimplyP_vx-xx.ipynb' within the 'SimplyP/Current_Release/vx-xx' folder and run

   ```
   jupyter notebook
   ```
2. then click the link to open 'Run_SimplyP_vx-xx_LongExample.ipynb'. You should now be able to work through the notebook, running the code cells interactively. More instructions are given within the notebook itself.

When you have finished working with the model, click 'File > Close and Halt' (remember to save any changes first, if desired), then close the browser tab. Close the 'Home' tab too, then CTRL + C' twice at the Anaconda prompt to shut down any active Python kernels.

9.3.3. Adjusting inputs

9.3.3.1. Model Parameters

These are defined in an Excel sheet. See the Example_Data file for a template. The file can have any name. The path to the file is entered at the top of the Jupyter notebook used to run the model.

The sheet names must not change, nor must the parameter names within the 'Param' column. See the 'readme' on the first sheet of the parameter file for more guidance.
9.3.3.2. Meteorological data

This should be stored in .csv format with column headings:

<table>
<thead>
<tr>
<th>Date</th>
<th>Precipitation</th>
<th>T_air</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/01/1998</td>
<td>12</td>
<td>9</td>
<td>0.9</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Description of variables:

- Precipitation: total precipitation (rain plus snow), (mm)
• T_air: air temperature, (degrees Celsius)
• PET: potential evapotranspiration, (mm)

See the Example_Data file for a template.

If the time series in this file is longer than the period defined by the start and end dates in the parameter file ('Setup' sheet, parameters 'st_dt' and 'end_dt'), then it will be automatically truncated to coincide with the desired start and end dates. N.B. it must cover the period defined by the start and end dates.

If PET data is not provided, it will be calculated by the model using the Thornthwaite method. Note that this method may provide biased results but has been chosen as a first approximation of PET as it is simple to implement and has low data requirements.

9.3.3.3. Observed discharge & water chemistry

0. Create separate Excel files for discharge and water chemistry data. Files can have any name (the path to the files is entered by the user in the parameter 'Setup' sheet).

1. Within the files: insert data for separate reaches on separate sheets, and number the sheets with the reach number (e.g. 1, 2,...) ONLY (the model code expects sheet names
to be integers, and will return an error if not). Each sheet within the file should have the headings:

1.1. **Discharge data:**

<table>
<thead>
<tr>
<th>Date</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/01/1998</td>
<td>12</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

1.2. **Water chemistry data** (include any of these you have data for):

<table>
<thead>
<tr>
<th>Date</th>
<th>TP</th>
<th>PP</th>
<th>TDP</th>
<th>SRP</th>
<th>SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/01/1998</td>
<td>2.7</td>
<td>2.3</td>
<td>1.0</td>
<td>0.98</td>
<td>3.1</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

where:

- **Q** is the discharge (m3/s)
- **TP** is total P (mg/l)
- **PP** is particulate P (mg/l)
- **TDP** is total dissolved P (mg/l)
- **SRP** is soluble reactive P (mg/l)
- **SS** is suspended sediment (mg/l)

Any columns in the sheet with names aside from these will not be read in (but need not be deleted from the file). As with the meteorological input data, observations are automatically truncated to the start and end dates given in the parameter setup sheet. See the Example_Data file for templates.