

# Unsaturated zone travel time to groundwater on a vulnerable site

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## ABSTRACT

A bromide (Br) tracing experiment was conducted to ascertain unsaturated zone travel time to groundwater on a site with a karstified limestone aquifer overlain by a thin free-draining overburden. Br tracer was applied to areas surrounding two boreholes; soil solution and groundwater Br concentrations were monitored. Bromide was first detected after eight and 34 days in the soil solution and groundwater. The quick break-through of the applied Br in the soil solution and groundwater indicates the presence of preferential flow in the soil at this site. The time to maximum groundwater Br concentration supports a dominant matrix flow path through the overburden and then preferential flow through the unsaturated limestone bedrock. The results indicated that the transport of conservative contaminants, such as nitrate, can be expected to occur in a single recharge season. The occurrence of preferential flow raises concerns over rapid transport of non-conservative contaminants such as faecal coliforms and this merits further investigation.

**Key index words:** bromide, tracing; preferential flow; dual porosity; travel time; groundwater vulnerability; karst; Fermoy.

## Introduction

This study is concerned with the use of bromide (Br) as a tracer to determine the travel time of water and mobile anions through the unsaturated zone, as part of a wider study of nitrate leaching to groundwater in an Irish limestone aquifer. While many tracer studies have been undertaken in Ireland to determine travel times associated with point recharge to karst aquifers (e.g. Gunn, 1982; Drew, 1988 and 1992) this constitutes a rare attempt to quantify the travel time of diffuse recharge through the soil and unsaturated zone in an Irish context. Ryan (1998) presented preliminary evidence of preferential flow in an Irish soil based on dye tracing which demonstrated preferential movement of the applied dye to a depth of 0.9m. A study in the Gort lowland, Ireland, estimated a recharge travel time of up to four years using tritium analyses (Bowen and Williams, 1972). A study of Crag Cave, southwest Ireland reported a rapid travel time, varying from hours to days, from soil surface to groundwater, due to presence of preferential flow through the soil (Tooth and Fairchild, 2003).

Water percolating through soil/subsoil may travel by two pathways, a slower pathway through the soil matrix (matrix flow) and a faster pathway (preferential flow) bypassing the soil matrix (Flury *et al.*, 1994). Matrix flow occurs via displacement where a volume of effective rainfall displaces an equal volume of soil water vertically downwards. Preferential flow or bypass flow results in a rapid movement of water through soil and subsoil bypassing the main soil matrix. This flow type through soil/subsoil is influenced by soil macropores formed by a number of processes such as soil fauna, plant roots, cracks and fissures and natural soil pipes (Beven and Germann, 1982). Similarly water can move by slow and fast pathways in bedrock often referred to as primary and secondary permeability. The majority

of Irish bedrock aquifers have only fast flow pathways or fissure permeability; in the case of karst limestones such pathways may be particularly rapid due to solutional widening of the openings. Preferential flow of water through soil and bedrock has significant human health and environmental implications as it leads to the bypassing of the potential attenuation properties of the soil/subsoil or bedrock matrix. The occurrence of preferential flow in both soil/subsoil and bedrock increases the potential transport of contaminants such as faecal microorganisms (McLeod *et al.*, 2001), pesticides (Brown *et al.*, 1999), herbicides (Elliot *et al.*, 1998), phosphorus (Simard *et al.*, 2000).

Travel times are a critical factor in determining groundwater vulnerability and producing groundwater protection schemes. Travel time can be defined as the length of time it takes for water to get from the soil surface to the aquifer and/or from one point to another within an aquifer. Many groundwater protection schemes involve the determination of travel times through the saturated zone to groundwater supplies, with time-of-travel zones being designated, for example the British 50 day zone (NRA, 1992) and the Irish 100 day zone (DELG/EPA/GSI, 1999). Vertical travel times through the unsaturated zone are more rarely incorporated however, with a range of surrogates and indices being employed instead. For example, in the widely used DRASTIC scheme developed in the USA (Aller *et al.*, 1987), the index of groundwater vulnerability incorporates rankings according to depth to the water table, soil type and impact of the vadose zone media, while the British scheme includes a ranking of soil leaching susceptibility based on soil properties such as texture (Robins *et al.*, 1994). In Sweden, quantification of groundwater vulnerability has been attempted by Maxe and Johansson (1998), who present a table of vertical travel times through different geological materials for a worst-case scenario assuming a liquid spill under saturated conditions and unit gradient (with reduced travel times for cohesive soils with potential for macropore flow). In the current Irish methodology, vulnerability zones used in both source and resource protection are ranked in four classes from extreme to low vulnerability based primarily on the thickness and lithology of the Quaternary deposits (subsoils) (Daly and Warren, 1998). In Ireland an attempt has been made to quantify the permeability corresponding to some of the subsoil types on a pilot research basis (Swartz *et al.*, 2003), but direct measurements of travel time using tracers are not well documented.

Traditionally Br has been used as a tracer for the study of water and solute transport as it does not adsorb to negatively charged soil particles. Background Br concentrations are generally very low in the aquatic environment making it an ideal tracer. Groundwater Br concentrations have been reported to vary between 0.01 and 0.32 mg/l (Houghton, 1946; Bathhurst *et al.*, 1980; Luong *et al.*, 1980; Lundstrom and Olin, 1986; Flury and Papritz, 1993). In the UK, groundwater Br concentrations range from 0.06 to 0.09 mg/l (Luong *et al.*, 1980). Lundstrom and Olin (1986) reported Br concentrations ranging from 0.016 to 0.08 mg/l from springs sampled in Sweden. Soil and groundwater Br concentrations decrease with increasing distance from the sea (Yuita, 1983).

Many authors have used Br tracing in field and laboratory investigations to examine the importance of preferential flow as a mechanism of water movement through soils to recharge aquifers (Everts *et al.*, 1989; Jabro *et al.*, 1994; Caron *et al.*, 1996; Schuh *et al.*, 1997; Kelly and Pomes, 1998; Timlin *et al.*, 1998). Many of these studies have been limited to investigations in the unsaturated zone with no linkage to the saturated zone (Schuh *et al.*, 1997; Owens *et al.*, 1985; Owens and Edwards, 1992) did look at groundwater Br breakthrough. On a coarse loamy glacial till, Schuh *et al.* (1997), observed increases in groundwater Br

concentration of one order of magnitude within 10 days of surface application and this was attributed to preferential flow through the soil to the water table which varied from 3 to 4.8 m below ground level (bgl).

The longevity of Br in a catchment after a single surface application was noted by Schuh *et al.* (1997) who observed elevated concentrations in saturated till for three years (the end of monitoring) after a single, surface application. Owens *et al.* (1985) observed no significant decrease of groundwater Br concentrations for 4.5 years following a single, surface-applied Br application.

Bromide is not a totally conservative tracer as a number of workers have reported crop uptake rates of 27 percent to 32 percent for Br applied to crops (Owens *et al.*, 1985; Schnabel *et al.*, 1995; Kessavalou *et al.*, 1996). It should also be noted that Br can have serious health effects, for example Owens *et al.* (1985) observed that nineteen cattle, in a herd of 25, died after grazing a plot which had received 168 kg Br/ha two weeks earlier. Therefore great care is needed in the use of Br as a tracer in ruminant grazing areas such as in this study.

### Study area

An investigation of nitrate leaching to groundwater from intensive dairy production commenced in 1985, on a 55ha dairy farm near Fermoy, co. Cork (Sherwood *et al.*, 1987). A phase of detailed investigation, including the tracer work reported here, commenced in 1993 (Richards, 1999).

The site is located on a thin soil derived from shallow Quaternary deposits, with depth to bedrock ranging from 0.6 m to > 3 m. The soil is a free draining acid brown earth of sandy loam texture. The mean soil infiltration capacity on the farm was 33 mm/hour (Richards, 1999). The Quaternary deposits, described by Shearley (1988), are fluvio-glacial deposits consisting of alternating poorly-sorted, coarse to fine gravels and cross-bedded sands with angular rock fragments of mainly sandstone, siltstone and mudrocks. Soil properties for the fraction < 2 mm, associated with the two study boreholes, are shown in Table 1.

Table 1: Soil properties of the two experimental sites, borehole 1 and 2. Particle size analysis based on the soil fraction <2mm.

Borehole	Depth (m)	Soil Horizon	Particle size analysis (%)			Dry bulk density (g/cm <sup>3</sup> )
			Clay	Silt	Sand	
1	0-0.3	A	12.4	31.3	56.3	1.15
	0.3-0.6	B	12.1	36.7	51.2	1.22
	0.6-0.9	C	8.4	46.5	45.1	0.88
2	0-0.15	A1	12.6	28.6	58.8	1.24
	0.34-0.46	B1	6.8	33.7	59.5	1.31
	0.46-0.6	B2	2.7	33.7	63.6	1.42
	0.6-1.3	Ct	15.1	39.1	45.8	1.59

The depth to bedrock on the site was assessed from borehole logs and trial hole excavations around the site (Figure 1). At the Br tracing sites (see Methods below) the depths to bedrock were 0.6-0.8 m at borehole 1 and 2.5 m at borehole 2.

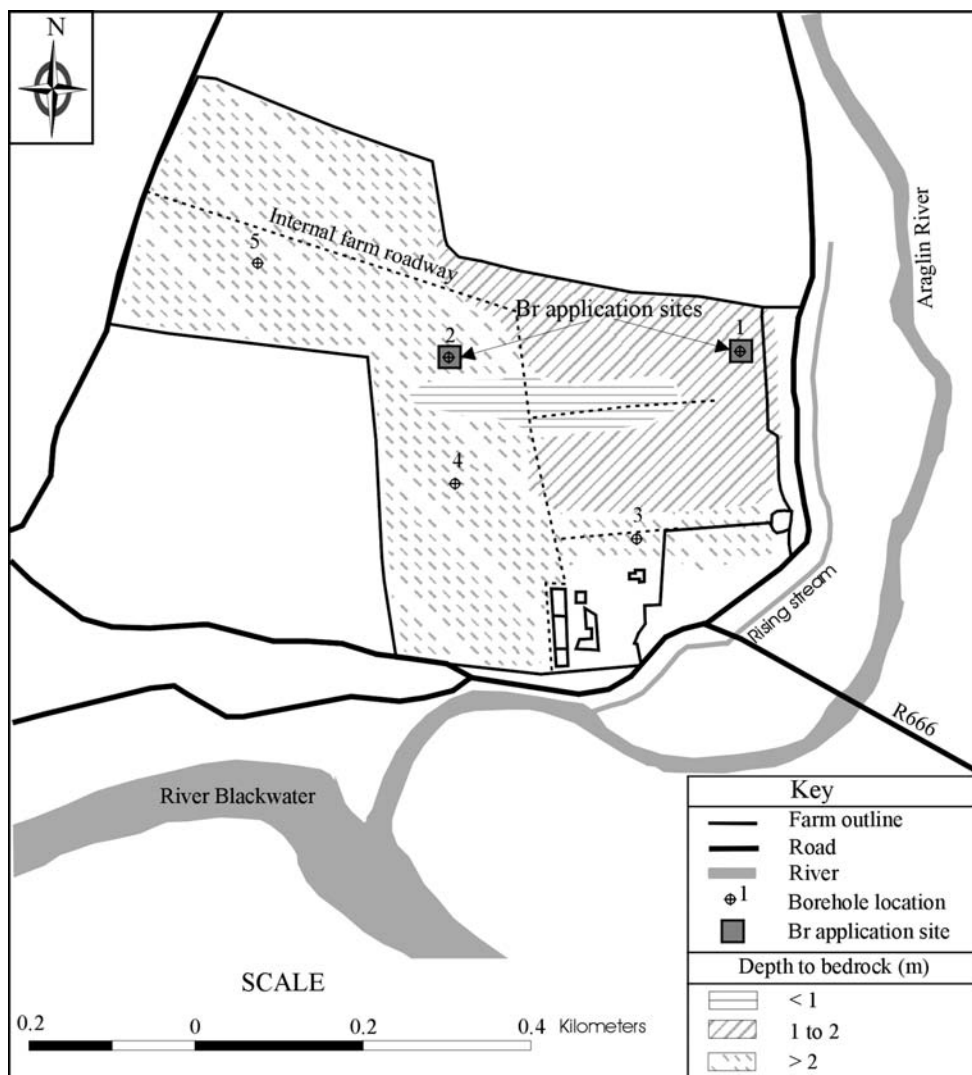


Figure 1: Study site borehole locations, bromide application areas and depth to bedrock (m).

The bedrock underlying the farm consists of folded limestones, shales and sandstones of Lower Carboniferous age (Figure 2). The bedrock underlying most of the study farm, including the two tracer sites, is the Ballysteen Limestone formation, which is a shaley/cherty limestone with intermittent beds of thin shale. The Ballysteen Limestone formation has been classified as a locally important aquifer which is moderately productive only in local zones (Daly, 2004). This overlies the Ringmoylan formation (a shale bedrock with intermittent limestone beds). Boreholes 1 and 2 are located on the same synclinal line, which plunges  $15^{\circ}$  W (Shearley, 1988). The total depth of boreholes 1 and 2 are 37.8 and 48 m, respectively and the standing water table heights at the start of the experiment were 22.4 m and 24.7 m bgl.

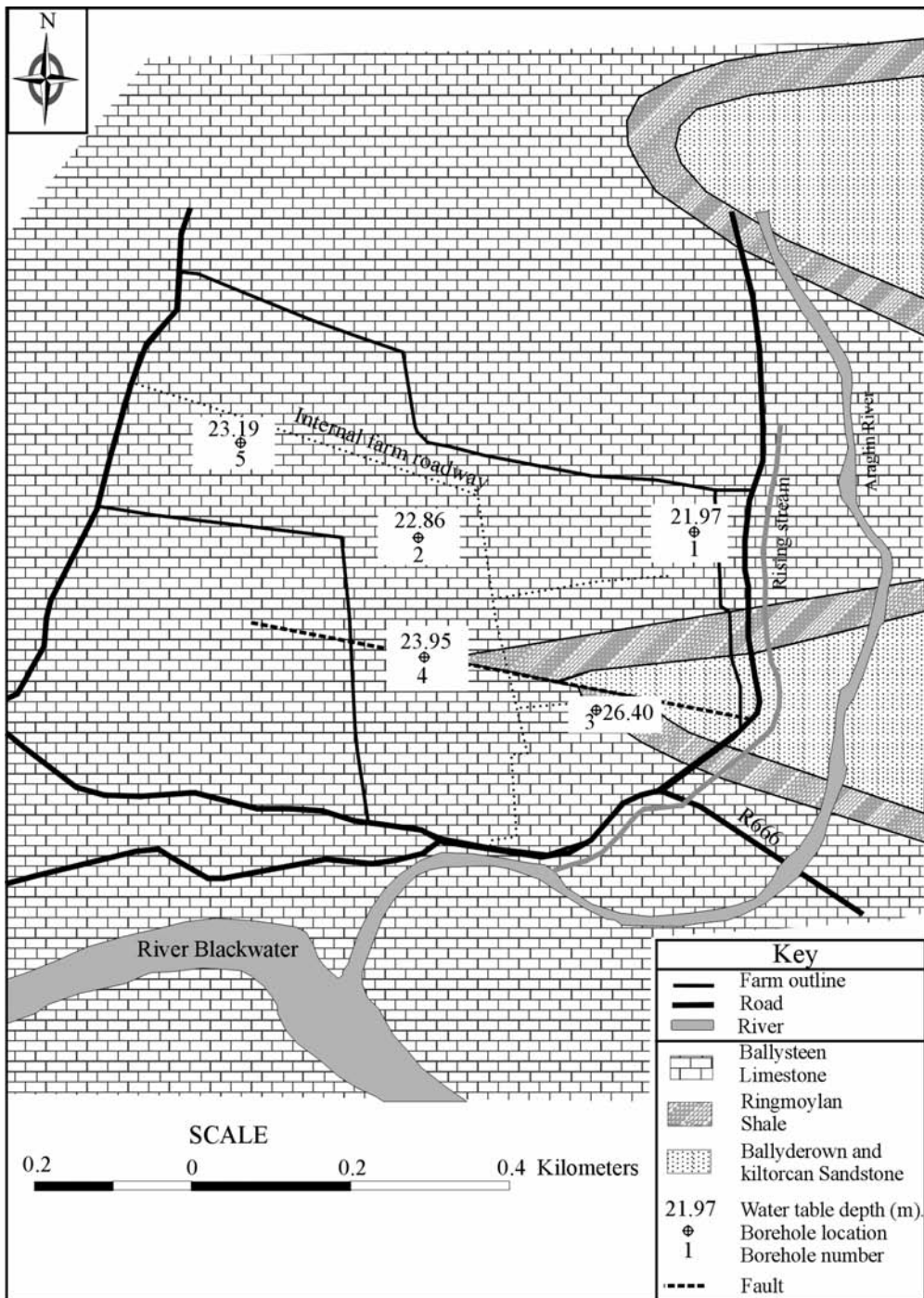


Figure 2: Study farm bedrock geology, borehole locations and standing water levels (m) when the bromide tracer was applied.

## Methods

The objective of the main study was to investigate and quantify nitrate leaching to groundwater on an intensively stocked dairy farm. Five monitoring wells were located on the farm. Wells were core-drilled to a depth of 50m bgl, geological cores were removed and logged. A 50mm PVC casing was installed in each borehole and the bottom 20m was slotted. The soil/bedrock interface was sealed with a bentonite cement. In 1993 ceramic cups (Soil Moisture Inc.) were installed at a distance of 3m from the five boreholes, at three depths of 0.5, 1 and 1.5m bgl. Originally there were three replicate cups per depth but when this experiment was begun only one cup per depth produced soil solution samples, as the other cups had ceased functioning. Due to the shallow bedrock at borehole 1, ceramic cups were only installed at a depth of 0.5m. Each cup had a bentonite seal installed 0.3 m above each cup to prevent edge flow along the cup sides.

At the beginning of January 1996, background water samples for Br analyses were taken of (a) soil solution at boreholes 1 and 2 and (b) groundwater at boreholes 1, 2, 3 and 4. Borehole 5 was not used as a monitoring well for this experiment as another experiment using optical brightener was being conducted simultaneously and this would have caused problems with the ion exchange column used in the Br analysis.

On 16 January 1996, KBr was applied at boreholes 1 and 2. A grid, 100 m<sup>2</sup>, was marked out on the soil surface at each borehole site, with the borehole in the centre of the grid. The grid was subdivided into 4 m<sup>2</sup> blocks; each block, with the exception of the block with the borehole contained in it, had two litres of deionised water containing 208 g KBr spread evenly over it giving a total of 5 kg KBr per 96 m<sup>2</sup> grid. The solution was applied evenly using a 4 l watering can with a T-bar attached to the outlet to ensure even irrigation of the Br solution. The Br application rate and hydraulic loading were equivalent to 349.5 kg Br/ha and 0.5 mm, respectively.

The soil solution was sampled weekly at each site from 10 January 1996 to 27 April 1996. The groundwater, in boreholes 1 to 4, was sampled using a 1 l hand-bailer and one well volume was removed prior to taking a 500 ml sample that was stored at 4°C for transport to the laboratory. A dedicated bailer was used for each borehole sampled to ensure no cross-contamination. Analysis of Br was carried out in the Environmental Sciences Unit, Trinity College Dublin by ion chromatography using a Dionex ion chromatograph.

Meteorological data from Teagasc, Moorepark, which is 1.5 km from the experimental site, was used to calculate effective rainfall or drainage which is an estimate of the quantity of water that percolates through soil to groundwater. Potential evapotranspiration (Pe) was calculated using the FAO Penman-Montieth equation (Allen *et al.*, 1998) and this was converted to actual evapotranspiration (Ae) using an Aslyng scale recalibrated for Irish conditions (Schulte *et al.*, 2004). Effective rainfall was calculated by subtracting daily actual evapotranspiration from daily rainfall (assuming no overland flow losses due to the high infiltration capacity of the soil on this site).

## Results

At the start of the experiment the soil was at field capacity as the area had received 151 mm rainfall, equivalent to more than one month's normal rainfall, in the first two weeks of January. During the experimental period, 16 January 1996 to 27 April 1996, there was a total of 366.3 mm rainfall and 245 mm of effective rainfall. In total, 32 of the 102 days during the

experiment had effective rainfall events and 98 per cent of the effective rainfall occurred during five short drainage periods. These events are numbered in Figures 3, 4 and 5. The total rainfall during the period January to April 1996 (517.2 mm) was higher than the 30-year average (1961-90) of 342 mm (Table 2).

Table 2: Monthly calculated effective rainfall, total rainfall and the 30-year average monthly rainfall (Fitzgerald and Forrester, 1996).

Month	Effective rainfall 1996 (mm)	Total rainfall 1996 (mm)	30-year average (mm)
January	177.2	185.8	117.0
February	101.8	117.8	87.0
March	122.3	148.6	79.0
April	44.0	65.0	59.0
Total	445.3	517.2	342.0

*Soil Solution*– The soil solution Br concentration results can be seen in Figure 3. Prior to tracer application, the background soil solution Br concentrations ranged from 0 to 0.04 mg/l. At borehole 1, at 0.5 m, Br concentrations had increased from a background concentration of 0.02 to 0.22 mg/l when the first soil solution sample was taken after tracer application (day 8). The corresponding travel time of first Br occurrence was  $6.3 \times 10^{-2}$  m/d. Drainage event 1 had a total of 26.3 mm of drainage which was evenly distributed between 2 and 4 days after application. Soil solution Br concentrations increased steadily over the monitoring period before peaking at 227 mg/l on 21 March 1996, 65 days after application. The maximum observed concentration had a travel time corresponding to  $7.7 \times 10^{-3}$  m/d. The maximum observed Br concentration in the soil solution at borehole 1 occurred after drainage event 3 (89.3 mm) and cumulative drainage of 206.3 mm, since the start of the experiment. After drainage event 4 (22.1 mm), the soil solution Br concentration decreased to 0.11 mg/l, 102 days after Br application.

At borehole 2, the 0.5 m soil solution Br concentration increased from 0 to 1.25 mg/l, eight days after tracer application which was similar to the soil solution Br breakthrough at borehole 1. The maximum observed soil solution Br concentration of 120 mg/l occurred on 19 February 1996, 34 days after application and 128.5 mm of cumulative drainage was estimated during this period. The soil solution Br concentrations at the 1 and 1.5 m depths increased simultaneously on 12 February 1996, 27 days after application, equivalent to travel times of  $3.2 \times 10^{-2}$  and  $5.5 \times 10^{-2}$  m/d, respectively. The concentrations at the 1.0 and 1.5 m depths were very similar and peaked on 21 March 1996, 65 days after tracer application. The maximum Br concentration in the soil solution at the 1 m depth was only 5 mg/l greater than the peak at the 1.5 m depth. At both sampling depths the Br concentrations in the soil solution decreased to 0.53 and 1.13 mg/l or less when sampling ceased on 27 April 1996, 102 days after tracer application.

*Groundwater*– The groundwater Br results are presented in Figure 4. Background groundwater Br concentrations ranged from 0.05 to 0.09 mg/l and the mean of the four boreholes was 0.07 mg/l. On 19 February 1996, 34 days after tracer application, the groundwater Br concentration at borehole 1 increased from 0.09 to 0.19 mg/l, corresponding to a travel time of  $6.6 \times 10^{-1}$  m/d. The maximum Br concentration of 15 mg/l was observed on 02 April 1996, 77 days after

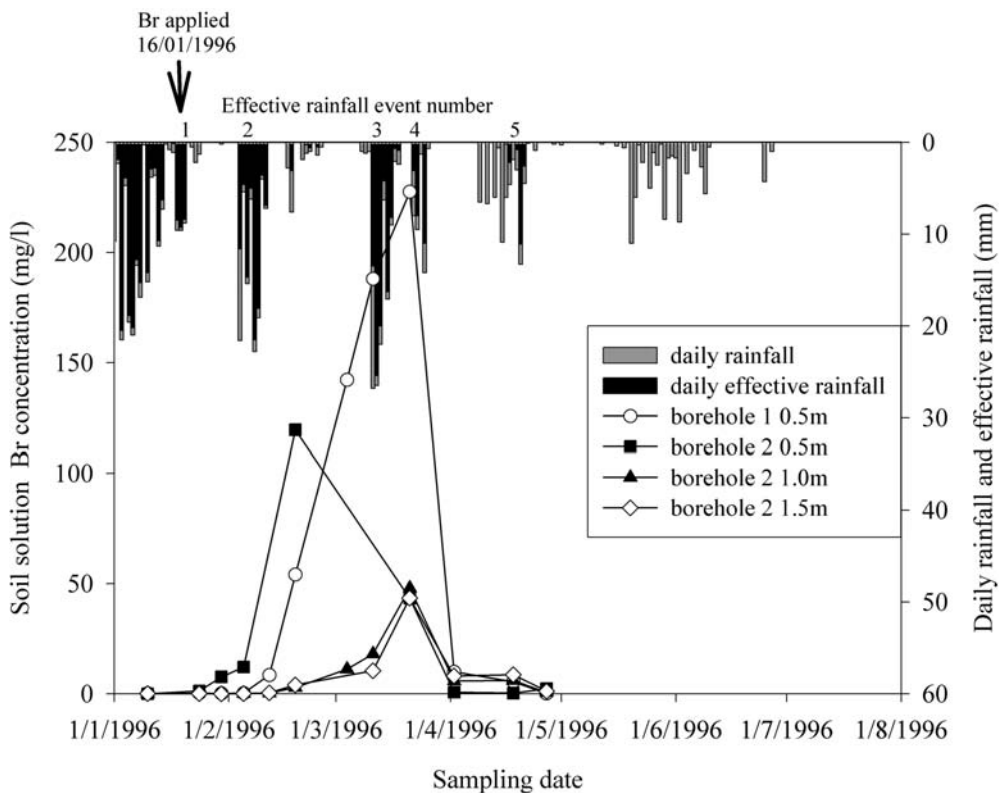


Figure 3: Soil solution Br concentrations at depths of 0.5, 1.0 and 1.5 m below ground level at borehole sites 1 and 2 plotted against daily rainfall and daily effective rainfall from 1 January 1996 and 1 August 1996.

application and 252 mm of cumulative drainage, equivalent to a travel time of  $2.9 \times 10^{-1}$  m/d. Groundwater Br concentrations subsequently decreased to 0.13 mg/l on 27 April 1996, 102 days after tracer application and 25 days after the maximum observed concentration. A summary of the observed time of travel for soil solution at 0.5 m and groundwater Br in borehole 1 is presented in Table 3.

Table 3: Summary Br trace time to first observed Br occurrence and time to maximum observed Br concentration (m/d) in soil solution at 0.5 m and in the groundwater at borehole 1.

	Day no. and time to Br occurrence m/d	
	First observed occurrence	Max. observed occurrence
Soil solution (0.5m)	Day 8, $6.3 \times 10^{-2}$	Day 34-65, $1.4 \times 10^{-2}$ - $7.77 \times 10^{-3}$
Groundwater borehole 1	Day 34, $6.6 \times 10^{-1}$	Day 77, $2.9 \times 10^{-1}$

The temporal variations in groundwater Br concentrations at boreholes 2, 3 and 4 were all very similar to each other. Groundwater Br concentrations in these boreholes increased from background concentrations of  $<0.1$  mg/l to maximum concentrations of 0.53, 0.48 and 0.25 mg/l, respectively, 102 days after Br application. The increase in groundwater Br



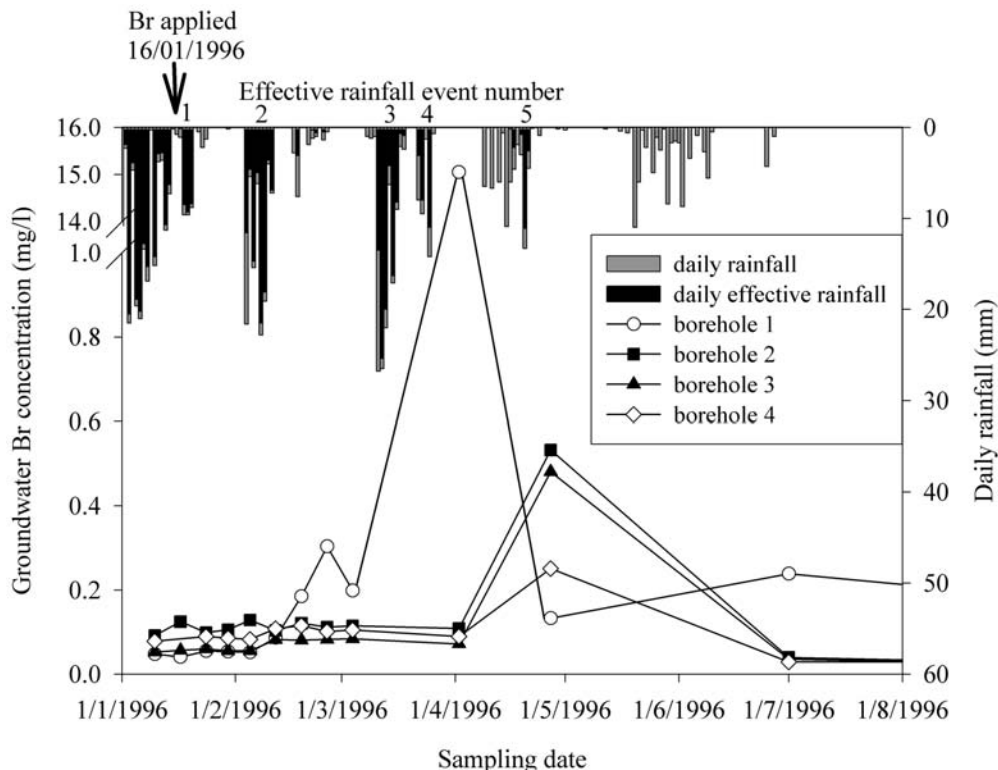


Figure 4: Groundwater Br concentrations plotted against daily rainfall and daily effective rainfall between 1 January 1996 and 1 August 1996.

concentrations at these boreholes occurred simultaneously with the decrease to <1 mg/l at borehole 1.

Water table heights, expressed as m above Ordnance Datum (m aOD), observed at each borehole are presented in Figure 5. The water table height increased in all boreholes twice during the experimental period, 19 February 1996 and 2 April 1996. On these dates the water table heights in borehole 1 increased by 0.63 and 0.21 m whereas in borehole 2 the increases were 1.27 and 0.41m. The total water table height ranges (1990 to 1997) observed in boreholes 1 and 2 were 1.89 and 2.81m. The two water table increases observed during the experimental period occurred after effective rainfall events 2 and 4. The first occurrence of Br in borehole 1 on 19 February 1996 was 34 days after Br application and seven days after the first observed increase of water table height. The second increase on 2 April 1996 was 77 days after Br application and corresponded with the maximum observed groundwater Br concentration in borehole 1.

The groundwater was re-sampled on a number of dates one year after Br tracer was originally applied and all the groundwater Br observations for the study are presented in Figure 6. Groundwater Br concentrations in borehole 1 ranged from 0.23 to 0.47 mg/l when re-sampled between 20 January 1997 and 27 March 1997, 370 and 436 days after application. Groundwater Br in boreholes 2, 3 and 4 remained at around the background concentration observed before the experiment was begun, ranging from 0.04 to 0.07 mg/l, during the same sampling period.

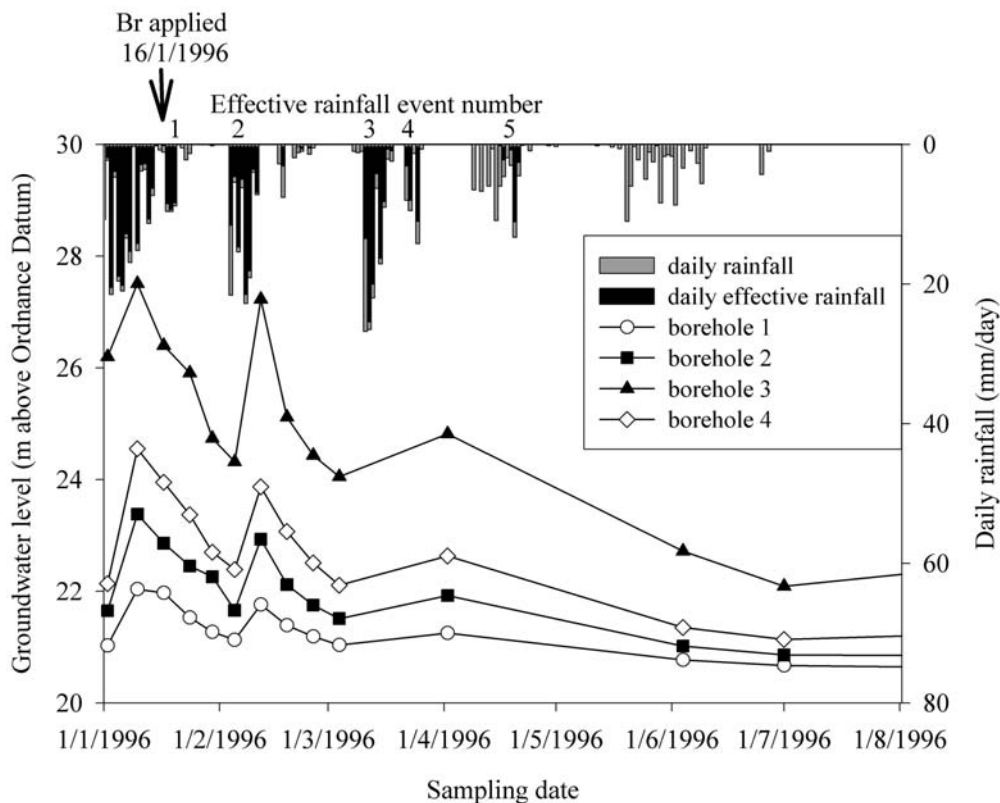


Figure 5: Groundwater level expressed as m above Ordnance Datum (m aOD) plotted against daily rainfall and daily effective rainfall (mm/day) between 1 January 1996 and 1 August 1996.

### Discussion

The soil solution Br concentration results indicate the rapid movement of applied Br from the soil surface to depths of 0.5, 1 and 1.5m bgl. At both borehole sites the soil solution sampled at the 0.5m depth increased eight days after tracer application, corresponding to a flow velocity of  $6.3 \times 10^{-2}$  m/d. The tracer solute front was estimated to have moved to a depth of 0.08 m during the eight-day period, assuming saturated conditions (i.e. hydraulic gradient of 1), porosity of 0.35 and a drainage volume of 27.4mm. The difference between the observed first Br occurrence and the estimated leaching depth indicates that the soil solution sampled did not move through the total porous annular space in the soil. This difference is also supported by the soil solution Br results from the 1 and 1.5m depths which showed first occurrence of applied Br 27 days after application.

At borehole 1, elevated groundwater Br concentrations were observed 34 days after application. During the first 34 days of the experiment there were two drainage events totalling 115.6 mm and this was sufficient to transport the applied Br solute front to the water table 22.96 m bgl (21.39 m aOD, Figure 5), increasing groundwater Br concentrations. The first Br occurrence in borehole 1 corresponded with an increase in the water table height at borehole 1 (Figure 5). Based on the effective rainfall volume it is estimated that the solute front moved 0.33 m over this 34 day period and so would not have reached the soil-bedrock

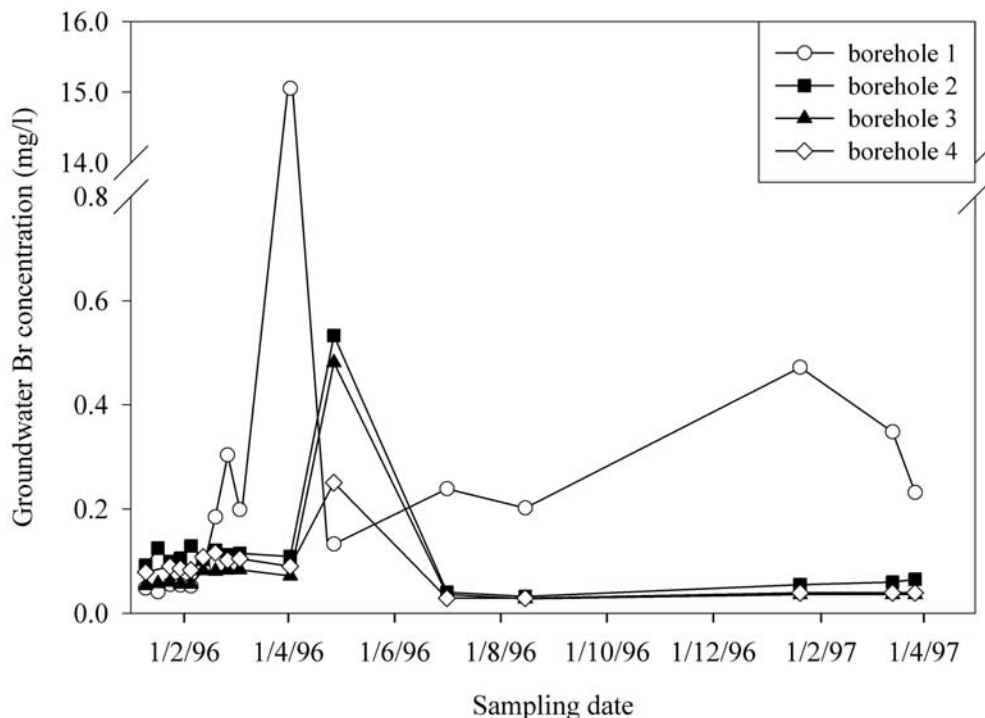


Figure 6: Groundwater Br concentrations from 1 January 1996 to 1 April 1997.

interface. Therefore, as with the results for first appearance in the soil solution, the timing of first appearance of Br in the groundwater implies that some of the applied Br did not move through the entire pore space of the soil (0.35) but moved preferentially to the water table.

Travel times to the maximum observed Br concentration in the soil solution (65 days) and groundwater (77 days) differed by only twelve days, during which time there was 4.9 mm of drainage. Based on the 252.2 mm of drainage during the first 77 days of the experiment and a porosity of 0.35, it is estimated that the solute front moved 0.71 and 0.72 m. Due to the shallow overburden depth at borehole 1 (0.6-0.8 m) it is likely that the maximum observed Br concentration in the groundwater, 77 days after tracer application, can be explained by matrix flow in the overburden and rapid movement of the solute from the soil/bedrock interface to the water table. Rapid solute movement through the unsaturated bedrock would be expected at this site as recharge in karst aquifers occurs almost entirely via secondary permeability openings (joints and bedding partings). At this site, solutionally enlarged secondary permeability openings were observed in bedrock core samples of the Ballysteen Limestone.

The findings of the current study compare favourably with the findings of Schuh *et al.* (1997) who observed an increase in Br concentrations in soil solution and groundwater (at 6.8m deep) within ten days of application on a similar glacial soil. The rapid transport of the applied Br was attributed to preferential flow following the first rainfall event after application (Schuh *et al.*, 1997). In contrast to the present study, Larsson *et al.* (1999) concluded that impact of preferential flow was minor as only a marginal increase of groundwater Br concentration at 1.55 m bgl was observed.

The antecedent meteorological conditions are important in determining the travel time of surface-applied chemicals such as Br. It was clear that the antecedent rainfall during the current study was the driving mechanism for Br delivery through the unsaturated zone to groundwater. There were two water table responses during the experimental period and these coincided with Br delivery to the groundwater, first by preferential flow and secondly by matrix flow. Schuh *et al.* (1997) also noted the importance of rainfall in rapidly transporting Br through the unsaturated zone to groundwater resulting in water table responses and coinciding with Br breakthrough.

The similar low Br concentrations observed at boreholes 2, 3 and 4 may indicate the same Br source. The results demonstrate that the Br applied was transported from topographic high (boreholes 1 and 2) to topographic low (boreholes 3 and 4). The elevated Br concentrations observed in boreholes 3 and 4 can not be explained by saturated flow from the input sites, as water can not flow up hydraulic gradient (see groundwater levels in Figures 2 and 5). It is likely that unsaturated flow transported the applied Br to boreholes 3 and 4. It is hypothesised that unsaturated flow occurred between bedding partings, such as limestone/shale interfaces, where lateral flow must occur above the more impermeable shale beds. Thus unsaturated flow down bedrock dip from boreholes 1 and 2 would be expected. It is also possible that unsaturated flow occurred from borehole 1 down the strike of the fold plunging west at 15° towards borehole 2. It was not possible to identify the exact source of Br in either borehole 3 or 4 and to do that the experiment would have to be repeated with only one input site. Thus it is important that tracer studies should have a single tracer input site to allow flow directions to be verified.

When the groundwater was re-sampled one year after Br application, borehole 1 still had elevated Br concentrations indicating that the tracer experiment was still affecting groundwater chemistry. Br concentrations had decreased close to background when sampling ceased 436 days after first application. The results indicate that there was a prolonged effect of the Br tracer, supporting the longevity of Br tracing experiments on groundwater Br concentrations observed by a number of workers (Owens *et al.*, 1985; Owens and Edwards, 1992 and Schuh *et al.*, 1997). Owens and Edwards (1992) reported that it took nearly ten years for groundwater Br concentrations to return to background. Schuh *et al.* (1997) observed elevated concentrations in saturated till for three years (the end of monitoring) after a single surface application. In the current study groundwater Br concentrations returned to background quicker than this reflecting the higher permeability soil/subsoil and aquifers in comparison to the studies mentioned.

The results from this tracing experiment confirm the extreme vulnerability designation of this site according to the Irish groundwater protection scheme (DELG/EPA/GSI, 1999). The bulk of Br transport through the soil appears to be by matrix flow (with peak concentrations at 0.5 m depth reached after 34-65 days), but the shallow glacial overburden and fissured, karstified bedrock means that peak concentrations in groundwater are reached rapidly (77 days at borehole 1). Therefore at this site conservative contaminants such as nitrate from the soil can be expected to reach groundwater within a single recharge season.

The trace also provides important evidence of preferential flow through the soil and glacial overburden (with first arrival of tracer at 0.5 m depth within eight days at both sites, and at 1.5 m depth within 27 days). While this flow route is quantitatively much less important for the Br (and presumably for other soluble conservative constituents), its

existence opens the possibility of rapid transfer of non-conservative contaminants such as faecal microorganisms. Other workers have recommended that caution must be used in interpreting the risk of microbial transport based on the results of conservative tracer studies (Dong *et al.*, 2002; Mawdsley *et al.*, 1995 and McLeod *et al.*, 2003). Given the concern over faecal microbial contamination in Irish aquifers (e.g. Thorn and Coxon, 1992 and Page *et al.*, 2004), such preferential flow paths clearly merit further investigation.

The geographic extent of the indications of preferential flow observed in this study is currently uncertain; the proportion of Ireland with similar conditions to the study site, extremely vulnerable underlain by karst bedrock, has been estimated at 4.6 per cent (Daly, 2005). Areas that may exhibit similar soil/subsoil and groundwater flow patterns would be north Clare, east Galway, north and south Cork. The geographic extent and soil/subsoil properties that contribute to preferential flow in Ireland need further investigation in order to identify land areas susceptible to these fast flow pathways.

### **Conclusions**

The findings in this study support the extremely vulnerable designation of this site due to the rapid transport of recharge to groundwater. There were indications of preferential flow through the overburden as time to first occurrence in the soil solution at 0.5m was eight days. There were also indications of preferential flow to the saturated zone, 22.96 m bgl, as Br was first detected in groundwater 34 days after tracer application. On the study site it appears that matrix flow through the overburden and preferential flow through the unsaturated bedrock is quantitatively more important for transport of conservative tracers such as Br and nitrate to groundwater. Conservative tracers such as nitrate can be expected to be transported through the unsaturated zone within one recharge season and this allows for temporal changes in groundwater chemistry to be related to land use practices on the farm. The occurrence of preferential flow through the unsaturated zone raises concerns over the rapid transport, to groundwater, of non-conservative contaminants such as faecal coliforms and this merits further investigation.

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