Nitrate fluctuations at the water table: implications for recharge processes and solute transport in the Chalk aquifer

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Abstract

This study investigates fluctuations in nitrate concentration at the water table to improve understanding of unsaturated zone processes in the Chalk aquifer. Sampling was conducted using a novel multi-level sampler during periods of water table rise over five years. The sampler allowed near continuous sampling at a vertical resolution of 0.05 m. Nitrate concentration increased as the water table seasonally recovered, with similar interannual trends with depth. The rising water table activated horizontal fractures facilitating the delivery of water elevated by up to 10 mg/L of nitrate with respect to the adjacent groundwater below. These fractures are considered to activate via piston displacement of water from the adjoining matrix. Hydrograph analysis identified sixteen events which significantly perturbed the water table within 24-48 hours of rainfall. Consistent nitrate concentrations indicate recharge through persistent fracture flow from the surface was not generally the primary driver of the rapid water table response during these events. Instead, the response was attributed to the piston displacement of porewater immediately above the water table. However, a single event in November 2012 delivered relatively dilute recharge indicating rapid persistent fracture flow following rainfall was possible to a depth of 14-15 m. Decreases in porewater nitrate concentration around fracture horizons and the dilution of many groundwater samples with respect to porewaters indicate a fresher source of water at depth. This was considered most likely to be a result of near surface water bypassing the matrix frequently because of widespread mineralisation on fracture surfaces, which retard water and solute exchange. Therefore, persistent fracture flow maybe considered a frequent process in, operating independently of the matrix, and is not necessarily event driven.

Keywords: nitrate, chalk, recharge, piston displacement, fracture flow, contamination

1. Introduction

Understanding the mechanisms of contaminant migration through the unsaturated zone is important for assessing the degree of attenuation and risk to aquifers. This is particularly relevant for fractured aquifers which can sometimes exhibit rapid delivery of contaminants from the surface to the water table (Nimmo et al. 2002, Mellander et al. 2013). The Chalk aquifer is the most important source of freshwater in Northwestern Europe and fracture flow can occur within the unsaturated zone (Downing et al. 1993). However, there is ongoing uncertainty over its significance (Price et al. 2000, Ireson et al. 2006, Van den Daele et al. 2007, Ireson and Butler 2011, Keim et al. 2012) and persistence with depth (Gooddy et al. 2001, Haria et al. 2003, Ireson et al. 2012).

The Chalk is a fine-grained soft limestone with low permeability, moderate to high porosity and very small pore diameters. It is commonly intersected by high angle joints and numerous horizontal discontinuities associated with bedding and secondary structures (Downing et al. 1993). It also includes thin horizontal clay-rich horizons known as marl bands. Together, these features make it a complex dual porosity medium for the transport of water and solutes.

Groundwater in the Chalk unsaturated zone is generally considered to move perennially under gravity through the aquifer matrix, with rapid, fracture flow (also termed fissure, preferential or bypass) occurring episodically (Mathias et al. 2005, Ireson et al. 2009a). Fissure flow has been suggested to account for 15-30% of total recharge (Smith et al. 1970, Jones and Cooper 1998, Mathias et al. 2006), with its onset dependent upon the duration and intensity of rainfall events and antecedent soil moisture content of the near surface (Ireson and Butler 2011).

Price et al. (2000) postulated that fracture flow is not generated by water migrating down from the surface, but from suction within the matrix declining to a level where water begins to accumulate on fracture surfaces. This was considered most likely towards the water table where suctions are lowest, with fracture flow likely to extend upwards with increasing recharge. However, it has also been demonstrated that marl horizons produce localised areas of low suction throughout the unsaturated zone (Gallagher et al. 2012), which can be where fracture flow is initiated (Zaidman et al. 1999). Alternatively, (Keim et al. 2012) proposed that fracture flow dominated throughout the winter in the Yorkshire Chalk, facilitated within numerous smaller features in the upper 5 m of the unsaturated zone. These converged into fewer solutionally enhanced features within 5-15 m of the surface, which persisted up to 45 m below ground level. This was despite the water table residing around 90 m below the surface.

There is also evidence for lateral flows within the Chalk unsaturated zone. Barraclough et al. (1994) suggested this from the loss of ^2H and ^{15}N tracers from below field plots. Additional support comes from cores below land that had never been fertilised, yet showed high concentrations of NO_3 similar to those in neighbouring arable fields (Lawrence 1985). Rutter et al. (2012) suggested that such lateral flows could be rapid, as they may be associated within solutionally developed horizontal fractures overlying marl horizons.

Nitrate (NO_3) is a groundwater contaminant of particular concern in many developed and developing countries (Almasri and Kaluarachchi 2007, Ledoux et al. 2007, Orban et al. 2010, Hosono et al. 2011, Barhoum et al. 2014). Within the UK, there is a legacy of NO_3 storage within the Chalk unsaturated zone resulting from historical fertiliser applications (Foster et al. 1982). This migrates through the matrix and fractures, with diffusive exchange between the two (Barker and Foster 1981, Mathias et al. 2005), but only at a rate of 0.3 to 1.4 m/year (Geake and Foster 1989, Chilton and Foster 1991). Consequently, peak NO_3 concentrations have yet to reach the water table in 60% of the UK Chalk (Jackson et al. 2008, Wang et al.

2012). This will occur over forthcoming decades with implications for groundwater bodies failing to obtain 'good status' defined by the Water Framework Directive (Rivett et al. 2007).

Stuart et al. (2008b) proposed four theoretical mechanisms for NO_3 transport to the water table: i) the establishment of rapid fracture flow in the winter/spring period containing enhanced concentrations of leached NO_3; ii) recharge to the saturated zone by piston flow through the unsaturated zone matrix releasing NO_3 stored in the unsaturated zone (Wellings and Bell 1980); iii) the flushing out of "stored" unsaturated zone NO_3 by rising groundwater levels (Brouyere et al. 2004, Hong et al. 2007); iv) the isolation of shallow highly permeable flow paths during periods of low water level reducing the amount of newer high NO_3 water which can move laterally to an abstraction point.

The objective of this paper is to characterise nitrate fluctuations at the water table to improve understanding of unsaturated zone processes in the Chalk. This is undertaken through novel high resolution sampling over five years.

2.   Methodology

2.1 Site setting

The study site is located to the southeast of Winchester, Hampshire, UK (51.025^o N, 1.278^o W). It is at an elevation of about 55 m above Ordnance Datum Newlyn (ODN) on the southeastern slopes of a dry valley which runs southwestwards towards the River Itchen, 2.7 km to the west (Figure 1). The surrounding area is in a Nitrate Vulnerable Zone (NVZ, Osborn and Cook 1997) and comprises predominantly arable and unimproved grassland, with cattle grazing in the valleys. The immediate area around the study site was "set-aside" for some years and is now headland.

At the site, the Seaford Chalk Formation is at outcrop and is underlain by the Lewes Nodular Chalk Formation. The Seaford and Lewes Nodular formations are around 25 and >50 m thick, respectively, and consist of soft-to-firm white chalk with common flints. The site is on the south flank of the Winchester Anticline which dips to the south at about 5° (Hopson 2001). Erosion of the Chalk surface has resulted in an outcrop of chalk of increasing age to the north climaxing in the window of Zig Zag Chalk Formation at the core of the anticline (Figure 1).

Groundwater flow is to the southwest towards the river but is influenced by abstraction from a   public   supply   pumping   station   (38 m above ODN)   to   the   west (Institute of Geological Sciences 1979). The long-term autumn minimum water level is approximately 25 m above ODN and levels show marked seasonal fluctuations of up to 20 m. The unsaturated zone is therefore predominantly in the Seaford Chalk. The Chalk in Hampshire is generally highly transmissive with a median value of 2600 m^2/day and pumping tests within the Itchen valley indicate values of up to 4500 m^2/day (Allen et al. 1997).

Groundwater levels from a monitoring borehole at the base of the dry valley (51.025^o N, 1.284^o W) and NO_3 concentration data from the local pumping station indicate a good relationship between the two (Figure 2), which was a prerequisite for site selection. High groundwater levels and NO_3 concentrations were observed particularly during the wet winters of 2001-2 and 2012, with NO_3 exceeding the UK drinking water standard of 50 mg/L. Lower concentrations of NO_3 occurred in the dry periods of 2006 and 2011.

2.2 Study boreholes

Borehole A was drilled in May 2006 to a depth of 75 m below the surface. This borehole was fully cored at 150 mm diameter and core was sampled for porewater hydrochemistry and aquifer physical properties. This borehole was completed with two 50 mm diameter piezometers, with 6-m screened sections located at around 30 and 60 m below datum (m bd). The borehole datum is ground level.

Borehole B was located 10 m away and was drilled at 200 mm diameter in October 2008 to a depth of 70 m bgl. This was completed with steel casing to 12.7 m below the surface, to the base of the weathered chalk, and with open hole below. This borehole was used for geophysical logging, dilution testing and multi-level groundwater sampling. The borehole datum is the top of the casing.

2.3 Hydrological fluxes

Daily rainfall data were retrieved from the UK Meteorological Office MIDAS site (2013) 4km from the study boreholes at Otterbourne Water Works (51.008^{o} N, 1.336^{o} W). Daily potential evaporation data were calculated from observations collected in Wallingford (51.603^{o} N, 1.111^{o} W) using the Penman-Monteith equation. Both datasets extended from 1st December 2006 until 31st December 2012.

The Penman Grindley (PG) methodology was used to estimate potential recharge (drainage from the base of soil zone) using the above observations to drive the simulation. The methodology was run within the ZOODRM modelling package (Hughes et al. 2008).The crop root constant, wilting point and runoff coefficient were set to 200 mm, 251 mm, and 5%, respectively. Actual evaporation was assumed to be 10% of potential evaporation between the root constant and the wilting point. Bypass flow was neglected, which could potentially result in an underestimation of potential recharge. This parameterisation was previously used at a similar Chalk site by Sorensen et al. (2014), who evaluated the performance of the PG approach against soil moisture observations and other recharge models. Soil moisture data were reproduced well and potential recharge was within 10% of that simulated by a more complex Richards equation based model in four out of six years.

2.4 Hydrograph analysis

The lag and amplitude of the water table response to precipitation is considered to reflect the mode of recharge in the Chalk. Ireson et al. (2009b) considered lags of >100 days to be recharge through the matrix, c. 20-30 days to be both through the matrix and partially saturated fractures, and a large <1 day response to be persistent fracture flow from the near surface. This analysis was based on a single chalk borehole where the water table fluctuated between 28 and 14 m bgl. Lee et al. (2006) attributed many lags of <2 days to fracture flow through a large part of the unsaturated zone at two sites with average water tables of 26 and 66 m bgl. Thereafter, they considered the subsequent water table rise after 19-26 days to be a separate matrix pulse.

Accordingly, groundwater level responses following precipitation were investigated for evidence of persistent fracture flow. This was considered to be an event resulting in a 0.1 m/d increase in the rate of water table rise within 24-48 hours of precipitation. Groundwater levels were monitored within the shallow piezometer at Borehole A using a pressure transducer. These data were corrected to frequent manual dip measurements, due to the inaccuracies associated with transducers (Sorensen and Butcher 2011).

2.5 Borehole characterisation

Core sampling and analysis

Porewater was sampled every 0.25 m by removing 10-15 mm of the core outer surface and then breaking the remainder into approximately pea-sized pieces. These were centrifuged under refrigeration at 14,000 rpm in Delrin[TM] buckets with titanium filter discs, filtered at 0.45 μm and aliquots taken for analysis. Core moisture content was determined by weight loss after oven-drying at 105 °C for at least 24 hours (Butcher 1990). Major anions were measured using a Dionex[TM] DX-60 Ion Chromatograph. Aquifer properties were determined on 25-mm oven-dried core plugs using the methods described by Butcher (1990). Gas permeability tests were performed under steady-state conditions using nitrogen and porosity using a liquid resaturation method (Butcher 1990). Only summary core data are reported for the purposes of this study, and the reader is referred to Stuart *et al.* (2008a) for full details, including depth profiles.

Borehole geophysics

An optical image of the borehole was recorded using a Geovista Electromind OPTV sonde, which provides a continuous 360-degree image of the borehole wall with a north-south orientation. This was used to identify features which could potentially be delivering water to the borehole. To provide evidence on whether these features were active, ambient fluid temperature and specific electrical conductivity (SEC) measurements were made with a Geovista[TM] TCME probe. Temperature and SEC vary between fractures as a result of differences in groundwater circulation pathways, e.g. deeper fractures tend to be warmer, and also have a greater SEC due to longer residence times resulting in enhanced rock-water interaction. Temperature and SEC measurements were made on the run down before any disturbance in the water column in March 2009 at a groundwater level of 14.1 m bd.

Dilution tests

Single borehole dilution tests (SBDT) involve injecting a tracer (salt in this instance) into a borehole water column and collecting depth profiles of tracer concentration with time to monitor its dilution (Maurice et al. 2011). The characteristics of the tracer dilution can reveal inflows to, and vertical flows within, a borehole (e.g. Mathias et al. 2007, Sorensen et al. 2013). SBDTs were performed at groundwater levels of 16.1 and 14.7 m bd in July 2012 and April 2013, respectively. These entailed injecting salt uniformly through the water column to a depth of 28-30 m bd, and multiple point injections to confirm vertical flows. Depth profiles of specific electrical conductance (SEC) were obtained to monitor the salt dilution with time.

2.6 Water table sampling

A multi-level sampler, based in principle on that first described by Gooddy et al. (2001), was deployed during periods of water table rise. The objective was to sample groundwater arriving at the water table prior to any mixing within the saturated zone. However, it is also possible that groundwater could arrive at the water table via fractures intercepted by the borehole above the saturated zone (Gallagher et al. 2012), or through upward flow promoted by fractures below the water table (Butler et al. 2009). Furthermore, there is the possibility of diffusive exchange between water within the borehole and the surrounding Chalk matrix prior to sample capture.

The sampler comprised a series of 30 ml Sterilin[TM] containers attached to a piece of plastic tracking. The containers included floating-ball seals, which would isolate each inundated container from the surrounding groundwater during a rise in the water table allowing samples at discrete depths to be obtained (Figure 3). The sampler was 4 m in length with 39 containers

at intervals of about 0.1 m. A supplementary set of 39 containers were attached on the opposing side of the sampler at the same interval, but offset by 0.05 m, to enable a sampling resolution of 0.05 m. A pressure transducer, with direct read cable leading to the surface, was attached to the base of the sampler. This enabled it to be positioned at the water table on each site visit. During these site visits bailed samples from the water table were also collected directly from the borehole.

The sampler was deployed during five successive hydrological years between October 2008 and December 2012. Where there were minor recessions, particular intervals were often resampled during subsequent water level rise. Major anions in all samples were measured using a Dionex^{TM} DX-60 Ion Chromatograph. This included nitrite and phosphate which could be indicative of water arriving rapidly at the water table from the soil zone, although NO_2 could also originate from others areas of nitrification of denitrification.

3. Results

3.1 Borehole characterisation

Core analysis

There was no evidence of large-scale solution enlargements of fractures in the Borehole A core, although in the unsaturated zone some high angle fractures with mineralised faces were found. The saturated hydraulic conductivity of the chalk matrix was in the range of 3 to 7×10^{-3} m/d in the upper 4-30 m of the borehole and declined with depth to 1×10^{-3} m/d. This implies that an infiltration capacity exceeding *c.* 3-7 mm/d over several days would be necessary to initiate fracture flow, neglecting the role of any soil layer, which is likely to attenuate rainfall.

The chalk in this area has the highest mean pore-size for UK chalk (0.65 µm) (Allen et al. 1997). Porosity values are in the range anticipated for this part of the Chalk ranging from 37.8 to 48.4% in the unsaturated zone with a mean of 41.8%. The high porosity means that vertical movement (V_m) through the matrix is likely to be low for the White Chalk (Equation 1). An annual potential average recharge (R) of 266 mm and the mean porosity (φ) suggest a rate of 0.64 m/year with a range of 0.38 to 0.79 m/year (**Error! Reference source not found.**):

$$V_m = R/\varphi \quad (1)$$

The NO_3 porewater profile displayed a large peak of 71.7 mg/L at 4.3 m below the surface, a low value of 28.3 mg/L at 6.8 m, a slow increase to 68.6 mg/L at 13 m, before a steady decline with depth to 50 m bd (Figure 4). Nevertheless, there are other notable transitory decreases in concentration at other depths, for example 25 m bd, which are concomitant with active fracture horizons (Table 2). The chloride profile showed a similar trend within the typical unsaturated zone (above 26 mbd), but the subsequent decrease with depth was less pronounced.

Borehole flow regime

Analysis of the optical image identified 14 potential inflows to Borehole B between 14 m and 26 m bd and a single marl band at 17 m bd (Table 2). Subsequent temperature and conductivity logs, and dilution tests suggest that 13 of these potential inflows actively contribute groundwater to the borehole (Figure 5). In particular, fractures at 20.3 and 25.5 m bd showed large dilution of the tracer within the borehole suggesting significant inflows.

The dilution tests highlight the predominance of downward flow from an inflow around 19 m bd to outflows at 24.3 and 25.5 m bd (Figure 5 D and E). A deeper point injection proved this downward flow continues to an outflow at around 60 m bd. Above 19 m bd, continued dilution of the tracer presumably results from multiple cross-flowing fractures. There was no evidence of a change in the hydraulic regime between dilution tests. Downward flow is likely to be seasonally persistent as a result of abstraction at the pumping station, which is located downgradient within the valley. There is no evidence of upward flows within the borehole.

3.2 Hydrograph analysis

Groundwater levels ranged between around 10 and 26 m bd, with considerable year-to-year variability (Figure 6).The rises during the winters of 2010/11 and 2011/12 were subdued due to low recharge. Thereafter, the considerable summer rainfall in 2012 produced significant summer recharge, and minimised soil moisture deficits before the onset of the main recharge season in October (Error! Reference source not found.). Consequently, the water table rose rapidly to the highest recorded level during the monitoring period by the end of December 2012.

The lag and magnitude of the water table response to precipitation events depends on their size and intensity, with examples shown in Figure 6, but the lag was always less than 15 days. Figure 7A shows a lag of around 12 days for two relatively low intensity precipitation events with changes limited to 0.2 m/d. Figure 7B illustrates a lag of around 5-10 days and response rate of up to 0.5 m/d to slightly higher intensity events in January. More interestingly, following this, the water table responded within 48 hours at a rate of 1.4 m/d, which subsequently decreased to 0.6 m/d after a further 24 hours. Figure 7C highlights the start of the 2012 recharge season with an initial series of events causing a response rate of only up to 0.5 m/d lagged by around 5-10 days. Subsequently, >100 mm of precipitation over 7 days resulted in a response rate of over 1.3 m/d for three successive days which rapidly declined to around 0.6 m/d within 48 hours. The lag between the peak in precipitation and maximum response rate was 48 hours.

In total, 16 events were identified which were indicative of persistent fracture flow. The rate of water table response declined within 72 hours of onset on all occasions, although subsequently the water table continued to rise more slowly in 14 instances. These events occurred across a range of unsaturated zone thicknesses and there does not appear to be any correlation.

3.3 Nitrate fluctuations at the water table

There is a general increase in NO_3 concentration as the water table rises, with similar interannual trends (Figure 8). There are frequent stepped increases in NO_3 concurrent with particular depths where fractures are present (Table 2). For example, at 24.3 m, 21.6 m and 20.3 m bd the concentration increases by between 5 and 10 mg/l between successive samples. On multiple occasions, these rises are followed by a subsequent decrease in concentration.

There are also transitory decreases in concentration, which tend to be less consistent with depth year-to-year, although the fracture at 18.2 m bd consistently supplies lower NO_3 water. The most significant decrease in NO_3 occurs within November 2012 at a depth of around 15.4 m bd where a cluster of seven samples were captured which were 20-40% more dilute than the surrounding groundwater. This was associated with the recharge event in Figure 7C. Other less significant decreases in concentration were around 20.9 m bd in 2011/12 and 16.4 m bd in 2009/10.

NO$_3$ concentrations within the porewaters show a similar trend to the groundwater concentrations with depth (Figure 8). However, actual concentrations are only similar below 24.5 m bd, around the typical annual groundwater level minimum. Above this, groundwater is generally more dilute, particularly between 24.5 and 20.0 m bd with dilution in the order of c. 20%. The frequently observed increases in groundwater NO$_3$ concentration at 24.3 and 21.6 m bd are also observed in the porewater data. After the steeped increase in groundwater NO$_3$ at 20.0 m bd, concentrations are generally elevated in respect to porewaters temporarily. It should be noted that porewaters were measured in 2006 and will have evolved in the intervening time, although vertical movement is only estimated to have occurred at an average of 0.64 m/year.

Groundwater NO$_3$ and chloride concentrations are well correlated ($r^2 = 0.91$), but there are variations in the ratio with depth (Figure 9). The ratio is reasonably constant below 20 m bd with a good correlation with the porewater ratio. However, between 20 and 15.5 m bd, the ratio is generally elevated in groundwater in every year. Above 14.5 m bd in 2009/10 the groundwater ratio is depleted due to high chloride concentrations. There is noticeable scatter in the data in 2012/13.

NO$_2$ was greater than 0.1 mg/L in 47 of 686 groundwater samples, with 9 of these samples collected in November 2012. There is no correlation between NO$_2$ and depth. Anomalous hydrogen phosphate was only detectable (>0.2 mg/L) on five occasions with no correlation with depth or significant recharge events.

4.   Discussion

4.1 Persistence of fracture flow from the surface during events

A rapid response to precipitation (frequently < 1 day) was identified on 16 occasions, which has been suggested to be a result of fracture flow which is persistent from the near surface (Ireson and Butler 2011, Ireson et al. 2012). Therefore it could be expected that recharge arriving at the water table would contain anomalous concentrations of nitrate at these times. This assumes that water flowing through the fractures does not rapidly and continually equilibrate with the matrix through diffusion. However this appears unlikely as, although the diffusive flux through chalk can be rapid over several hours if a sufficient concentration gradient exists (Gooddy et al. 2007), complete equilibration is unlikely within 24-48 hours.

Only a single event in November 2012 seemingly affected the concentration of NO$_3$ at the water table, with numerous dilute samples captured. This water could have originated from the near surface or have been released from the matrix higher within the chalk profile, where low concentrations were observed in the porewaters, and transported through the fracture network. However the presence of elevated nitrite, which can be relatively high in soils as an intermediary product of nitrification and denitrification (Burns et al. 1996), supports the theory of persistent fracture flow from the near surface. Nevertheless, it is possible there was a contribution from a fracture around a metre above the water table (14.3 m bd), but there are no other potential flowing features intersected by the open section of the borehole above this. Either way, the evidence suggests persistent fracture flow to a depth of 14-15 m bgl is possible following intense rainfall.

This event differed from all previous given the persistence and sheer volume of precipitation that fell beforehand: an unusually wet summer proceeded by 243 mm between 1st October and 24th November 2012. Therefore it was likely that suctions throughout the unsaturated zone remained low, permitting fracture flow following 41 mm of precipitation over 2 days. The persistence of fracture flow to a depth of 14-15 m has implications for the transport of

near surface chemical and biological contaminants to the water table with minimal attenuation.

4.2 Cause of rapid water table response

The rapid response of the water table to precipitation, yet no significant change in NO_3 concentration (with the exception of November 2012), suggests that fracture flow is unlikely to be the primary driver. Therefore, it should be considered that the response is usually a result of a piston displacement mechanism. In other words, because the matrix is at or close to saturation, a pressure wave can migrate through the unsaturated zone causing a reduction in suction and release of waters from the matrix just above the water table (Ireson et al. 2006).

This conceptualisation is further supported by estimating the characteristic time for diffusion through a matrix block (Barker, 1993):

$$t_{cb} = b^2 S_s / K_s \qquad (2)$$

Where: t_{cb} is the characteristic time for pressure diffusion, S_s is specific storage , K_s is saturated hydraulic conductivity. Defining b as 13-26 m, S_s as 1.5×10^{-5} m^{-1} (Chalk in southern Britain for a water table 0-30 m below the surface, Allen et al. 1997) and K_s as 6-8×10^{-3} m/d reveals a t_{cb} of 0.3-1.7 days. Therefore, rapid water tables responses of <48 hours can be explained via this mechanism.

4.3 Mechanisms of nitrate delivery to the water table

There is no clear trend of increasing NO_3 concentration at the water table between years, which would be expected as the stored NO_3 within the unsaturated zone migrates vertically. However, estimates of the rate of vertical movement are low (0.38 to 0.79 m/year) and the water table does not vary within the same range every year. Therefore, it is probable that sampling would need to extend for further years to provide evidence of this mechanism, which is already well established within the literature (Smith et al. 1970, Geake and Foster 1989, Chilton and Foster 1991)

NO_3 concentrations at the water table appear generally controlled by the presence of horizontal fractures in the unsaturated zone. As the water table rises to the elevation of the fracture, they appear to activate and modify the concentration. Certain deeper fractures (24.3, 21.6, 21.0 m bd) usually increase the concentration, where the porewater data also indicate higher concentrations within the matrix. This suggests that water held within the matrix is released into the adjacent fractures as the water table rises, i.e. piston displacement resulting in the flushing of stored NO_3.

Between 15.5 and 20 m bd, the N:Cl ratio of the groundwater is elevated with respect to the adjacent porewaters. Moreover, at 20 m bd groundwater nitrate concentrations exceed that of the porewater in three years. This is unlikely to be a result of the slow vertical migration of solutes through the matrix since the porewaters were analysed. Moreover, its year-to-year prevalence suggests it is unlikely to be a result of a fractured connection to alternative sources of NO_3 and chloride shallower within the profile. Therefore these observations suggest an alternative source of water, which is considered to be lateral flows within the unsaturated zone. With the lack of marl horizons, which have previously been considered the main driver (Gallagher et al. 2012, Rutter et al. 2012), mineralisation of fracture surfaces is considered to permit lateral flows.

Decreases in porewater nitrate concentration around some fractures, notably 25.5 m bd, indicate a diffusion gradient from the matrix into the fracture water can occur in places. This

could only be facilitated by more dilute water flowing through such fractures, at least, on occasions. Such a conceptualisation is corroborated by the capture of many groundwater samples that were more dilute than the adjacent porewaters. Therefore the question arises: how might apparently 'fresher' water flow through these fractures at depth?

It could be considered that the matrix and fractures are not in equilibrium due to the development of coatings on the fracture surface, which could retard water and solute exchange. Indeed, analysis of core at Twyford Down (51.040^{o}N, 1.310^{o}W), 3 km northwest of the study site, showed extensive mineralisation on hydraulically active fractures relating to clay complexes, calcite, and manganese hydr(oxides) (Shand and Bloomfield 1995). Furthermore, these coatings, which could remain wet throughout most the year, could also promote frequent persistent fracture flow through the unsaturated zone, whilst retarding diffusion, i.e. delivering fresher water that would dilute the bulk matrix signal. An alternative explanation is the lateral movement of lower nitrate waters from upgradient, although this is more unlikely given the extensive arable agriculture across the catchment.

There is no evidence of rapid fracture flow containing enhanced concentrations of NO_3. This suggests that the emergence of significant quantities of water from the matrix, higher within the unsaturated zone, or directly from the near surface, and rapid vertical transport through the fracture system without being re-absorbed in into the matrix is not a viable mechanism for recharge or solute transport in this location.

4.4 Application of a multi-level sampler

An array of techniques are available to investigate groundwater recharge (Scanlon et al. 2002). Chalk recharge studies are often limited to soil moisture and suction observations, combined with numerical modelling. Their conclusions regarding the varied contribution of fracture flow are then used to postulate over the vulnerability of the chalk to contamination. However, these studies do not conduct hydrochemical observations at the water table, which is a major limiting factor for inferring vulnerability, or indeed for understanding unsaturated zone processes. The multi-level sampler developed here provides a potential solution: allowing large numbers of samples to be obtained easily, economically, and from a known depth within the aquifer. However, the hydrogeological regime of the borehole must be established before deploying such a system to obtain ambient groundwater samples in a multi-layered or fractured aquifer.

In our study, the hydrogeological regime was assessed by undertaking multiple SBDTs which revealed the absence of significant upward flows within the borehole between 14.7 and 25.5 m bd. Thus, as the water table rises, samples should be obtained from new fractures as they are activated. This is confirmed by the stepped changes in NO_3 concentration at depths concurrent with fractures. Nevertheless, at intervals between fractures it is unclear if the hydrochemistry of the groundwater sampled represents that of: water flowing through the shallowest saturated fracture, water of the adjacent matrix, or a mixture of the two. There is no clear evidence of water entering the borehole from fractures several metres above the borehole.

The impacts of diffusive exchange between the water column within the borehole and the adjacent walls before the sample capture remain unquantified. However, during recharge events the rate of water level rise is typically at least 0.2 m/d, and given the likely small existing concentration gradient between the water column and borehole walls, diffusion is unlikely to significantly impact any interpretation.

5.   Conclusions

High temporal and spatial resolution groundwater sampling at the water table was undertaken to investigate NO_3 unsaturated zone processes. This was undertaken using a novel multi-level sampler which facilitated large numbers of samples to be obtained easily and economically. NO_3 concentrations increased as the water table rose during all five years, with a similar interannual trend with depth. Horizontal fractures exerted a strong control and frequently resulted in sudden increases of 5-10 mg/L where the water table rose to an elevation to activate a new fracture. This was considered to indicate piston displacement of matrix waters into adjacent fractures. There was also evidence of lateral flows within an unsaturated zone profile largely free of marl horizons, which have previously been considered the main process driver.

Recently, multiple studies have implicated that a rapid water table response following precipitation is indicative of persistent fracture flow through the Chalk unsaturated zone. However, on every occasion but one where this occurred, there was no resultant decrease in NO_3 (bypassing of rainwater through the unsaturated zone) or increase in NO_3 (leaching from higher within the unsaturated zone profile/soil zone). The water table response could be explained by piston displacement of porewater immediately above the water table. However, a single event in November 2012 resulted in dilute samples arriving at the water table, highlighting that persistent fracture flow following rainfall was possible to a depth of 14-15 m. This was attributed to heavy rainfall and wet antecedent conditions, including during the previous summer.

The majority of groundwater samples were depleted with respect to nitrate compared to the adjacent porewaters suggesting matrix waters are frequently diluted by a fresher source. This is considered to be a component of frequent persistent fracture flow from the near surface, not necessarily driven by intense rainfall events, which impacts the bulk composition of groundwater at the water table. A possible mechanism facilitating this is the widespread mineralisation on fracture surfaces which may retard both water and solute movement. Thus, the fracture system may allow water to flow, even when suctions are below that expected to trigger fracture flow, and prevent solutes in the matrix and fracture fully equilibrating.

The dominant mechanisms controlling NO_3 fluctuations in recharge are considered to be piston displacement and the flushing of NO_3 within the unsaturated zone by rising groundwater levels. The two processes will naturally be interlinked. With no evidence for changes in concentration with time, NO_3 removal from matrix storage appears insignificant, and it is therefore likely to pose a threat to groundwater supplies for decades to come.

Acknowledgements

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Table 1 Observed rainfall, simulated hydrological fluxes, and estimated vertical migration rate of NO$_3$ through the unsaturated zone (mm)

Period	Rainfall	Actual evaporation	Runoff	Δ soil storage	Potential recharge	Migration rate of NO$_3$
Apr 08 - Oct 08	459	420	23	-62	77	184
Oct 08 - Apr 09	414	96	21	43	254	608
Apr 09 - Oct 09	298	453	15	-171	0	0
Oct 09 - Apr 10	631	91	32	191	317	758
Apr 10 - Oct 10	230	371	12	-165	13	31
Oct 10 - Apr 11	419	87	21	150	160	383
Apr 11 - Oct 11	383	458	19	-94	0	0
Oct 11 - Apr12	300	111	15	82	92	220
Apr 12 - Oct 12	601	416	30	-26	181	433
Oct 12 - Dec 12	425	37	21	52	315	754
Hydrological year average	740	424	37	13	266	636

Table 2 Evidence for active fractures and their impact on NO₃ concentrations. I, D and - denote increase, decrease, and no data, respectively. A blank cell refers to no significant change.

Depth (m bd)	Optical televiewer analysis	TCME	SBDT	Change in NO$_3$ concentration				
				2008/9	2009/10	2010/11	2011/12	2012/13
14.3	Horizontal fracture	Minor	Not tested	-		-	-	
15.4	Sub-horizontal solution enhanced feature	Minor	No	-		-	-	D
15.9	Horizontal fracture	Minor	Minor	-	I	-	-	I
16.9	Horizontal fracture	Major	Minor		D	-	D	
17.8	Minor horizontal fracture	Minor	Minor		I	-	I	I
18.2	Horizontal fracture	Minor	Minor	D	D	-	D	-
19.0	Composite flint band	Minor	Minor	I	D	-	I	-
19.4	Horizontal open fracture	Minor	Minor			-	I	-
20.3	Sub-horizontal fracture with complex higher angle features	Minor	Major	I	I	I	I	-
21.0	Horizontal fracture, possible solution enhanced	Minor	No	-	I	I	I/D	-
21.6	Series of sub-horizontal minor fractures	No	No	-	I	I	I	-
24.3	Sub-horizontal solution enhanced feature	Major	Major	-	I	I	I	-
25.5	Sub-horizontal solution enhanced feature	Major	Major	-	-	-		-
25.7	Minor sub-horizontal fracture	No	Minor	-			-	-

Contains Ordnance Survey data © Crown copyright and database right 2013
NEXTMap Britain elevation data from Intermap Technologies

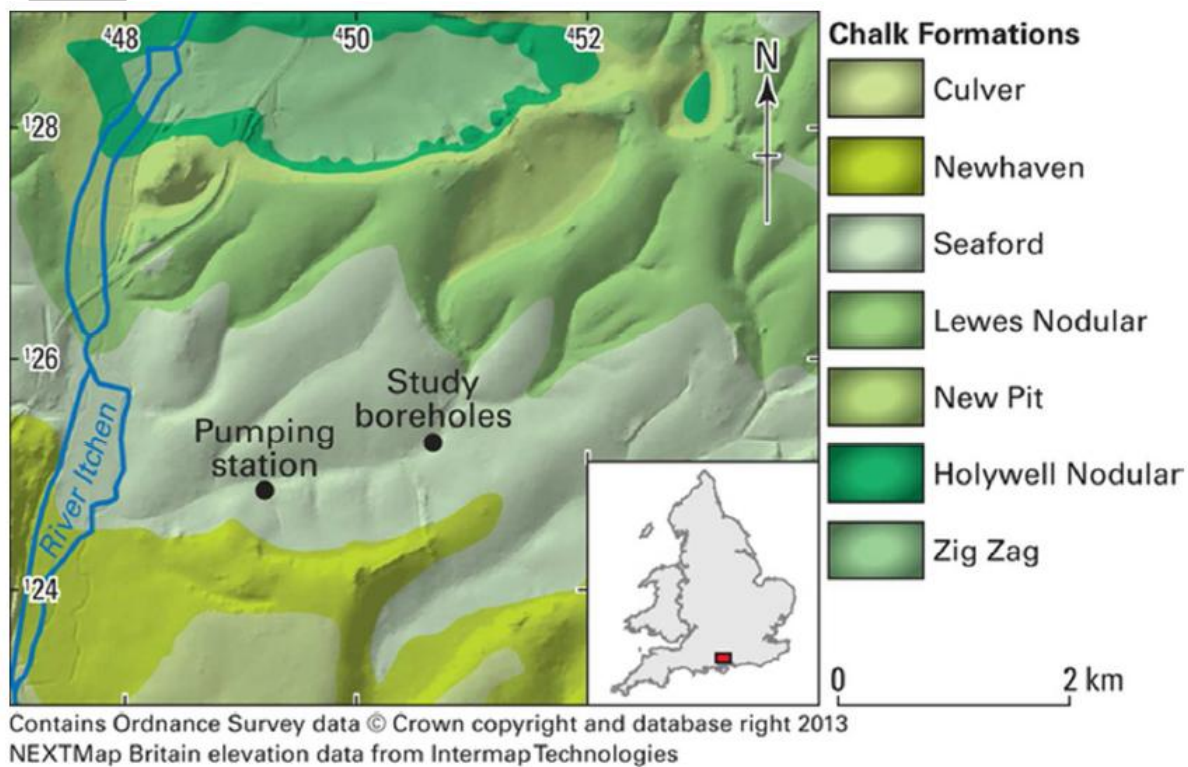**Figure 1 Study site setting**

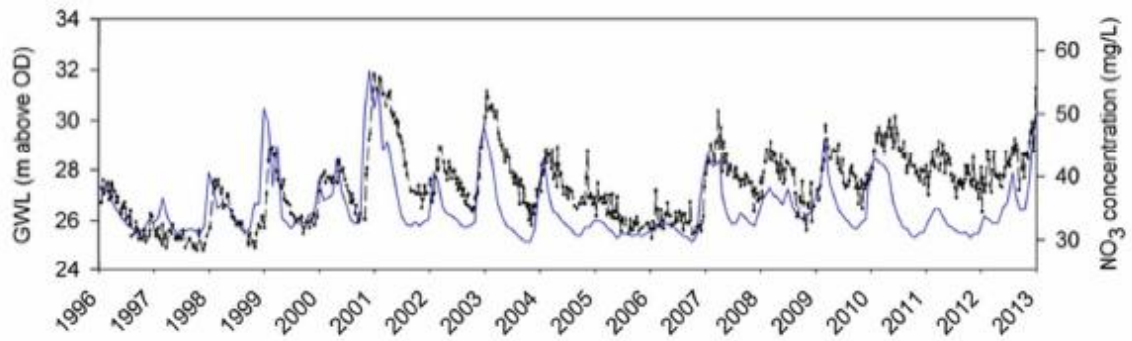**Figure 2 NO$_3$ concentrations at the pumping station (black) and water levels (blue) at a nearby Environment Agency monitoring borehole**

Rising water table ▽
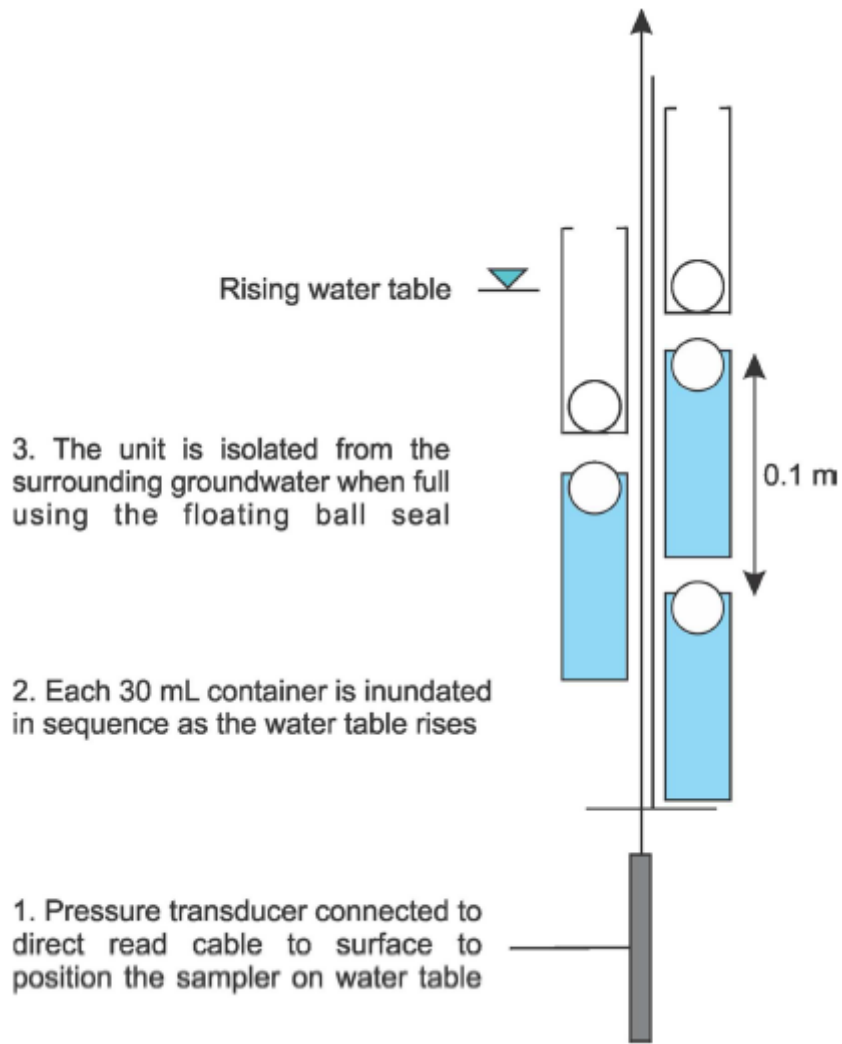
3. The unit is isolated from the surrounding groundwater when full using the floating ball seal

0.1 m

2. Each 30 mL container is inundated in sequence as the water table rises

1. Pressure transducer connected to direct read cable to surface to position the sampler on water table

Figure 3 Schematic diagram of multi-level sampler
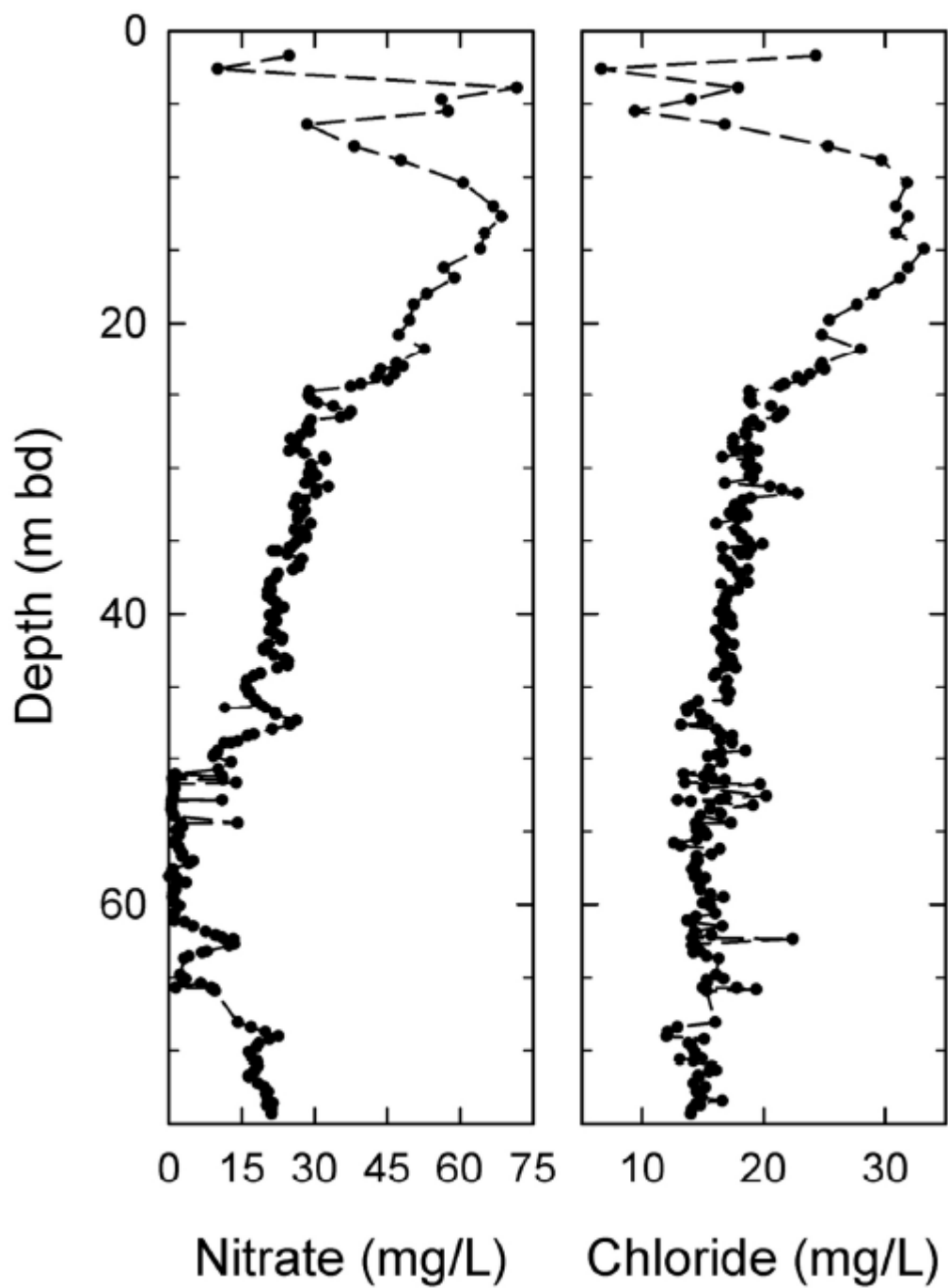
Figure 4 Porewater profiles of nitrate and chloride obtained from Borehole A in 2006
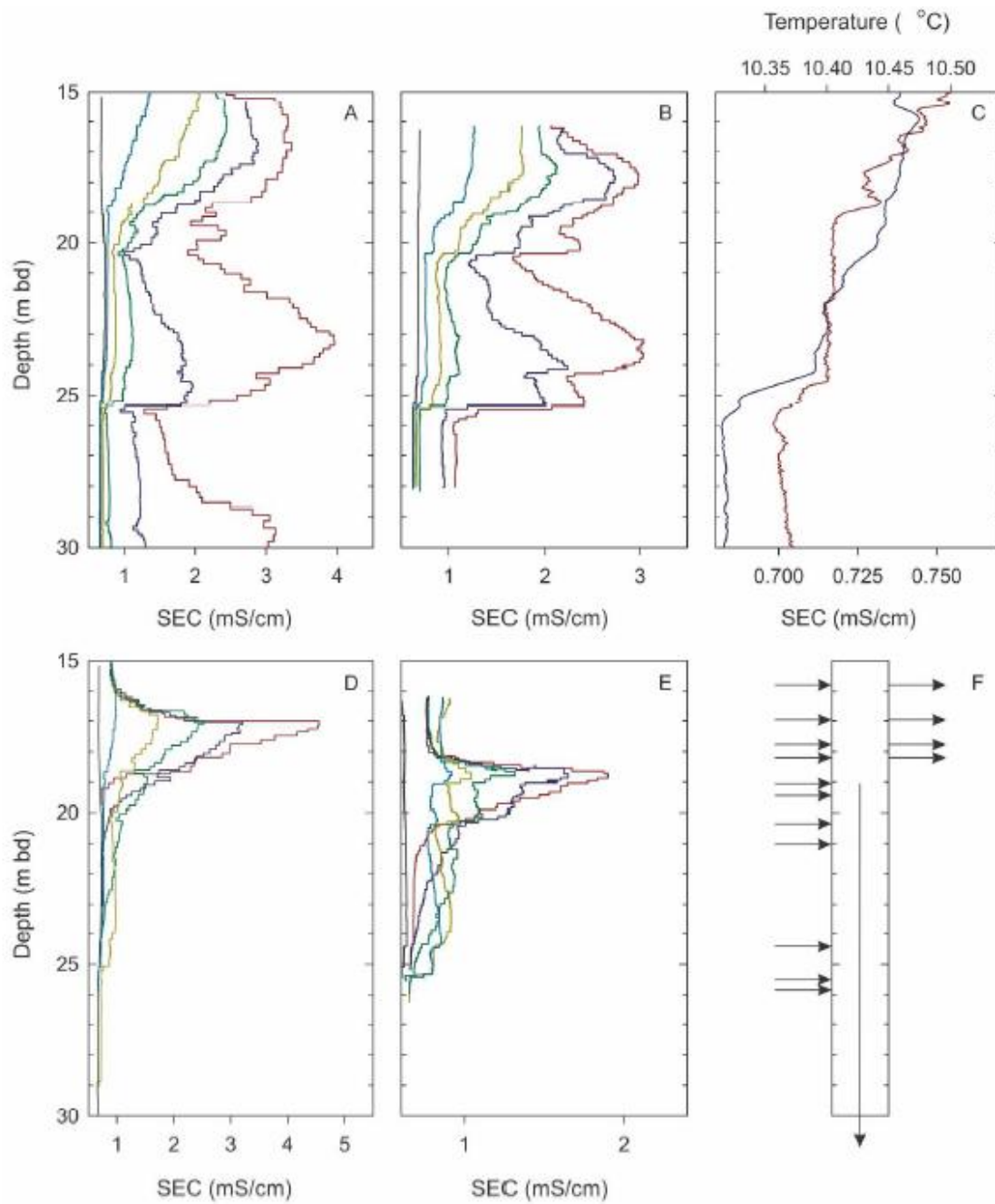
Figure 5 Characterisation of borehole flow regime (A) uniform SBDT in July 2012 at a water table depth of 16.2 m bd (B) uniform SBDT in April 2013 at a water table depth of 15.2 m bd (C) temperature (red) and SEC (blue) logs in March 2009 (D) point injection dilution test in April 2013 (E) point injection dilution test in July 2012 (F) interpretation
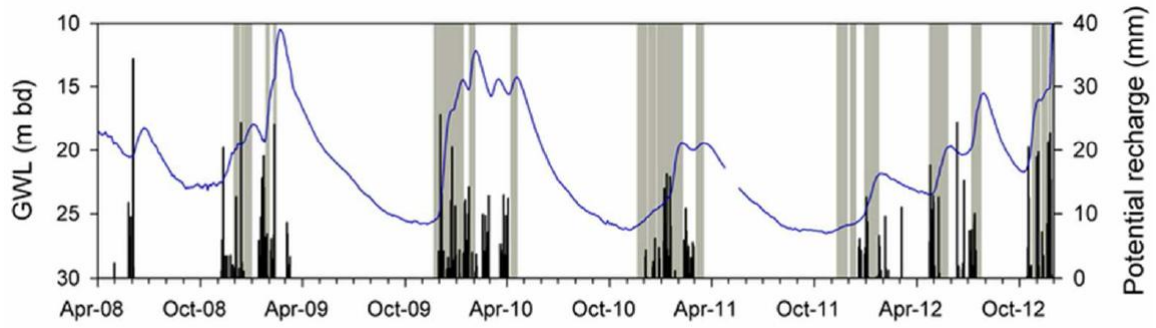
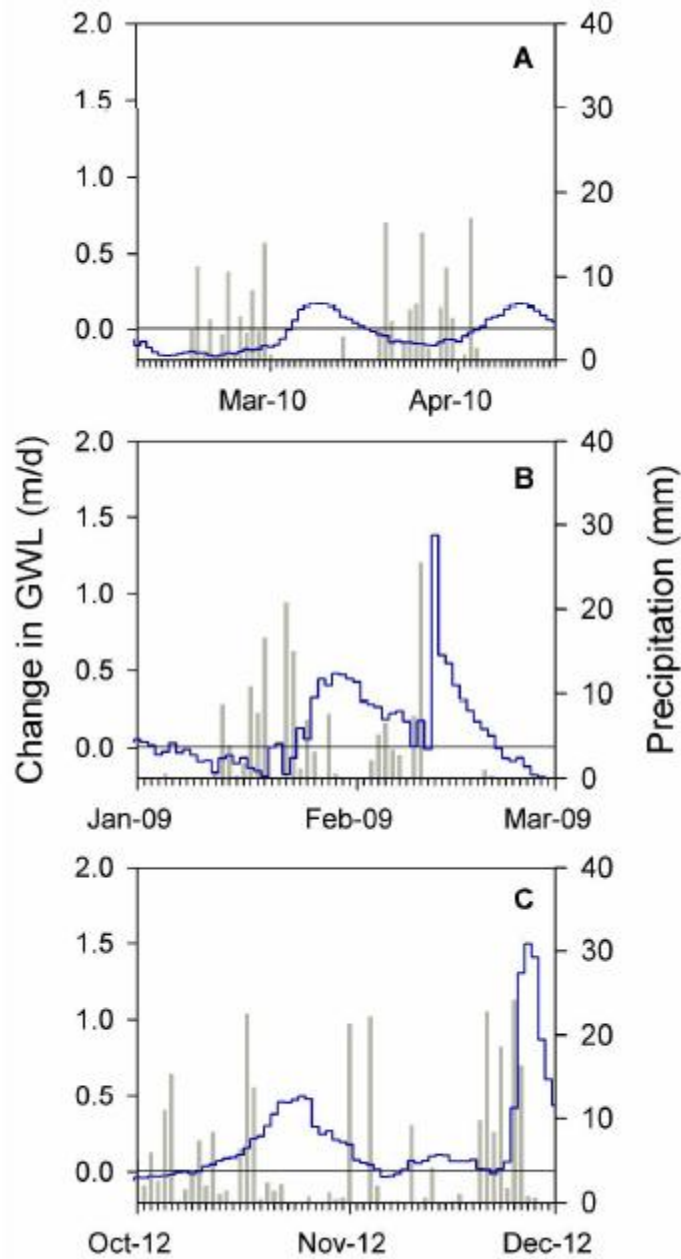**Figure 6 Groundwater hydrograph with simulated potential recharge. Greyed rising limbs indicate when samples were obtained**

Figure 7 Rate of water table response to precipitation (A) slow responses in 2009/10 at depths of around 15.5 m bd (B) slow and following rapid responses at depths of 19 m bd on 19/1/2009 and 14.4 m bd on 10/02/2009, respectively (C) slow and following rapid responses at depths of 21.8 m bd on 10/10/2012 and 14.6 m bd on 24/11/2012, respectively
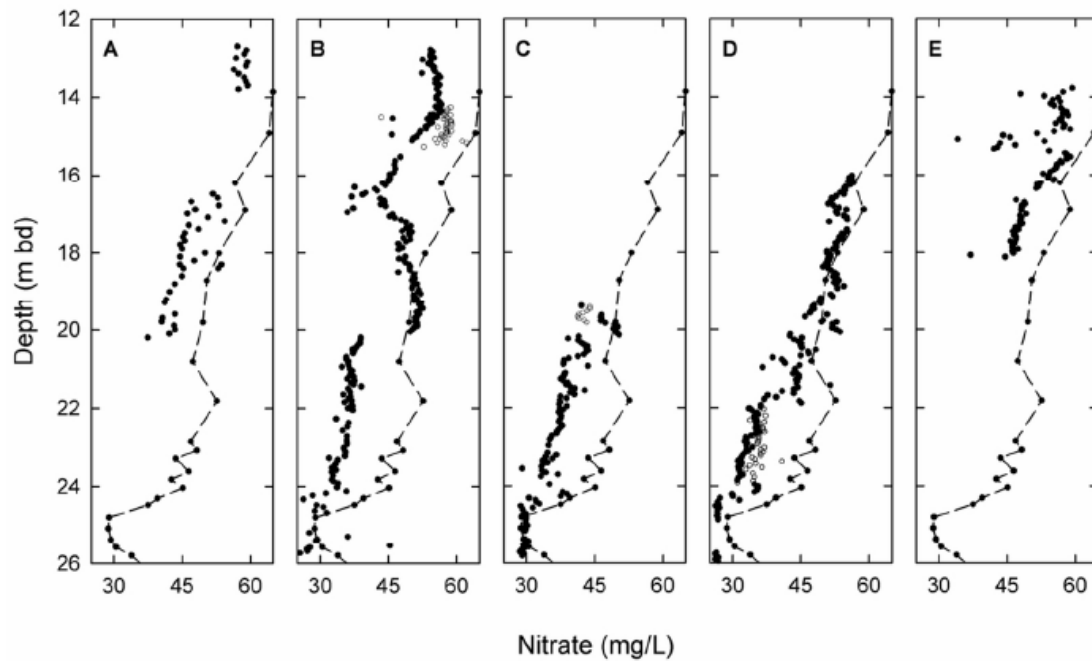
Figure 8 NO$_3$ concentration at the water table during five successive hydrological years (A) 2008/9 (B) 2009/10 (C) 2010/11 (D) 2011/12 (E) 2012/13. unfilled circles denote concentration after a fall and subsequent rise in water level to the same depth as the initial rise during the same hydrological year. Porewaters from 2006 shown as a reference.
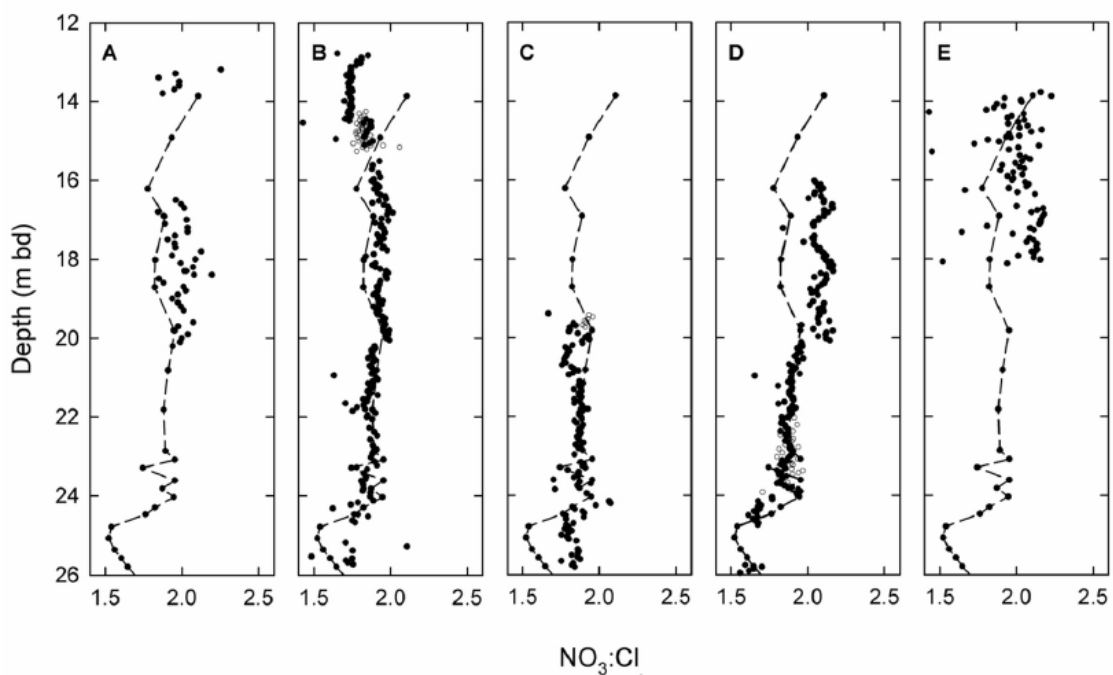
Figure 9 Ratio of NO$_3$ concentration to chloride concentration at the water table during five successive hydrological years (A) 2008/9 (B) 2009/10 (C) 2010/11 (D) 2011/12 (E) 2012/13. Unfilled circles denote concentration after a fall and subsequent rise in water level to the same depth as the initial rise during the same hydrological year. Porewaters from 2006 shown as a reference.