Investigation of rising nitrate concentrations in groundwater in the Eden Valley, Cumbria:

2. Unsaturated Zone Studies

Groundwater Systems and Water Quality
Commissioned Report OR/08/023N

Environment Agency Science Group
Project SC030113

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Investigation of Rising Nitrate Concentrations in Groundwater in the Eden Valley, Cumbria:

Catchment Water Quality Survey.

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View of research drilling in the Eden Valley looking west from near Penrith

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EXECUTIVE SUMMARY

This component Work Package of the Eden Valley Project was undertaken with the objective of estimating recharge rates and the timescale for water movement through the unsaturated zone where the Permo-Triassic sandstone aquifer is exposed at the surface (i.e. free of superficial deposits).

Given the inherent uncertainties and limitations associated with the various methods for estimating recharge, it was proposed to use three different and independent methods and to compare the results obtained.

The three methods proposed were:

(i) to date the pore water profile within the unsaturated zone using the historical tracer tritium

(ii) to date the pore water profile within the unsaturated zone using nitrate and chloride, released from the soil following the change in land-use from rough grazing to intensive pasture.

(iii) To estimate recharge using a soil moisture water balance approach.

The pore water profile data (needed for the tracer method for estimating recharge) was obtained from a cored borehole at a site to the east of Penrith where a deep unsaturated zone (c. 120m) was present. The site had a good record of land-use history which showed that a sudden change in landuse, from rough grazing to intensive grass pasture, occurred in 1976 and continued until the present. It was anticipated that this land use change would produce a recognisable ‘step change’ in pore water concentrations for both nitrate and chloride.

The reason for selecting a site with such a deep unsaturated zone was to maximise the likelihood that infiltration from c. 1962 (when tritium concentrations occurred) would be present in the unsaturated zone, the depth of penetration of the 1962 recharge was variously estimated to be between 80 and 160 m depth, depending on what recharge rate and what moisture content (for the sandstone) is assumed.

The borehole was drilled to a total depth of 122m in August 2004. The pore water chemistry results indicated that elevated nitrate and chloride concentrations, associated with 1976 recharge, had penetrated to about 100 m depth (this is equivalent to an average recharge rate of about 468 mm/y). The 1962 recharge is believed to have migrated below the water table and therefore tritium could not be used to ‘date’ the pore water profile within the unsaturated zone.

The average recharge (for the period 1976-present) was estimated using the soil moisture water balance (deficit) approach, to be 368-424 mm/y depending on the value of the ‘root constant’ selected and rainfall monitoring station data applied. This is equivalent to a depth of penetration of between 79 and 90 m for the 1976 recharge. The higher recharge rate (or deeper penetration depth of the 1978 recharge) is preferred for estimating recharge at this site because this was based on data from the nearest rain gauge (at a site at a similar elevation to that at the drillsite). The rainfall data at this latter gauge was c. 6% higher than the main rainfall monitoring station in Penrith (which had a longer monitoring record).

The average recharge rate is therefore likely to be in the range 424-468 mm/y and the rate of water movement through the unsaturated zone is c. 3.5-3.85 m/y. Based on this estimate of water movement in the unsaturated zone, the travel time for recharge to migrate from the soil to the water table (or the delay imposed by the unsaturated zone) over the highest ground (where unsaturated zone thickness can be in excess of 175m) the travel times could exceed 50 years. However, over large areas of the Eden valley, the recharge currently arriving at the water table is of post 1990 origin. Thus an important conclusion is that, over most of the Eden valley, nitrate concentrations arriving at the water table are unlikely to substantially increase. This does not mean of course that nitrate concentrations will not increase at abstraction boreholes (or in the baseflow to the streams). Indeed, it is anticipated that nitrate concentrations at groundwater outflows will continue to rise until most of the pre 1990 origin recharge has been flushed out; this is likely to take many decades.

Similar possibly slightly slower rates of water movement through the unsaturated zone may be anticipated where thin (<2m) but relatively permeable cover overlies the sandstone. Where the superficial cover exceeds 2m thick, and especially where it is clay-rich, recharge rates may be significantly reduced. The influence of the lithology and thickness of superficial cover on recharge rates is an important issue and one that needs to be investigated at a later stage.

Of interest, although not directly relevant to the objectives of this Work Package is that the pore water of the unsaturated zone had a different water chemistry to the groundwater in the saturated zone. The former are of mixed ionic composition with low bicarbonate concentrations whilst the latter are a Ca-HCO_3 type water. This suggests that any carbonate cement that may have been present in the unsaturated zone has been removed; a process which will have modified the porosity and permeability of the aquifer and which would have been enhanced by acid rain deposition.

1. INTRODUCTION

1.1 Project objectives

The objectives of the project ‘Investigation of Rising Nitrate Concentrations in Groundwater in the Eden Valley’ are to identify the causes of rising nitrate concentrations in groundwater in the Permo-Triassic sandstone aquifer of the Eden Valley area and to gain a better understanding of the groundwater and surface water flow system. This includes identifying the sources of the nitrate contamination and the processes controlling nitrate movement, so that possible management options for reversing this trend can be considered.

The main objectives of this Work Package (Work Package 2 “Estimating the nitrate flux through the unsaturated zone”) are to estimate rates of recharge to the Permo-Triassic sandstone aquifer (and rates of water movement through the unsaturated zone) where these sandstones are exposed at the surface (i.e. free of superficial deposits) in the Eden Valley, Cumbria. An estimate of recharge rates and unsaturated zone travel times are required when attempting to model the movement of water and solutes from the soil zone through the subsurface to aquifer outflows (e.g. abstraction boreholes or groundwater baseflow to streams).

This report considers ‘direct recharge’ only, that is water added to the groundwater reservoir, in excess of soil moisture deficits and evapotranspiration, by direct vertical percolation through the vadose zone (Lerner 1990). This report does not consider recharge to the Permo-Triassic sandstone aquifer where it occurs as (i) subsurface flow from adjacent permeable rocks, (ii) leakage from surface water bodies or (iii) recharge through superficial deposits. The latter issue, which is known to be important in the Eden Valley, is dealt with later in this project as part of Work Package 4.

The Eden Valley (Figure 1) lies between two upland areas; the Pennines to the east and the Lake District to the west. It is aligned approximately northwest-southeast, is 56 km long and varies in width from 5 to 15 km. Much of the valley is underlain by Permo-Triassic sandstone, which forms the major aquifer in the region. Approximately 20% of the sandstone outcrop is free of superficial deposits. The remainder is covered by various superficial deposits, including Till (dominant), glacial sands and gravels and river alluvium. The superficial cover is generally thin; comprising Till deposits, less than 2m thick, which occur over 60% of the bedrock. Deposits are thicker around Appleby and also to the west of Brough where a distinctive “hummocky” topography with mounds in excess of 30m of relief can be identified (Humpage 2005). The till is variable in composition but can be surprisingly sandy and therefore potentially permeable. The water table is relatively deep over most of the Eden Valley and, in areas free of superficial deposits, virtually all the water that passes below the root zone can be assumed to continue downwards to the water table. Nevertheless, given the large area of outcrop that is covered by thin superficial deposits, the influence of these deposits on recharge rates is of crucial importance and is an issue which will be addressed later by this project.

Agriculture has modified the quality of recharge water and has resulted in elevated concentrations of nitrate in pumped groundwater from some boreholes in the sandstone aquifer (Butcher et al. 2005). Specific questions that this project seeks to answer are i) what is the distribution of nitrate in the subsurface? ii) how long does it take for recharge to migrate from the soil zone to the various groundwater outflows? and iii) does this observed distribution of nitrate agree with modelled predictions? Estimating recharge rates, and their spatial distribution is a crucial first step.

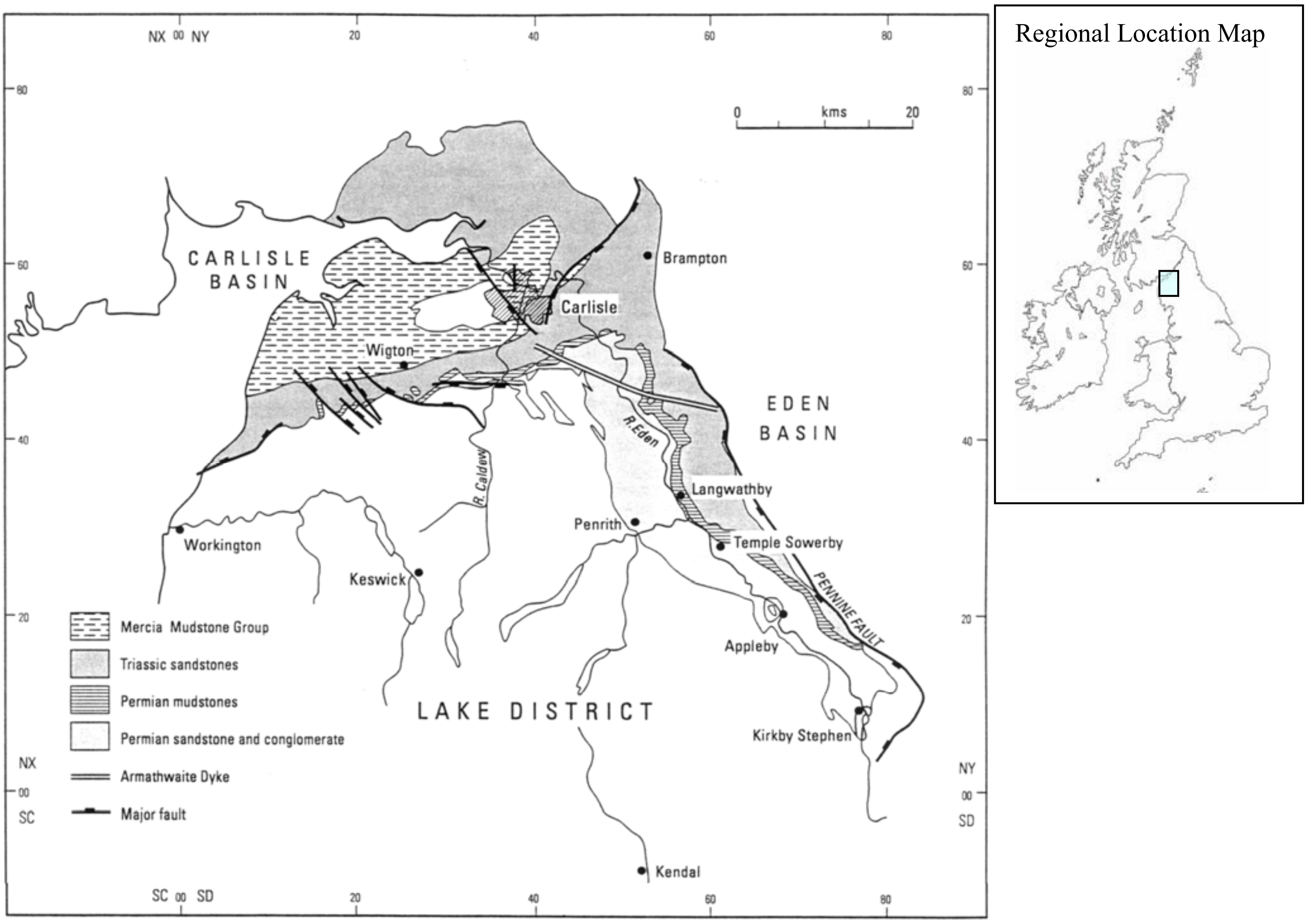

Figure 1. Location map of the Eden Valley

1.2 Recharge estimation

A 'piston flow' mechanism for recharge is assumed for the Permo-Triassic sandstones. Recharge moves down through the unsaturated zone in a series of discrete layers; the addition of recharge at the base of the soil zone pushes an equal volume of water in the layer immediately below until water in the last layer of the unsaturated zone is added to the saturated zone (Kruseman GP 1997).

Various techniques are available to quantify recharge and choosing the appropriate technique requires consideration of the ease and reliability of data collection, an understanding of the recharge processes and the purpose of the recharge estimation. In general it is often helpful to use several independent techniques and to compare results using these difference techniques. Significant differences in recharge estimates between these methods may indicate poor initial conceptualisation or errors in data collection/ analysis.

1.2.1 Understanding recharge processes

In humid regions it is generally assumed that recharge occurs when there is an excess of water available from rainfall after taking the runoff, potential evaporation and the soil moisture deficit into account.

Runoff occurs instantly after rainfall, the quantity depending on soil conditions, rainfall intensity and land slope. The actual evapotranspiration may be different to the potential evaporation when there is limited soil moisture and will vary with soil type, crop type and growth.

Once below the root zone, recharge will not be affected by evapotranspiration and, in the absence of near surface deposits of low permeability, will continue to move vertically downwards to the water table. However, poorly- permeable layers within the sandstones may produce temporary perched water tables and, as a consequence some lateral flow. The significance of this to recharge, at the catchment scale, is probably small but will depend on the vertical hydraulic conductivity and lateral extent of the layer.

1.2.2 Recharge estimation techniques (unsaturated zone)

Various methods based on unsaturated zone studies can be used to estimate recharge (Lerner et al 1990, Scanlon et al 2002). For this study, 2 methods were proposed, based on the ease of data collection and simplicity and reliability of analysis. These are:

Soil moisture balance method. This method has proved to be reliable for estimating recharge in British aquifers over many years (Rushton and Ward 1979). Two widely used approaches are applied; the first is based on the work of Penman (1948) and Grindley (1967), while the second approach is based on the work of Allen et al (1998). Both approaches use data and information which is commonly available. The details of these are given in 2.2 of this report.

Historical environmental tracer method. This method uses tracers, which have been released to recharge (as a result of human activities) to 'date' the water moving down through the unsaturated zone. It is essential that the tracer represents 'an event' rather than a gradual build-up over time. The use of historical tracers to estimate groundwater recharge is not uncommon (Phillips et al. 1988; Scanlon 1992: Cook et al. 1994). Tracers that were considered to be potentially useful for dating recharge moving through the unsaturated zone in the Eden Valley were (a) tritium and (b) nitrate (and chloride).

TRITIUM

Tritium, which is an isotope of hydrogen, was released into the atmosphere following nuclear testing in the late 1950s and early 1960s. Peak concentrations of tritium occurred in rainfall during 1962/63 and these peak concentrations have been widely used for dating ground waters, especially in the unsaturated zone (Foster & Smith-Carrington 1980). Some decline in the 1962/63 peak concentrations will have occurred principally because of radioactive decay (½ life = 12 years) and the elapsed time (c. 50 yrs) nevertheless, a clearly defined peak corresponding to 1962/63 recharge can be anticipated (pers. comm. B Smith). The main disadvantage of tritium is that recharge associated with 1962/63 infiltration will have migrated beyond the water table by now in most areas.

NITRATE

Nitrate has been released in increasing quantities to recharge from agricultural soils following the intensification of farming in the 1960s and 1970s. In general, nitrate released from agricultural soils is a poor tracer because the increase in nitrate concentrations with time has been gradual. However, where land-use practices produced a 'step-change' in the nitrate concentrations released (e.g. from rough grazing to intensive cropping) then the use of nitrate as a tracer may be appropriate.

CHLORIDE

Chloride is present in many fertilisers and in animal slurry and therefore is potentially an useful tracer (Edmunds and Gaye 1994, Gates et al 2008).

1.2.3 Site selection

In order to estimate the depth of penetration of the historical tracers, a cored borehole is required to determine the porewater depth profile. The site for the cored borehole had to meet the following criteria:

- Permo-Triassic sandstone should outcrop with no/minimal drift cover.
- A deep unsaturated zone should exist (so that 1962/63 recharge may be present above the water table).
- A good record of land use history exists which shows a rapid and major land use change capable of producing a 'step change' in the concentrations of nitrate being leached from the soil.

A suitable site was identified near Penrith (map and cross-section). The site was underlain by Permo-Triassic sandstone and no superficial deposits were mapped. The adjacent drift-covered areas occupied lower ground and so runoff recharge from these covered areas onto the borehole site was not an issue.

The depth to water table was estimated to be about 120 m (Figure 2). It was considered possible that 1962/63 recharge might be present in the unsaturated zone as the depth to 1962/63 recharge was estimated to be between 80 and 160 m (depending on the recharge rate and the moisture content of the unsaturated sandstone assumed). At this site, there was a sudden and major land use change in 1976. Prior to that date, the land use was unfertilised grass with bracken and it was assumed that little nitrogen was leached from the soil. In 1976 the farmer sprayed the field to remove the bracken and significant quantities of nitrogen fertiliser were applied (250 kgN/ha/a). In 1982, following the construction of a gas pipeline, the field was levelled for more intensive use and the improved grass pasture was heavily fertilised with both slurry and chemical fertilisers. Procter and Metcalfe (2005) present details of land use changes and estimates of the quantities of fertiliser and slurry applied to the field; their report is included in Appendix 3

1.2.4 Land use and potential sources of groundwater nitrate

The Eden Valley is largely rural with a low population density of about 0.2 persons/ha. Livestock rearing is the main agricultural activity; in recent years the improvement of grasslands, cereal cropping and higher stocking densities have resulted in greater applications of fertilisers to grassland and fodder crops. The spreading of slurry wastes on grassland has increased, sometimes contravening Codes of Good Agricultural Practice, e.g for the Protection of Water, 'The Water Code' (MAFF 1998). Both the timing and quantities applied are more dictated by the need to dispose of the slurry than to meet the crops nutrient needs. However, within the Eden catchment there are also significant areas of semi-natural habitat including unimproved grassland and woodland.

Figure 3 indicates the estimated concentration of nitrate in hydrologically effective rainfall (HER), 'excess rainfall' (Lord and Anthony 2000), across the Eden Valley catchment, 2000 (where the sandstone is present at outcrop this would effectively equate to the nitrate concentration in recharge). These figures were produced by ADAS from the National Environment and Agricultural Pollution Nitrate (NEAP-N) framework model (Anthony et al, 1996 and Lord and Anthony, 2000) developed to predict nitrate leaching through the base of the soil zones. It can be seen that the amount of excess nitrate available for leaching is generally higher in the central and the northern part of the valley. This has increased since estimated values in 1970 (see Butcher et al 2005).

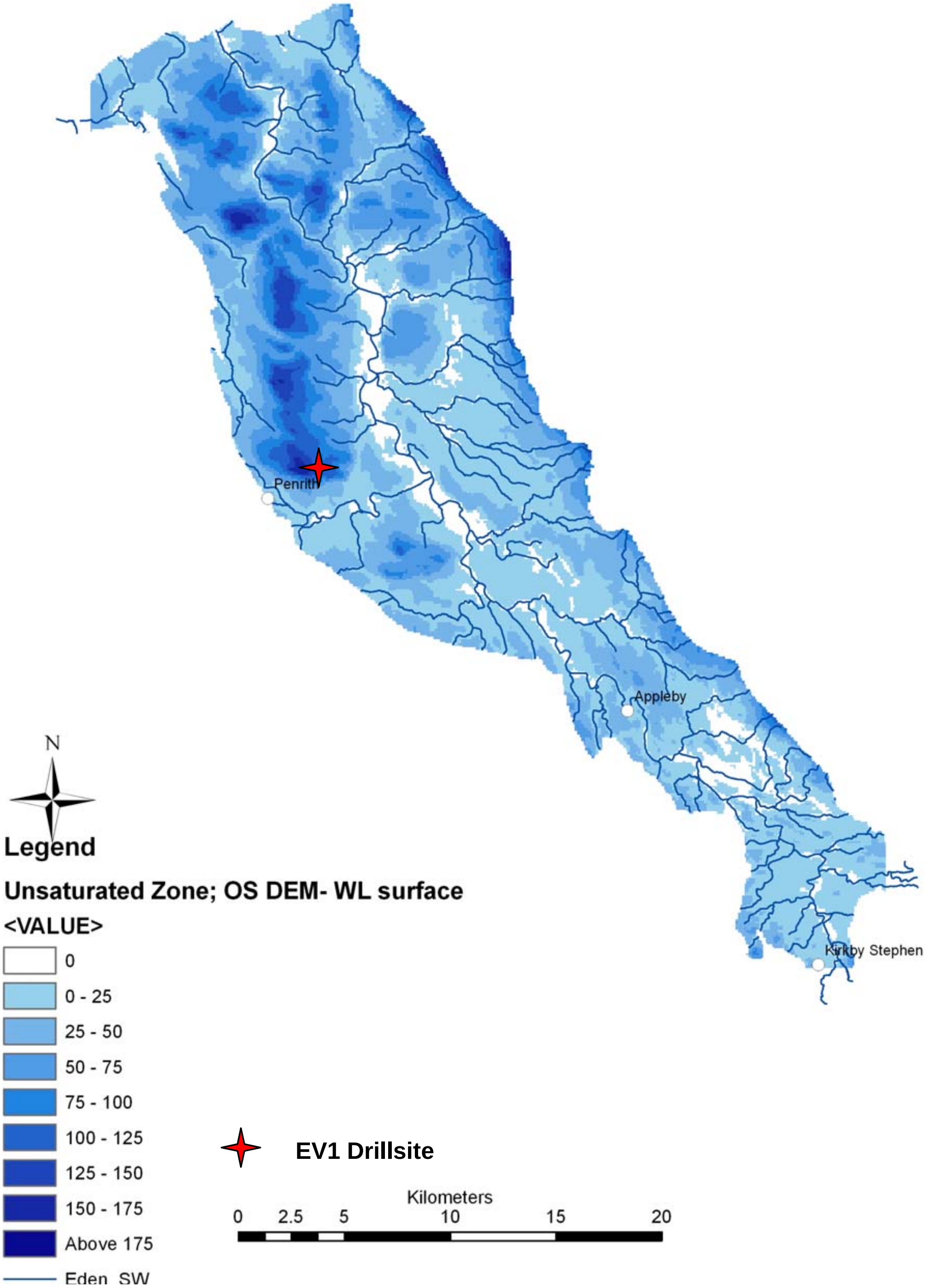

Figure 2. Modelled unsaturated zone thickness: depth to water table

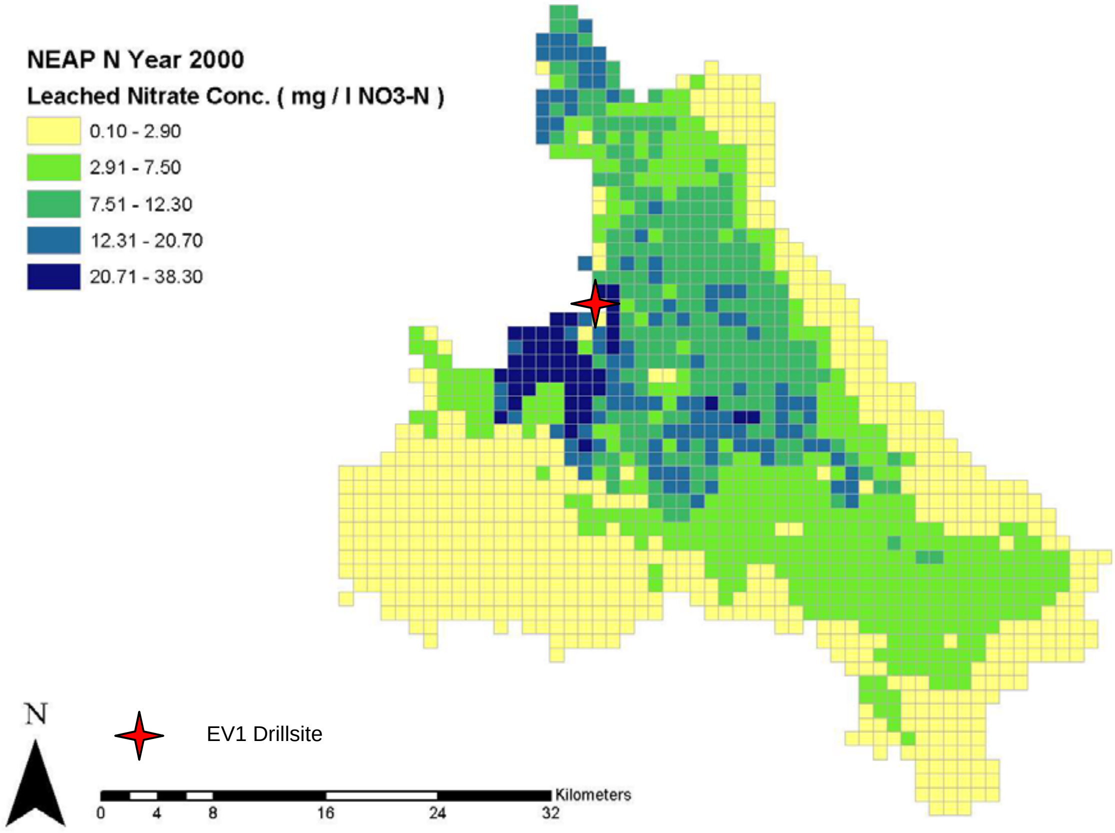

Figure 3. Estimated concentration of nitrate available as mg/l N in recharge across the Eden Valley catchment for the year 2000

In the Eden Valley, slurry is widely disposed of to grass pasture and in places at rates in excess of crop nutrient requirements. Rates of nitrogen application in excess of 200 kg N/ha/y are common. Leaching from these intensively cropped (mainly grass) fields is therefore considered to be the most likely source of the nitrate found in groundwater in the sandstone aquifer.

For large abstraction boreholes, slurry pits represent a relatively small point source of nitrogen within a large groundwater catchment and thus there is considerable potential for dilution (Gooddy et al, 2001). Thus high yielding abstraction boreholes provide an integrated sample of water recharged over the borehole catchment. The potential for contamination of low yielding farm boreholes from localised point source contamination is however much greater because of their smaller groundwater catchments, as they permit only limited dilution and can be skewed by local sources of contamination.

2. METHODS

2.1 Tracer method for estimating recharge

2.1.1 Field programme

The purpose of the drilling was to obtain core with as little disturbance as possible. This core was sub-sampled to a prioritised regime (**Table 1**) to obtain pore water chemistry (major ions, including nitrate and chloride; tritium) and the physical characteristics of the rock (moisture content, porosity and permeability).

Rotary coring using airflush was selected as the preferred drilling method to ensure minimum contamination of the pore waters in the rock core. Where drilling could only proceed with the addition of a fluid, a water-foam mix was used. Samples of the water and water foam mixture used were taken for chemical analysis to help, (a) identify depth intervals where the pore waters were contaminated (and the degree of contamination) and (b) assess which water chemistry parameters were unaffected by the addition of water-foam. The use of water-foam for drilling was kept to a minimum.

Drilling continued successfully down to a depth of 122 m below casing top (bct): the total length of core recovered was to 119m bct. This was coincident with the expected position of the water table. At this depth, it is thought that wet drill cuttings seized the core barrel in the borehole and this was not recovered. Drill rods were recovered and the borehole was back-filled with a bentonite and cement grout mixture to 1m below the surface of the field.

The diameter of the core recovered was c. 100mm which provides sufficient pore water (by centrifugation) to satisfy laboratory requirements (c. 2 ml per cm of core length). The core was obtained using ‘Geobore S’ 102mm core barrel with plastic sleeve lining.

The core was geologically logged at a field laboratory using BS5930 : Code of Practice for site investigations, (British Standards Institution 1999). Lithology, fractures, colour were noted and percentage core recovery.

The core was then sub-sampled, as described in. Samples of complete core of approximately 50 cm length were selected for tritium analysis. These samples were wrapped in foil and cling film and then sealed in labelled plastic bags and stored in a refrigerator. Samples for physical characterisation were selected and sealed in labelled plastic bags. Samples for moisture content determinations were sub-sampled, weighed, crushed and placed in an oven for 24 hours prior to re-weighing. Moisture content was expressed as the weight of water per weight of wet rock. This was then converted to moisture content per unit volume of wet rock.[1]

Samples of core for porewater major ion analysis were selected and the outer edges of the core, which are more susceptible to disturbance/contamination, were removed. The inner portion of the core was crushed, weighed and packed into centrifuge buckets. These were then placed in a Beckman J2 21Centrifuge and spun at 14000 rpm for about 40 minutes. The centrifuged porewater samples were filtered, on-site pH, SEC and HCO_3 determined and then samples were split for subsequent analyses with a proportion acidified by 1% nitric acid. The samples were stored in a refrigerator at the field laboratory and then transported to BGS hydrochemical laboratories at Wallingford for analysis.

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[1] This was estimated assuming a grain density of 2.65 and an average porosity of 25%.

Figure 4. EV1 Drillsite field looking west and showing typical use prior to drilling.

Figure 5. EV1 Drillsite looking east over Eden Valley floodplain towards Pennine uplands.

Figure 6. EV1 Drillsite looking west towards plantation, golf course and Penrith.

Figure 7. Recovering core material.

Figure 8. Inserting core barrel

Figure 9. Encountering 'moist' rock at c. 76m.

Table 1. Sampling regime for drilled core

Priority	Requirement	Sampling Interval	Sample Size	Sample Handling
1	Centrifuging of porewater	Every metre on the metre. Extra samples at obvious changes in lithology	Sufficient to provide required amount of porewater (see table above), dependant on saturation	Process as soon as possible. Store pending samples (bagged and heat sealed) in fridge until processed. Return residue to core run.
2	Moisture content	As above, plus c.20 extra samples to cover range of lithologies	Regular = c.100 gm Extra = c.30gm lump from uncentrifuged sample	As above
3	Tritium Analysis	GL to 50mbgl, every 5m. 50mbgl to TD, every 2m	Stick of core c.0.50m long	Store (foil wrapped, bagged and heat sealed) in fridge until transported to Wallingford
4	Aquifer Properties	Every 2m from GL to TD	Stick of core c.0.30-0.50m long	Store (bagged, heat sealed or taped) until transported to Wallingford
5	“Alternate samples“	Every 2m from GL to TD, alternating with AP samples above	Stick of core c.0.30-0.50m long	Store (bagged, heat sealed or taped) until transported to Wallingford
6	“Additional detailed sampling”	Three to be chosen between (say): 10 and 20m 60 and 70m 100 and 120m	Complete c.2m between centrifuge samples.	Store (bagged and heat sealed) in fridge until transported to Wallingford
7	Geochemical Samples	Selected number – to be advised	Can be spun residue from centrifuging	Store (bagged and heat sealed).

2.1.2 *Laboratory programme*

WATER CHEMISTRY

Porewater concentrations of Cl, NO_2-N, TON and NH_4-N were determined by automated colourimetry using a Skalar SAN^{++} Analyzer. The samples were filtered through a 0.45µm filter but were not acidified. HCO_3 pH, and SEC were determined in the field laboratory by mobile field metres and titration.

Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to determine 27 analytes (**Table 2**). Total concentrations of each element are determined irrespective of different oxidation states. Concentration ranges and detection limits vary for different elements and analyte wavelengths vary with concentration. Samples were acidified with 1 % nitric acid prior to analysis and a minimum volume of 20 ml is usually required for routine analysis. In exceptional circumstances, such as with low volume pore-waters, 5-10 ml is adequate. Some samples were also analysed by ion chromatography to establish whether all the sulphur determined by the ICP-OES method is attributable to the sulphate ion.

Table 2. Analytes for EV1 borehole hydrochemical analysis of porewater samples

Determinands	**Test Method**
Determination of the major and minor cations (27 elements: Ca, K, Mg, Na, S (as SO_4, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, La, Li, Mn, Mo, Ni, P, Pb, Si, Sr, V, Y and Zn	ICP-OES
Determination of major anions Cl, SO_4, NO_3, NO_2, F, PO_4	Ion chromatography
Determination of inorganic nitrogen species	Automated colorimetry
Total iodide	Colorimetry analysis
Dissolved organic carbon	OC analyser

The recovered pore water was filtered and split, one portion being preserved with 1% nitric acid. The unacidified sample was analysed for alkalinity and conductivity immediately by potentiometric titration, and then the samples were collated for the following laboratory analyses:

PHYSICAL CHARACTERISATION

Samples selected for physical characterisation (porosity, permeability determination) were sub-sampled by drilling c. 25mm diameter core plugs in vertical and horizontal orientations. These were oven dried for a minimum of 24 hours prior to testing for porosity, vertical and horizontal permeability.

PERMEABILITY

Gas permeability tests were performed on samples under steady-state conditions using a pressurised coreholder. A full description of the methodology and discussion of the correlation between gas and liquid permeability in sandstones can be found in Bloomfield and Williams (1995).

In the standard test, samples are constrained in a core holder and a pressure-regulated supply of nitrogen gas was applied to one end of the sample (the downstream end of the sample was held at atmospheric pressure). A soap-foam flow meter was used to measure the outflow of nitrogen from the downstream end of the sample. Gas permeability was calculated using the measured sample dimensions, differential pressure, and the steady-state gas flow rate as follows:

$$k_g = \mu\ Q\ L\ P_o/[A\ (P_i^2-P_o^2)]$$

where k_g is gas permeability, μ is gas viscosity, Q is the volumetric gas flow rate measured at atmospheric pressure, L and A are the sample length and area respectively, P_o is the downstream (atmospheric) pressure, and P_i is given by $P_i = P_o + P_g$, where P_g is the absolute pressure of the regulated nitrogen permeant. The effective errors associated with the gas permeability measurements are about +/- 2.5% of measured sample permeability.

POROSITY

Porosity (and bulk and grain density) were measured using a liquid resaturation method based on the Archimedes principal. The methodology is described in detail in Bloomfield et al. (1995). A sample to be tested is weighed and then placed in a resaturation jar. The jar is evacuated then flooded with propanol. Propanol is used as it is relatively inert with respect to the core and reduces the potential for swelling clays to modify the porosity during testing. The sample is allowed to saturate for at least 24 hours. The saturated sample is then weighed, firstly immersed in the propanol and then, still saturated with propanol, in air. For each sample its dry weight (w), its propanol saturated weight in air (S_1) and its saturated weight immersed in propanol (S_2) are recorded, in addition the density of the propanol (ρ_f) is noted. From these values sample dry bulk density (ρ_b), grain density (ρ_g) and effective porosity (ϕ) can be calculated as follows:

$$\rho_b = (w\rho_f)/(S_1-S_2)\ \text{g cm}^{-3}$$

$$\rho_g = (w\rho_f)/(w-S_2)\ \ \text{g cm}^{-3}$$

$$\phi\ = (S_1-w)/(S_1-S_2)$$

The effective errors on the porosity measurements are approximately ± 0.5 porosity percent.

The data is presented as depth profiles of physical characteristics and water quality with depth.

2.2 Soil-moisture water-balance approach for estimating recharge

The aim of the modelling was to undertake a single point recharge calculation for an approximate recharge estimation. No rivers and runoff routing are considered, one landuse type is specified and rainfall and evaporation data recorded at one raingauge station (Penrith Water Treatment Works (id 12999), are used. However, rainfall data for a more limited period was recorded at a second gauge station (Penrith Cemetry (id 12965)) closer, and of a similar elevation to the borehole site. Comparison of the rainfall data (derived from Met Office MIDAS database) between Penrith Water Treatment Works and the Cemetery rain gauges showed that the latter had, on average, a higher rainfall (c. 5% higher). Recharge calculations were made using (a) the Penrith station data (as its records cover the period 1974-1999 with only minor interruptions) and (b) the Penrith Water Treatment Works station data multiplied by a factor of 1.06 (to allow for the higher rainfall that is believed to occur at the borehole site because of its higher elevation).

Two recharge approaches were considered; these are the conventional SMD approach and the revised approach adopted by the FAO. The details and assumptions of these approaches are discussed below.

2.2.1 Recharge estimation using conventional SMD approach

The conventional method of estimating recharge in humid areas is based on the work of Penman (1948) and Grindley (1967). This method calculates the recharge as the excess quantity of water available from rainfall after taking the runoff, the potential evaporation and the soil moisture deficit into account. Runoff is assumed to take place instantly after rainfall and its quantity is estimated as a fraction of the amount of rainfall. The potential evaporation is the maximum quantity of water that can evaporate under the given conditions of wind speed and solar radiation.

The Penman equation is usually used to determine the potential evaporation. This equation includes the value of evaporation from crop-covered soil (for the borehole site, and for most of the Eden valley, the crop is grass) with a freely available supply of water. If the value of the potential evaporation is, therefore, greater than the daily rainfall minus the quantity of runoff, water will be lost from soil by evapo-transpiration by plants. However, the quantity of water lost from soil is dependent on the Soil Moisture Deficit (SMD), which is the amount by which the soil moisture is below the field capacity, of the soil.

This technique calculates the change in Soil Moisture based on a relationship between Actual Evaporation (AE) and Potential Evaporation (PE). The relationship between AE and PE is derived from the Soil Moisture Deficit in relation to the Root Constant (C) and Wilting Point (D) as described in Figure 10. For temporary grass the root constant (C) is 56 mm and the wilting point (D) is 102 mm. Water is assumed to be freely available from the part of the soil located between the ground surface down to a horizon equivalent to the value of C, but only part of the water can be extracted from the soil when the SMD reaches or becomes greater than the value of C. No water is extracted from the soil if SMD reaches or becomes greater than the value of D. In the latter case, the value of SMD is considered to be equal to the value D.

When the SMD reaches a value of zero, the excess quantity of rainfall is considered as potential recharge.

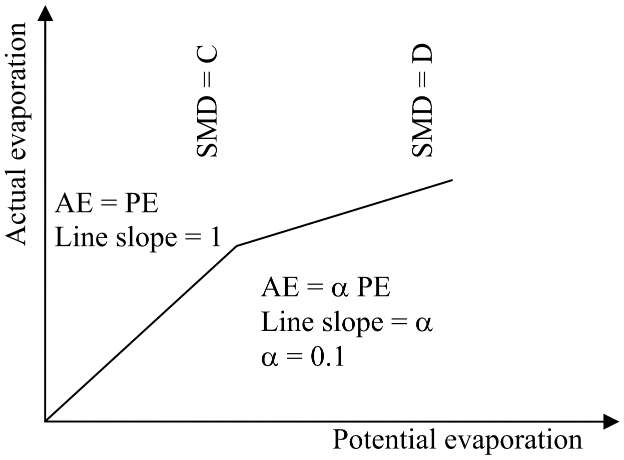


Figure 10. Relationship between Actual Evaporation and Potential Evaporation.

2.2.2 Recharge estimation using modified approach of FAO/EA

A review of recharge estimation for British aquifers carried out by Rushton (2005) includes the development of a new soil moisture balance recharge estimating approach. This approach attempts to improve the estimation of evapotranspiration of the crop by considering both the properties of the crop and the properties of the soil. A full description can be found in either the Groundwater Resources Modelling: Guidance Notes and Template Project Brief (Version 1) document prepared by the Environment Agency (EA) (EA, 2002) or Rushton (2003). The paper on estimating recharge in British aquifers (Rushton, 2005) provides a valuable summary of the FAO/Environment Agency approach and is in part reproduced below.

1. **Soil moisture balance:** moisture conditions within the soil are described by the soil moisture deficit as in the conventional approach.
2. **Properties of the soil:"** the moisture holding properties of the soil determine the availability of water for a crop. The upper and lower limits are θ_{FC} the moisture content at field capacity, and θ_{WP}, the moisture content at the wilting point when crop growth ceases. These critical moisture contents can be estimated from field samples. Alternatively a useful table is provided in the FAO report (Allen et al 1998), which indicates that for sand $\theta_{FC} - \theta_{WP}$ is typically 0.08, whereas for a silty clay 0.16 is a representative value."
3. **Properties of the crop:** "crops have different sowing dates, different durations of growth, different water requirements and different rooting depths, detailed information about these parameters can be found in the FAO report (Allen et al 1998). The crop water requirement (i.e. the potential evapotranspiration *PE*) on a particular day is estimated from a crop coefficient multiplied by the reference crop evapotranspiration (usually calculated from the Penman-Monteith equations see Allen et al 1998). During the mid-crop growth stage the crop coefficient for wheat and potatoes is 1.15 (grass is 1.0) but for apples the crop coefficient is 0.95".
4. **Crop under stress:"** when the soil moisture deficit is greater than a critical value called the readily available water *RAW*, the roots of the crop have difficulty in attracting water at a sufficient rate to meet the evapotranspiration demand. However, when the soil moisture deficit is equal to or greater than the total available water *TAW*, the roots are unable to attract any water and the crop wilts. *TAW* is calculated from the effective depth x ($\theta_{FC} - \theta_{WP}$); as the roots grow, *TAW* increases. *RAW* for most crops is 0.55 *TAW*. When the *SMD* is between *RAW* and *TAW* and there is no infiltration, the actual evapotranspiration is at a reduced rate, $AE = K_S\ PE$, where the stress coefficient K_S can be estimated from the graph in Figure 11.
5. **Evaporation from bare soil:"** during winter, either with no crop or limited crop cover for winter crops, bare soil evaporation is significant. Bare soil evaporation can be estimated as the reference crop evapotranspiration multiplied by 1.05 (Allen et al 1998). Reduced evaporation occurs when there is insufficient moisture near the soil surface. A coefficient similar to the stress coefficient (see Figure 11) applies with zero evaporation when *SMD* is greater than the total evaporable water *TEW* (which is smaller than *TAW* due to the limited depth of soil from which surface evaporation is effective).
6. **Occurrence of recharge:** recharge occurs when the soil moisture deficit falls to zero, the soil becomes free draining and any negative soil moisture deficit becomes recharge.

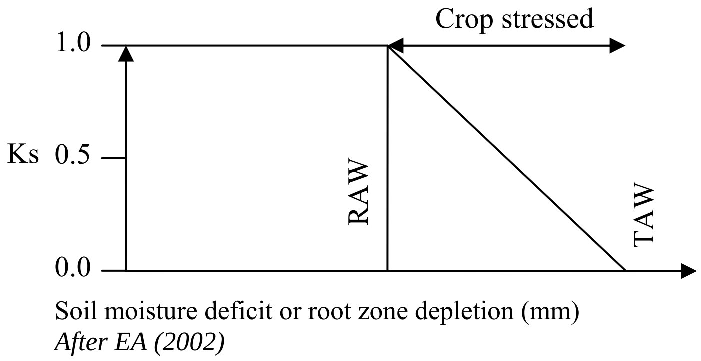


Figure 11. Relationship between Actual Evaporation and Potential Evaporation.

2.2.3 Runoff

It is assumed that a proportion of the rainfall is lost on the ground as runoff and the remainder of the rainfall infiltrates to the ground and becomes a potential recharge. The runoff coefficient can be defined in the model as a constant value or a value that changes on a monthly basis or can be related to the rainfall intensity and current soil moisture deficit as suggested by Rushton (2003). In this investigation, the model implements the same rainfall/soil moisture-runoff relation suggested by Rushton (2003) and explained in Table 3. This table shows that for dry soil conditions with soil moisture deficit greater than 60 mm no runoff occurs if the rainfall intensity is less than 20 mm day^{-1}. However, when the soil approaches field capacity with the soil moisture deficit less than 10 mm, substantial runoff occurs especially with higher rainfall intensity (Rushton, 2003). This approach of determining the runoff coefficient is used in the recharge calculation.

2.2.4 Recharge estimation: assumptions and parameters used

The calculation of recharge requires the definition of many parameters that describe the climate, ground and landuse characteristics of the study area. The parameters involved in this exercise and the values used are described in this section.

RAINFALL AND EVAPORATION DATA

As stated before rainfall and evaporation data that define the climate characteristics are obtained from the nearest available measurement. However, it is believed that the study area receives more rain than that recorded at the main rain gauge station and consequently the daily rainfall values are increased by approximately 6 %. This is because a comparison of rainfall at second gauge site which is close to the site and at a similar elevation than the main gauge site 1 in Penrith shows rainfall is approximately 6% higher, however the second site has data for a more limited period.

GROUND CHARACTERISTICS

The ground characteristics include the topography and the geology or soil type. While the topography characteristics control the overland water movement, they are ignored here because only one recharge node is considered.

The geology or soil type controls the runoff coefficient value. As described in Section 2.2 the runoff coefficient value is related to the rainfall intensity and the soil moisture deficit based on the criteria described in Figure 11. The soil type also affects the results produced by the FAO recharge method. This method involves three parameters related to the type of the soil. These are: the moisture content at field capacity, the permanent wilting point and the depletion factor. Values of 0.41, 0.24 and 0.39, which represent the characteristics of a clay soil, are used for these parameters respectively (Rushton, 2003).

LANDUSE TYPE

In addition to the climate characteristics of the study area the recharge calculation method is selected based on the landuse of the area the node represents. In this investigation it is assumed that the study site is covered by grass (permanent and temporary) at all times. Both the SMD and FAO recharge calculation methods are suitable in this case and they are both considered.

Table 3. Runoff for different rainfall intensity (Pr in mm day-1) and current soil moisture deficit after Rushton (2003)

	Rainfall intensity (Pr) (mm day^{-1})				
SMD (mm)	0-10	10-20	20-30	30-50	>50
0-10	0.0	0.2(Pr – 10)	0.15Pr	0.30Pr	0.5Pr
10-30	0.0	0.0	0.10Pr	0.20Pr	0.45Pr
30-60	0.0	0.0	0.05Pr	0.10Pr	0.40Pr
>60	0.0	0.0	0.02Pr	0.05Pr	0.30Pr

3. RESULTS

3.1 Core drilling and testing

3.1.1 Lithology

Core recovery was generally good (c. 90%); the core consisted of relatively uniform moderately strong, dark red, well-sorted, well-rounded, medium- to coarse-grained sandstones. Exceptions were observed and these included silt bands and more cemented sandstones but these made up a relatively small proportion of the total core recovered. The sandstones exhibited dune cross bedding typical of aeolian sandstone.

3.1.2 Moisture Content

The moisture content of the sandstones, expressed as weight of pore water per unit weight of wet core was also relatively uniform (5.8%). Moisture content can also be expressed by unit volume (volume of pore water per unit volume of wet core) as mentioned earlier. The estimated moisture content, in the depth interval from 0-100m, averaged 12.6%. by volume. The estimated fraction of the total porosity that was saturated was typically 50.4 %. Higher moisture contents were observed at 33m 78-80m and 84m although no obvious lithological differences were consistently observed which suggests that quite small changes in lithology (and/or degree of cementation) can have a significant impact on moisture content. These higher moisture contents do not appear to correlate with sections of the borehole where foam and small quantities of water were added to help drilling progress. The higher moisture contents are therefore not thought to be a consequence of drilling practices.

A 'step change' increase in moisture content was observed below 106m from MC c.6-25% although no obvious change in lithology or porosity/permeability was observed. The increase in moisture content below 106m is thought to be because the capillary fringe and later the water table had been encountered. However, no water was airlifted to the surface and this was probably because any water lifted was adhering to the borehole wall.

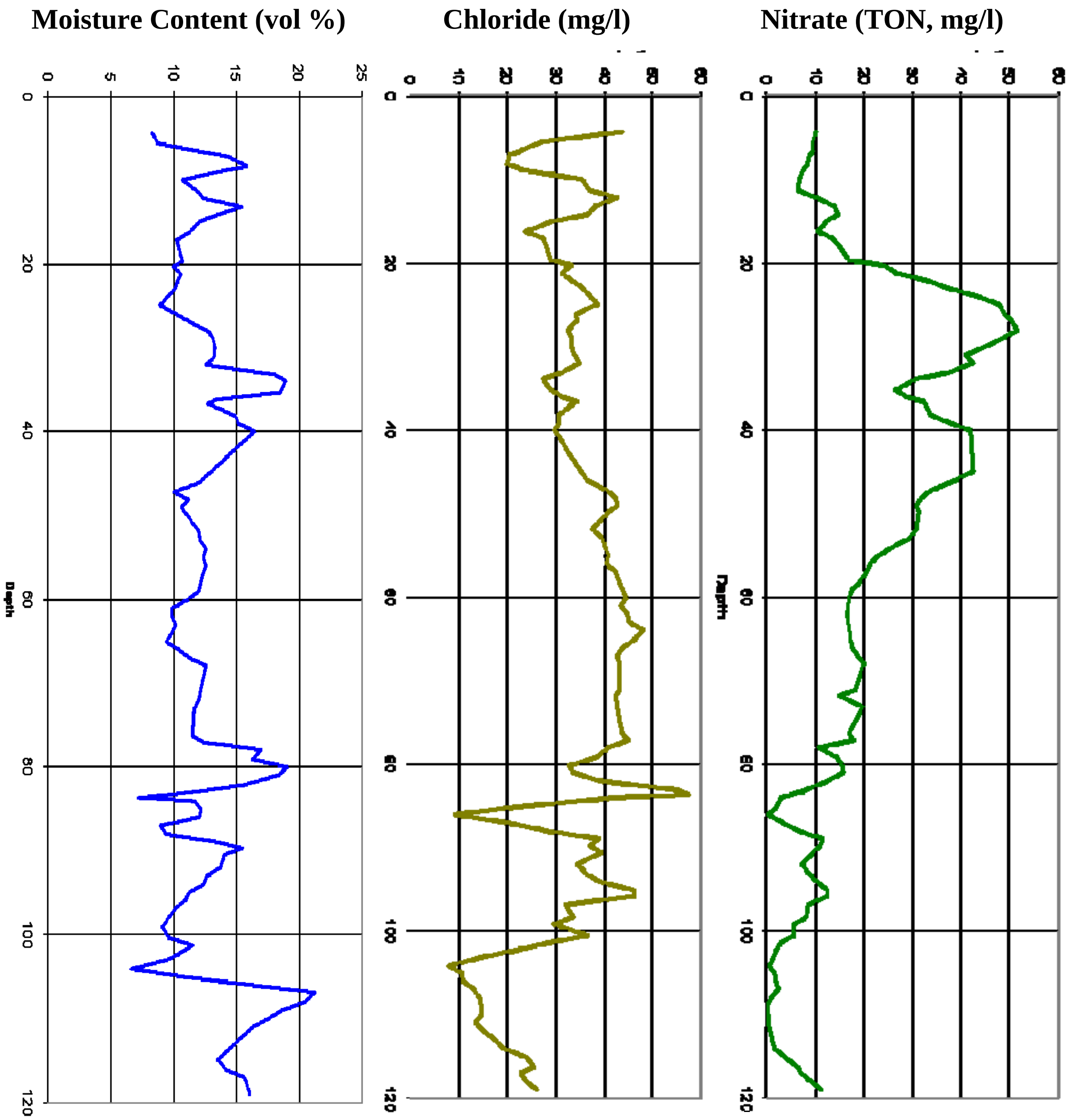


Figure 12. Moisture content (vol), Chloride (mg/l) and Nitrate (mg/l) profiles (3 point average)

3.1.3 Permeability and Porosity

Porosity and permeability results based on the laboratory testing of rock plugs (Table4) are consistent with previous results for Permo-Triassic sandstones in the Eden Valley (Allen et al 1997).

Table 4. Core porosity and permeability

Property	**Min**	**Max**	**Mean**
	mD	mD	mD
Kh	20	18400	3700
Kv	1.7	9800	2200
Ǿ	14.5	35.5	25.5

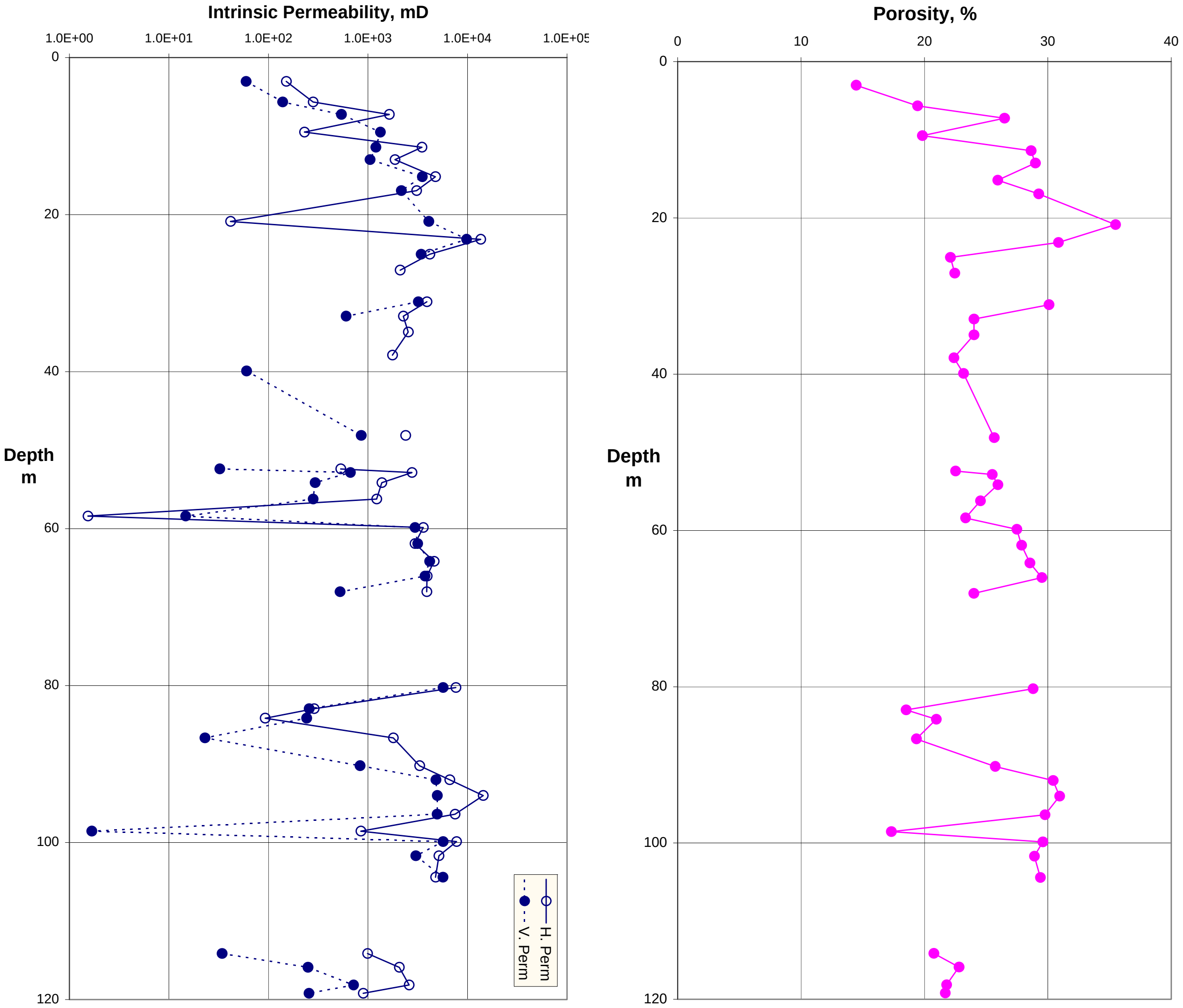


Figure 13. Porosity and permeability profile

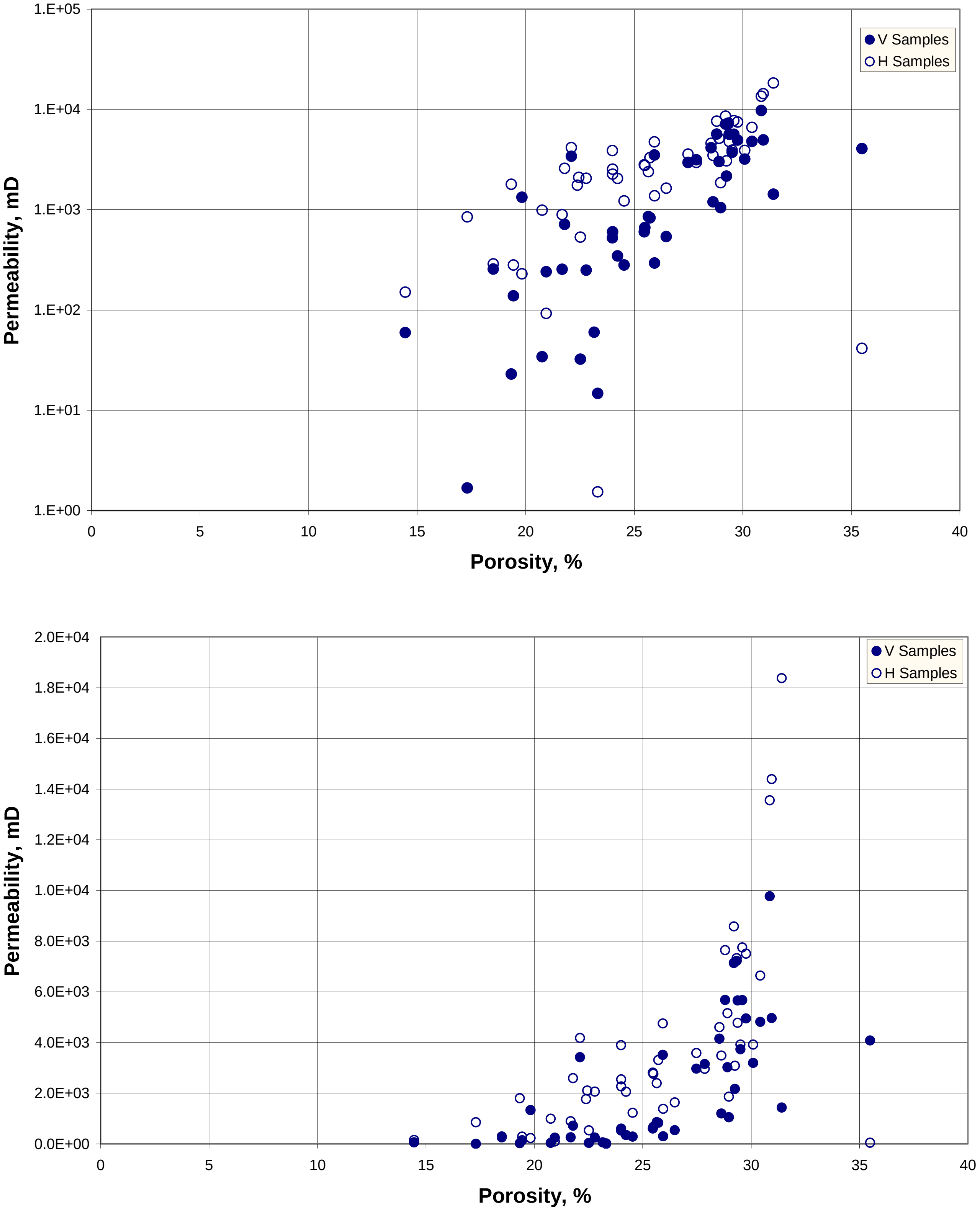


Figure 14. Porosity and permeability cross plots (log and linear permeability axes)

3.2 Water Quality

3.2.1 Water types, sources of contamination and ionic balances

A summary of the porewater analyses for the major and some minor ions are presented in Table 5; full analyses are presented in Appendix 1. Some analyses had poor ionic balances (<±5%) and these were generally associated with intervals where a mixture of water mist and foam had been introduced during drilling. Analyses of the water/foam, (Table 7) confirmed a distinctive composition including high concentrations of K, S, Na and P but only low Cl and NO_3 concentrations. The poor ionic balances associated with the use of foam in drilling, appear to be due to uncertainty about the speciation of sulphur. In several cases, the ICP-OES analysis showed a relatively high total sulphur concentration but analysis using ion chromatography established that this was not all attributable to the sulphate ion. The use of foam has not introduced nitrate or chloride into the porewaters and thus nitrate and chloride concentrations are probably representative of inputs derived from agriculture even where some contamination by water/foam is evident. However for three samples (in the interval 84-86 m) where total sulphur concentrations were greatest (and where contamination by water/foam is assumed to be most severe), nitrate concentrations were low (< 2.0 mg N/l) which can probably be attributed to dilution. One sample at a depth of 92 m exhibited some of the largest porewater concentrations of sulphate, magnesium, potassium, calcium and barium but these are isolated to a single interval. It is thought that this sample may have been contaminated by drilling additive residue from a previous activity.

Table 5. A statistical summary of the porewater quality in EV1 borehole

Determinand		**Units**	**Min**	**Max***	**median**	**Samples**
pH			5.26	7.13	6.5	102
SEC	conductivity	µmS/cm	95.5	799	290	102
Ca	calcium	mg/l	4.68	181	17.7	102
Mg	magnesium	mg/l	0.50	28.5	4.74	102
Na	sodium	mg/l	14.4	302	28.2	102
K	potassium	mg/l	4.08	12.6	6.45	102
Cl	chloride	mg/l	7.6	77.1	35.2	102
SO_4	sulphate	mg/l	0.23	1050	5.1	102
HCO_3	bicarbonate	mg/l	0.71	19.3	2.44	102
NO_3	nitrate as N	mg/l	0.065	49.6	14.6	102
Al	aluminium	mg/l	<0.01	0.41	0.03	102
B	boron	mg/l	0.24	3.85	0.83	102
Ba	barium	mg/l	0.22	5.09	0.55	102
Cu	copper	mg/l	<0.008	0.194	0.052	102
Fe	iron	mg/l	<0.005	0.06	0.012	102
Li	lithium	mg/l	<0.004	0.07	0.015	102
Mn	manganese	mg/l	0.004	1.42	0.03	102
Ni	nickel	mg/l	<0.005	0.016	0.008	102
Si	silicon	mg/l	3.46	9.72	6.05	102
Sr	strontium	mg/l	0.029	0.848	0.89	102
Zn	zinc	mg/l	0.018	0.820	0.095	

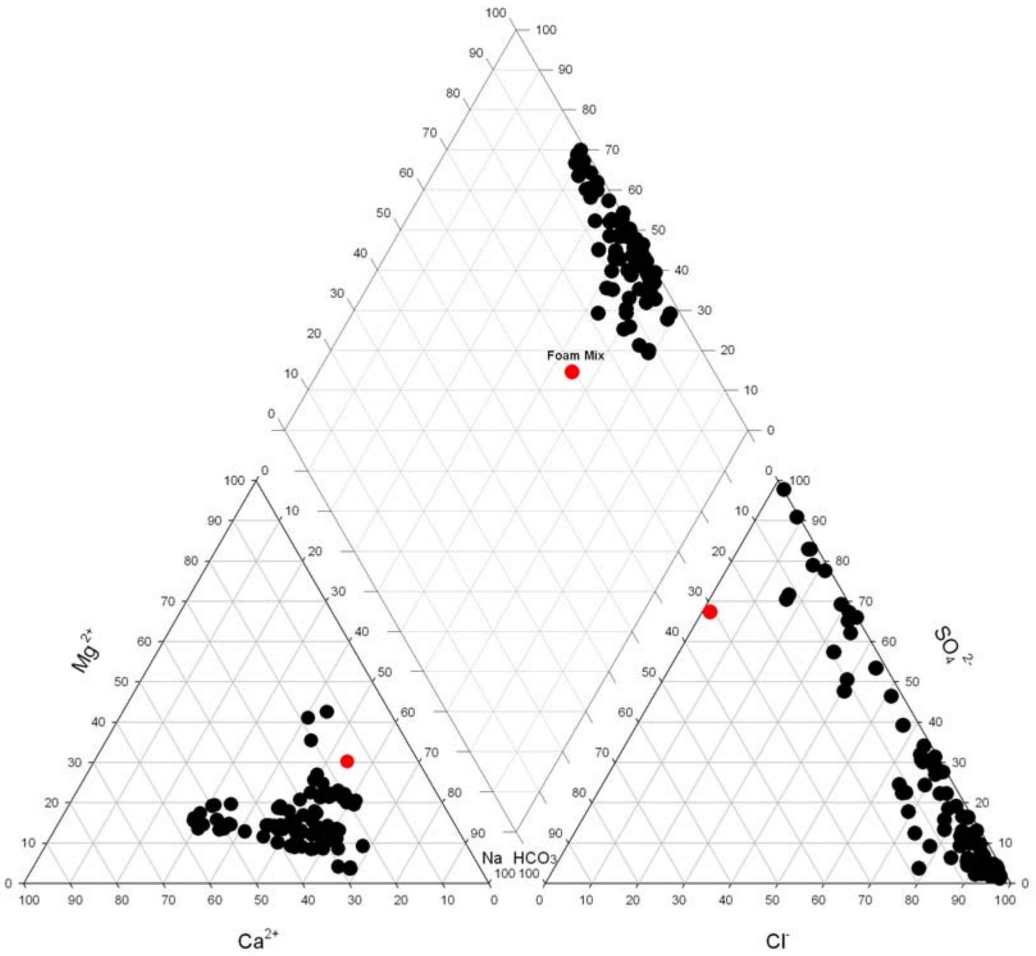


Figure 15. Piper diagram for porewaters from borehole EV1 and drilling foam

Table 6. Drilling water (mist) / foam analyses

Fluid / Analyte	**Ca**	**Cl**	**HCO_3**	**K**	**Mg**	**Na**	**SO_4**	**TON**
mixing water	19.4	7.6	172	4.97	1.61	4.0	4.36	< 0.2
foam	15.5	19.1	<1	188	0.94	12500	40400	0.66
foam water mix	18.8	7.3	174	6.25	0.688	71.4	293	< 0.2

The porewaters in the unsaturated zone are of a mixed water type (Ca/Na – Cl, (SO_4)), with low HCO_3 concentrations and contrasts with the groundwater sampled as part of the Catchment Water Quality Survey (Butcher et al 2005) which were predominantly of Ca – HCO_3) type (Figure 15). The low bicarbonate concentrations in the porewaters of the unsaturated zone suggest that there is little calcium carbonate cement or this has been removed by infiltration over time, a process that would perhaps have been enhanced by acid rain deposition and had an impact on rock properties.

3.2.2 Solute porewater depth profiles

The principal interest in this study is the movement of chloride and nitrate (derived from chemical fertilisers and animal slurry) through the unsaturated zone following the conversion of rough unfertilised grazing to intensive cropping (mostly grass). It was anticipated that there would be a 'step change' in the nitrate and chloride concentrations leached from the soil following this change in landuse and that the depth of penetration of the elevated nitrate and chloride concentrations (above background) should permit an estimate of recharge to be made. The profiles are presented in Figure 12 (Cl- and NO_3-N). The pore water chemistry results are presented in Figure 16 and tabulated in Appendix 1. However, a more detailed review of these pore water profiles and a comparison with the agricultural inputs is discussed in Chapter 4.

CHLORIDE

Sources of chloride in groundwater recharge can be both natural (including rainfall), and anthropogenic (principally derived from chemical fertilisers and animal slurry). The chloride depth profile shows that elevated concentrations (25-50 mgl^{-1}) occur down to depths of about 100m. Maximum chloride concentrations occur at c. 80m. From 106-110m, chloride concentrations are about 10 mg/l (approximately equivalent to baseline concentrations, Shand et al 1997). Below 110m, chloride concentrations gradually increase to 30 mgl^{-1}. The reason for this increase in chloride concentrations is thought to be mixing with groundwater below the water table. The chloride concentration is similar to those in some pumped groundwater from nearby boreholes, although these are pumped from deeper below the water table where there would be some dilution, see Table 7.

Background concentrations of chloride ($\leq$10 mgl^{-1}) occur at 84 -86m and 96.7 m. The lower chloride concentrations could be due either to dilution when water was added to the borehole (within the interval 84-86 m the high SO_4 concentrations indicate contamination by drilling foam) or to recharge by-passing the sandstone matrix.

NITRATE

Sources of nitrate are principally anthropogenic and derived from agricultural practices. The nitrate depth profile is somewhat different to chloride. Concentrations are modest (c. 10 mg N/1) in the upper 15 m of the profile before peaking (c. 50mg N/l) at 20-30 m depth. Below 30m nitrate concentrations show a steady decline to about 100m where concentrations reach baseline values (1-2 mg N/l). Below 110m, the nitrate porewater profile is similar to the chloride profile and shows a steady increase in concentrations with depth. Nitrate concentrations in the pore water below 110m increase and are slightly higher than those in some pumped groundwater from nearby boreholes although these are pumped from deeper below the water table where there would be some dilution, see Table 7.

The dip in nitrate concentrations at 84-86m depth which may be due to dilution by water, added to the borehole to improve drilling progress at this depth.

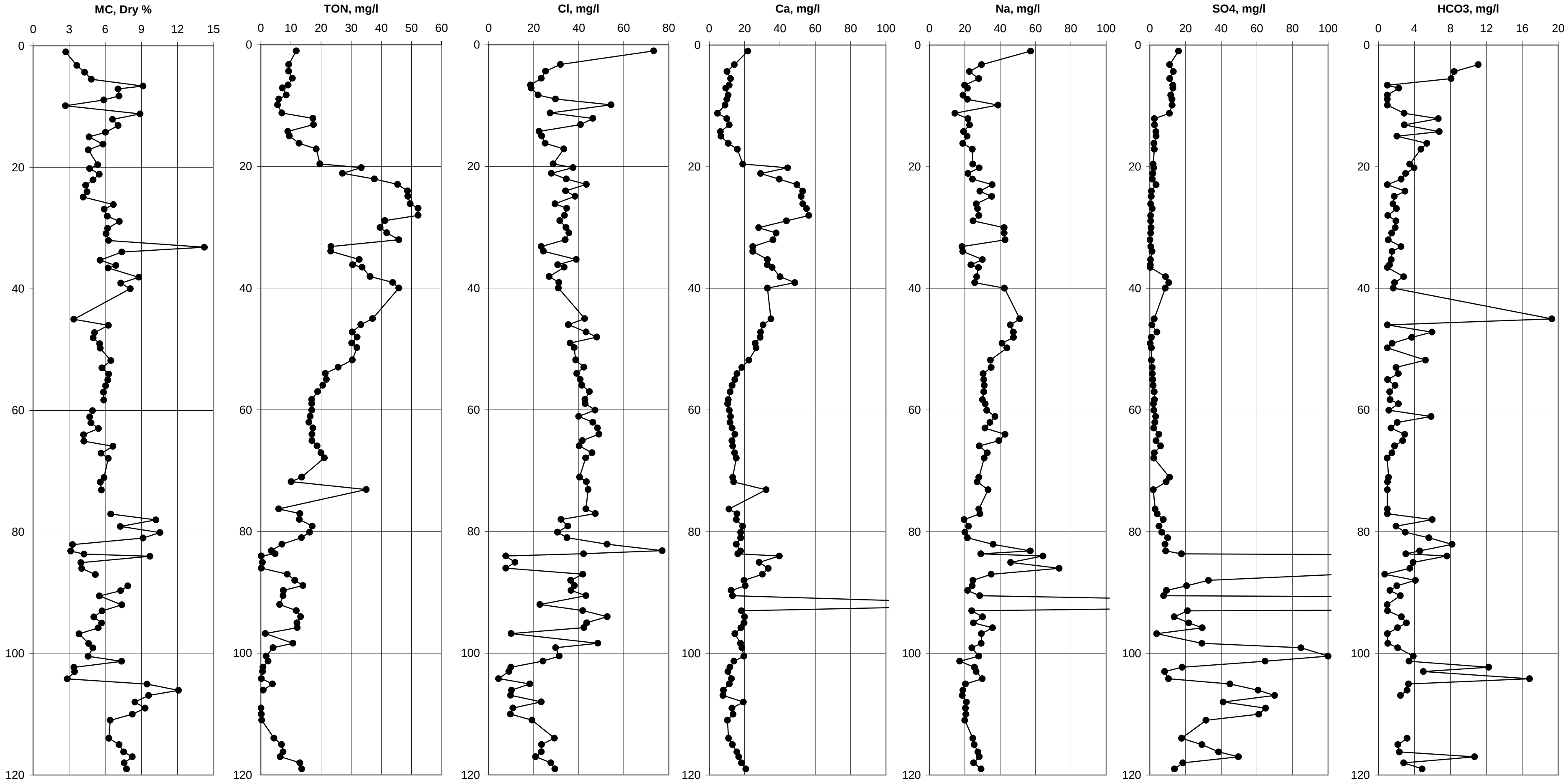
The nitrate and chloride profiles suggest that 1976 recharge has migrated down to a depth of approximately 100m. The difference in the shape of the nitrate and chloride profiles is attributed to different agricultural inputs of nitrogen and chloride. Further, during the early stages of intensive cropping, some of the nitrogen available for leaching (but not the chloride) may have been incorporated into the soil organic pool.

NITRITE/AMMONIUM

For groundwaters the ammonium and nitrite concentrations in the porewater profiles are relatively high. Ammonium is highest in the upper 50 m (0.1-0.6 mg N/l) and declines to less than detection below 90m. Nitrite concentrations are highest in the interval 50-80 m (Figure 16). Comparison of the ammonium and nitrite profiles suggests that ammonium is being converted (oxidised) to nitrite(e.g. nitrification).

Table 7. Comparison of water quality from neighbouring boreholes

Site	**Beaver Lodge Maidenhill**	**Greengill Farm**	**Greengill Foot Farm**	**Greengill Head Farm**	**Foresthall Farm**	**Inglewood Bank**	**Penrith Golf Club**
Well No.	NY53/42	NY53/30	NY53/43	NY53/50	NY53/45	NY53/46	NY53/38
NGR	5289 3290	5068 3344	5176 3161	5290 3253	5154 3403	5333 3432	5176 3161
NO_3 (mg/l)	19.9	10.8	8.1	23.5	18.7	33.0	2.3
Cl (mg/l)	11.4	9.8	10.8	22.6	68.2	33.0	11.0


MC, Dry %
0 3 6 9 12 15
TON, mg/l
0 10 20 30 40 50 60
Cl, mg/l
0 20 40 60 80
Ca, mg/l
0 20 40 60 80 100
Na, mg/l
0 20 40 60 80 100
SO4, mg/l
0 20 40 60 80 100
HCO3, mg/l
0 4 8 12 16 20
0
20
40
60
80
100
120

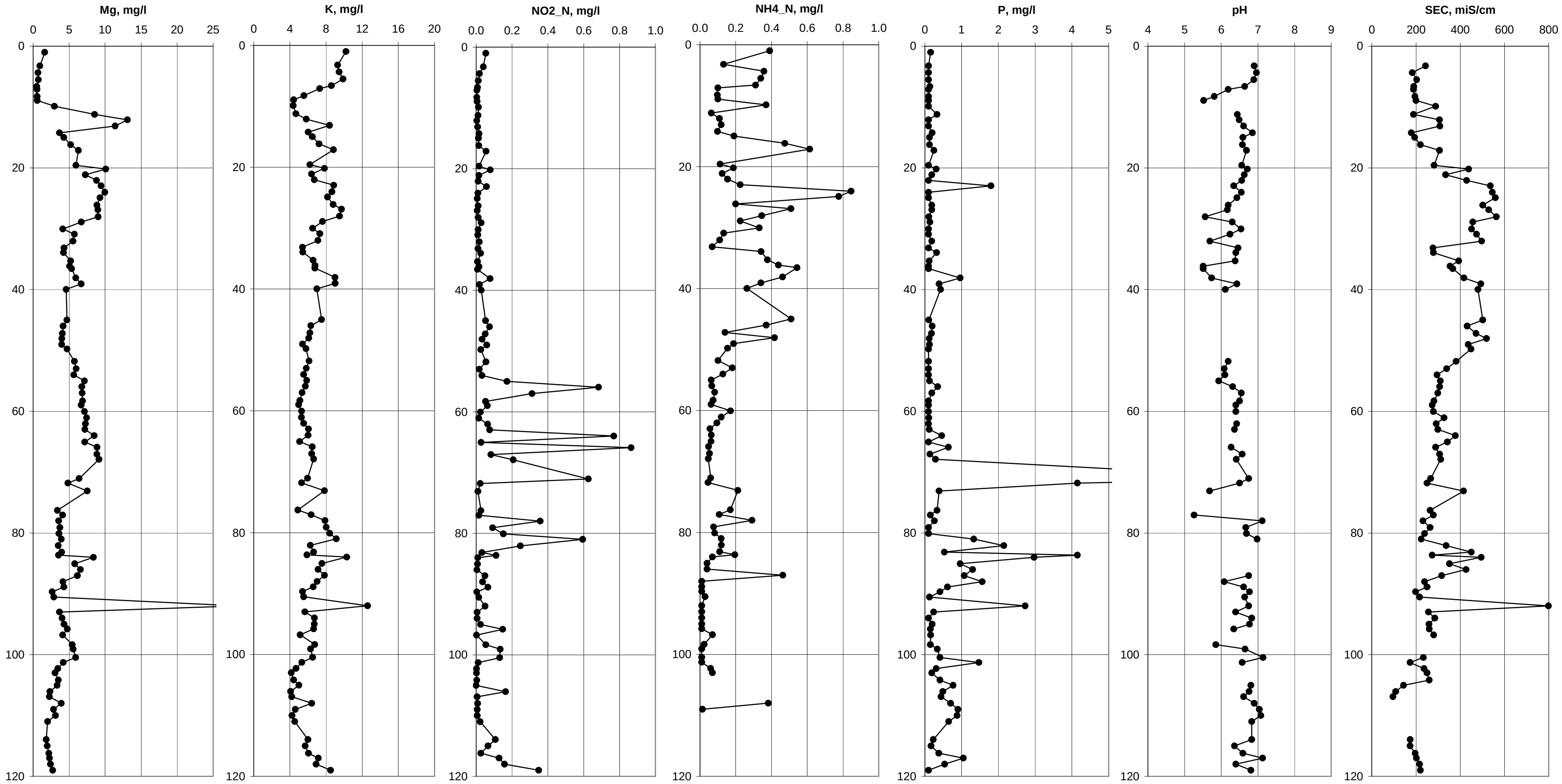


Figure 16. Porewater Profiles

3.3 Soil moisture –water balance modelling

The results of soil moisture-water balance modelling are presented in Table 8. For the Penman-Grindley approach, three crops were considered (‘temporary grass’, ‘permanent grass’ and ‘rough grazing’) and two rainfall regimes (one based on data from Penrith Sewage Treatment Works raingauge and the other is the same site raingauge data multiplied by a factor of 1.06 to allow for higher rainfall at greater elevation as discussed in section 2.2.5

The FAO/EA approach considered only ‘grazed pasture’ crop type and the two rainfall regimes above.

Runoff estimated by the model for both the conventional and the FAO methods were 1.4 10^{-2} mm/d (5 mm/y) which is low and consistent with the generally accepted view that runoff on sandstone at outcrop is small.

Table 8. Rainfall / recharge modelling approaches

Rainfall Station	**Penman Grindley Approach /Constants**			**FAO Approach**
	No. 12 Permanent Grass RC 76 WP127	*No. 13* Rough Grazing RC 13 WP 51	*No. 11* Temporary Grass RC 56 WP 102	Grazing Pasture
Penrith Sewage Wks Recharge mm/yr	368	445	386	370
Penrith Cemetery* Recharge mm/yr	405	481	422	408

*Penrith Cemetery c. 1.06 (6%) greater rainfall

4. DISCUSSION

4.1 Recharge estimate: tracer approach

A recharge rate of about 450 mm/a (and an average rate of water movement through the unsaturated zone of c 3.5 m/a) was estimated when using historical tracers (N, Cl) to date the recharge at the borehole site. The 1976/77 recharge could be 'dated' by the step increase in nitrate and chloride concentrations corresponding to the change in land use from unfertilised grass (with bracken) to intensive cropping (initially fertilised grass and later occasional fodder crops and improved pasture).

The two tracer profiles give similar depths of penetration for the nitrate and chloride 'fronts' which correspond to the 1976/77 recharge. The depth of these fronts was approximately 100 m. Below this depth, concentrations of nitrate and chloride (1-2 mgN/l and ~10 mg/l respectively) are similar to 'baseline concentrations (Shand et al 1997) and to minimum concentrations observed in the catchment water quality survey (Butcher et al 2005). This provides some confidence in the 'dating 'of the tracer fronts.

The relatively uniform nature of the sandstone, both in terms of its appearance when the core was logged and in its moisture content profile with depth, also provides confidence in the use of this tracer technique to estimate recharge. Nevertheless some anomalously low porewater concentrations (for nitrate and chloride) were observed in the depth profile (e.g. 84-86 m, 95 m). This could be attributed either to dilution, caused by using water/foam in the drilling operations or to recharge by-passing the sandstone matrix. The former is a more likely explanation, at least for the interval 84-86 m, but, even if by-pass flow has occurred, any impact on recharge estimates is probably small, given that the interval where the matrix appears to have been bypassed is relatively thin (1-2 m) compared with the total depth of penetration of the tracer front (approximately 100 m).

4.2 Detailed comparison of porewater profiles (in USZ) and agricultural record

It can be difficult to draw meaningful conclusions when comparing nitrate and chloride porewater concentrations in the USZ with agricultural inputs, not least because of uncertainties in quantifying the nutrient inputs at the borehole site over a 30 year period. Despite these practical difficulties it is probably worthwhile to attempt to compare the porewater concentrations with the land-use history for this site as a sensible correlation between the quantities of nutrients applied and leached would add to the credibility of the dating of the profile.

The chloride porewater profile, together with a best estimate of the quantities of nutrients added and the land-use record, is presented in Figs.16 and 17. From 1976-82, the pasture was unimproved (eg the grass was not of a standard suitable for intensive grazing) although chemical fertilisers were applied at a rate of approximately 250 kg N/ha/a and presumably other nutrients (P and KCl) were also added most years. This period, 1976-82, is approximately represented by the depth interval, 80-100 m (these depth intervals were estimated assuming that porewater at 100 m depth represents 1976/77 recharge and that each year recharge moves down at an average rate of 3.6m), where chloride concentrations average 35 mg/l. Allowing for background chloride concentrations of ~10 mg/l, the additional chloride (25 mg/l) is equivalent to a leaching rate of about 112 kg/ha/y which is probably a realistic rate when considering that most chloride applied to the soil will be leached since plant uptake is usually small.

From 1984-present, slurry was applied, in addition to the chemical fertilisers, at the rate 11m/ha/y with heavier applications (80 m/ha/y) in the 3 year period, 1984-86, and in 1997. The higher chloride concentrations (c 45 mg/l) in the interval, 60-78m, may in part be due to the heavy applications of slurry during 1984-86.

The reason for the generally lower chloride concentrations (c 30mg/l) from 10-40m is not immediately apparent although one possible explanation is that the quantities of other nutrients, including KCl, in the chemical fertilisers were lower than in previous years even though the N applications were higher. However, there is no evidence to support this.

The low chloride concentrations (18-25mg/l) observed over the depth interval, 5-10m, corresponds approximately to recharge that occurred during the period 2001-03. At this time, Foot and Mouth Disease (FMD) occurred (2001) and smaller quantities of both slurry and chemical fertilisers were applied to the field.

Dating of the USZ using the chloride ‘front’ at 100m depth to represent the 1976-77 recharge provides a reasonable match between the chloride porewater profile and the agricultural record from 1975 to the present day. This ‘reasonable match’ needs to be set in the context of the difficulties and uncertainties in (a) estimating rates of application of slurry to the field (it was based on averaging the total slurry produced over all the farm fields used for slurry spreading), (see Appendix 3) and (b) estimating the chloride content of chemical fertilisers when only the total nitrogen applied is recorded.

The variability of nutrient inputs over the field, especially where grazing animals also contribute to the nutrient inputs, makes direct comparison between porewater concentrations and agricultural inputs imprecise. However, the good agreement between the low chloride concentrations, in the porewater profile, at 5-10 m depth, and the estimated depth of penetration of the 2001-03 recharge (when agricultural inputs were low due to FMD) does provide some validation of the dating of recharge events in the unsaturated zone.

The nitrate porewater profile is different in shape to that of chloride. Comparing the nitrate porewater concentrations with the agricultural record has the advantages (over chloride) that at this site the nitrate inputs are better defined, but the disadvantage that the leaching behaviour is more complex as there are other significant losses of nitrogen from the soil which include volatilisation (from slurry) and plant uptake both of which may vary with season.

From 1976-82, nitrogen applications from chemical fertilisers, were 250 kgN/ha/y. Porewater nitrate concentrations between 80-100m depth, which are derived from recharge that occurred between 1976 and 1982, is about 8-10 mgN/l; this implies a leaching rate of about 30-40 kgN/ha/y. which is comparable to rates observed previously beneath fertilised grassland on sandstone outcrop (Parker et al. 1989).

Slurry was added to the field from 1984 onwards at rates of 80 m^3/ha (equivalent to 250 kgN/ha/y) for the period 1984-86 and thereafter up to 2001 at the rate of 11 m^3/ha (equivalent to 35 kgN/ha/y); chemical fertilisers continued to be applied at the rate of 250 kgN/ha/y up to 1986. Nitrate concentrations in the profile from 60-80m (and derived from recharge during 1982-87), averaged 15 mgN/l (equivalent to a leaching rate of 60 kgN/ha/y).

Between 60 and 40m (equivalent to recharge derived from 1987-93) the nitrate porewater concentrations increased steadily from 17 mgN/l to 45 mgN/l. Over this same period, chemical fertiliser applications had increased from 250 kgN/ha/y to about 300 kgN/ha/y although this increase had occurred as a step change in 1987 (Figure 17). This suggests that the process of leaching nitrate from the soil is not simple and may involve a delay between the application to, and the leaching from, the soil zone.

Peak nitrate concentrations in the porewater profile occur in the depth interval 20-40m (equivalent to recharge 1993-98) and average 40 mgN/l which implies a leaching rate of about 180 kgN/ha/y. Nitrogen applications during this period were typically in excess of 300 kgN/ha/y (from chemical fertilisers) and about 33 kgN/ha/y as slurry. However, 250 kgN/ha/y was applied as slurry during 1997 and additional nitrogen inputs may have occurred from cattle grazing on the field. Nevertheless a leaching rate of 180 kgN/ha/y does seem high even though leaching rates as high as 150 kgN/ha/y beneath intensive pasture has been observed elsewhere (Parker et al. 1989).

The relatively low nitrate concentrations (8-20 mgN/l) between 0 and 20 m depth (equivalent to recharge 1998-2004) are more difficult to explain. In part it is due to FMD, however low nitrate porewater concentrations are also observed at depths corresponding to recharge prior to FMD. It must be stressed that estimates of nitrogen applications are approximate only; slurry applications were estimated by dividing the total slurry produced by the area receiving the slurry to produce a farm average rate (Proctor & Metcalfe 2005). In reality, in any given year, some fields will receive significantly higher applications and others less. However it is not possible to say that this is the reason for the apparent discrepancy between the estimates of the nitrogen leached (obtained from the porewater profile) and the nitrogen applied to the field.

Hence the nitrate porewater-depth profile is broadly consistent with the agricultural record although some differences are apparent. These discrepancies may be due to inherent difficulties in estimating rates of nitrogen application to the land but may also suggest that processes controlling nitrate leaching, and possibly nitrate transport in the unsaturated zone flow, are more complex than is commonly assumed.

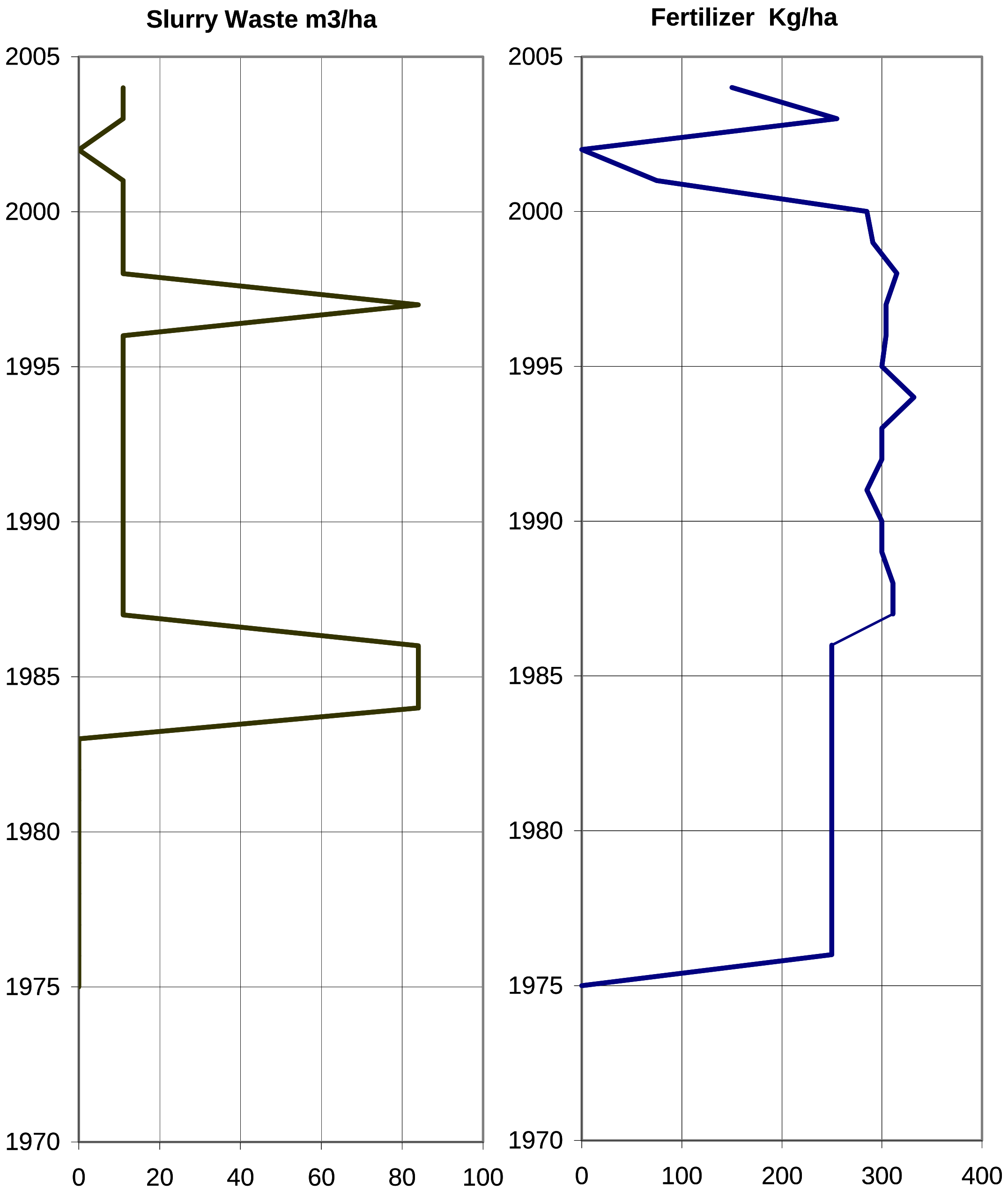


Figure 17. Slurry and fertiliser application history profiles

4.3 Recharge estimate: SMD method

This method provided a range of recharge estimates (368–481 mm/y) depending on the specific technique used, the crop type and the rainfall data (Table 8). When comparing with the recharge rate estimated by the tracer method it is probably more appropriate to use the higher rainfall data, as the borehole site was located close to the top of a hill (where the rainfall is higher). The recharge estimates, (for temporary or permanent grass) using the conventional SMD approach and the higher rainfall, are 405-422 mm/y which are similar to those obtained using the FAO/EA approach for grazing pasture (408 mm/y) and are broadly comparable to recharge estimates using the tracer technique (450 mm/y).

The soil moisture water balance approach, which is widely used and accepted in the UK, makes no assumption on subsurface conditions below the soil zone, other than all the potential recharge arrives at the water table. The recharge estimates, based on the soil-moisture water-balance approach, is applicable over large areas wherever the soil type, crop type and climatic conditions are similar. The reasonable agreement in recharge estimates for the two approaches (tracer approach and soil –moisture water-balance approach) provides a degree of confidence in these estimates. Thus for conditions similar to those at the borehole site, the recharge rate, beneath managed grass, on sandstone outcrop, may approach 425 mm/y. At lower elevations, the recharge rate on sandstone outcrop for managed grass is probably closer to 375 mm/y. The recharge estimate for rough grazing is 445-481 mm/y (depending on rainfall data used). All these recharge estimates, for grass, are higher than the rate (315 mm/y) suggested by Ingram (1978) but lower than the recharge estimate (c530 mm/a) of Monkhouse and Reeves (1977). The recharge estimates of both Ingram (1978) and Monkhouse and Reeves (1977) were catchment averages and not specific to a crop.

4.4 Chloride in rainfall

The chloride content of the rainfall has been measured at Bannisdale NY 515 504 and Cow Green NY 817 298 and is in the range 70-100µeq/l ~2.5-3.5 mg/l in 2000 (and in 1997 up to 7 mg/l (CEH 2000) Assuming a recharge rate of 400–450 mm/y(or approximately 50% of the annual rainfall), then the chloride concentration in recharge should be ~5-7 mg/l. This compares with a minimum (or baseline) chloride concentration in the unsaturated zone profile of 5–10 mg/l. This is a reasonable agreement and provides further confidence in the recharge estimates.

4.5 Nitrate flux to the water table

An important aspect of diffuse pollution in aquifer systems is the residence time of groundwater both within the saturated and unsaturated zones of the aquifer. Because groundwater residence times can be many years, decades or even longer, it raises questions as to where, and when, diffuse contaminants (e.g. nitrate) will reach peak concentrations. It is probably useful initially to predict the arrival of peak nitrate concentrations at the water table; this will require an understanding of:

(1) catchment land use history and rates of nitrate leaching from the soil with time.

(2) Denitrification processes in the unsaturated zone.

(3) Transit times through the unsaturated zone.

4.5.1 Catchment land use history

Models (e.g. NEAP-N) have been developed by ADAS to estimate nitrate fluxes leaving the soil zone, at the catchment scale, and are based on spatially distributed information on soil type, hydrologically effective rainfall(HER) and land use (Anthony et al. 1996; Silgram et al 2001). The NEAP-N model considers a maximum potential nitrate loss factor for individual crop and livestock types based on agricultural statistics data. Coefficients are based on generalised results from UK data and therefore represent typical land management practices (Silgram et al. 2005). The model is still being validated by field measurements but currently provides the best means available to estimate nitrate concentrations in aquifer recharge over time at the catchment scale. The agricultural census data suggests that in the Eden valley nitrate applications (mostly to grass) peaked during the late 1980s or early 1990s and have remained largely constant to the present day with the exception of the period 2001-03 during the time of FMD.

DENITRIFICATION

Denitrification is a microbial process in which nitrate is progressively reduced to nitrogen gas. Denitrification can be important in some aquifer systems (Foster et al. 1985) but is restricted to environments where dissolved oxygen concentrations are low, or absent, and is therefore more usually observed in confined aquifers (Lawrence & Foster, 1985) or within semi-permeable cover (Parker et al. 1985).

A previous catchment water quality survey in the Eden valley observed no evidence for denitrification and concluded that denitrification is not a significant process controlling nitrate concentrations in the sandstone aquifer (Butcher et al. 2005). Furthermore, evidence from the porewater chemistry of the cored borehole (EV1) described in this report suggests that in the unsaturated zone oxidation of ammonium to nitrite occurs instead. This is consistent with the normally aerobic conditions found in the unsaturated zone of permeable aquifers.

TRANSIT TIMES THROUGH THE UNSATURATED ZONE

Travel times to the water table have been inferred (Figure 18) and are based on an estimated recharge rate of 400 $mm.y^{-1}$ (equivalent to a downward rate of water movement through the unsaturated zone of 3.6 $mm.y^{-1}$) and the depth to water table observed within the Eden Valley (EA monitoring data). The estimated travel times to the water table are shown by solid lines where the sandstones are exposed and by dashed lines where thin drift (<2m) overlie the sandstone. Dashed lines are used to indicate the greater uncertainty associated with recharge rates (and therefore rates of downward water movement through the unsaturated zone) where the sandstone has a thin drift cover.

These results can also be presented in terms of the approximate age of the recharge currently arriving at the water table (Figure 18). This shows that over large areas of the Eden valley, the recharge currently arriving at the water table is of post 1990 origin.

Thus over most of the Eden valley, porewater nitrate concentrations arriving at the water table are unlikely to substantially increase. This does not mean of course that nitrate concentrations will not increase at abstraction boreholes (or in the baseflow to the streams). Indeed, it is anticipated that nitrate concentrations at groundwater outflows will continue to rise until most of the pre 1990 origin recharge has been flushed out which is likely to take many decades.

4.6 Future Work

OTHER RECHARGE ESTIMATION TECHNIQUES

Given the relatively uniform nature of the sandstones, it should be possible to estimate recharge rates using the Darcy flow equation applied to the unsaturated zone. This requires an estimate of the unsaturated, vertical hydraulic conductivity for the sandstones which is difficult to measure directly. However, the unsaturated hydraulic conductivity of the sandstones can be estimated from their capillary pressure-saturation relationship using the van Genuchten equation (van Genuchten, 1980). Although estimating recharge using the capillary pressure-saturation relationship is beyond the scope of this project, it might be a suitable topic for an MSc project and could be considered later.

RECHARGE RATES WHERE THE SANDSTONES ARE OVERLAIN BY THIN SUPERFICIAL DEPOSITS

Within the Eden Valley, some 40% of the Permo-Triassic sandstone outcrop is overlain by a thin (<2 m) cover of till. These thin till deposits can be relatively permeable, partly because they are weathered and fractured and partly because they can be sandy (having been largely derived from the scouring of sandstone bedrock by the ice sheet). Thus, recharge rates may not be significantly different to those estimated for exposed sandstone. Nevertheless, given that the area of thin till cover, within the Eden Valley, is appreciable, it is important to establish recharge rates for this setting, rather than assume rates similar to exposed sandstone. Therefore it is recommended that tracer tests, using an applied tracer (probably deuterium) be undertaken, in areas where the till cover is thin, to estimate the downward movement of recharge over a 1–2 year period. The estimated rate of movement of recharge through the unsaturated zone (c 3.5 m/a) where the sandstones are exposed suggests that a 1 – 2 year period should be sufficient to permit a sensible depth of penetration of the applied tracer to be observed. It is also recommended that at least one tracer test is carried out on exposed sandstone to provide a direct comparison with the recharge estimates described in this report.

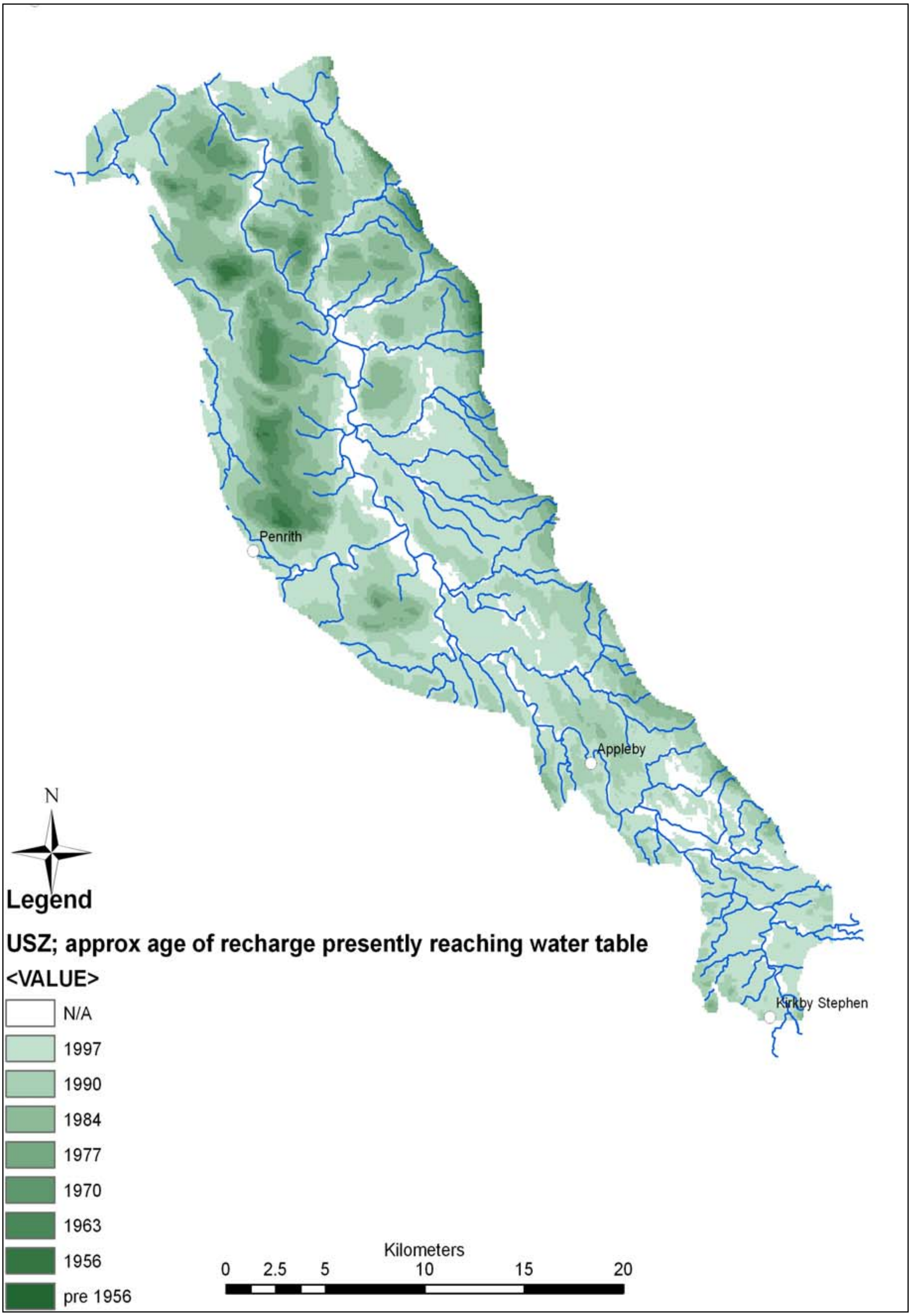


Figure 18. Approximate age of recharge presently reaching water table

5. SERIES REFERENCES

Allen D J, Brewerton L J, Coleby L M, Gibbs B R, Lewis M A, MacDonald A M, Wagstaff S J and Williams A T. 1997. The physical properties of major aquifers in England and Wales. Eds. Allen D J, Bloomfield J P and Robinson V K. British Geological Survey Technical Report WD/97/34; Environment Agency R&D Publication 8, British Geological Survey, Keyworth, Nottingham.

Anthony, S., Quinn, P. & Lord, E.I. (1996) Catchment scale modelling of nitrate leaching. Asp Appl Biol 46: 23–32.

Arthurton R S, Burgess I C and Holliday D W. 1978. Permian and Triassic in: The Geology of the Lake District edited by F Moseley. Yorks Geological Society Occasional Publication No 3.

Arthurton R S and Wadge A J. 1981. Geology of the Country around Penrith. Memoir for 1:50 000 geological sheet 24. British Geological Survey, NERC. HMSO.

Bott M H P. 1974. The geological interpretation of a gravity survey for the English Lake District and the Vale of Eden. *Journal of the Geological Society of London.* No 130, 309-331.

Butcher A S, Lawrence A R, Jackson C, Cunningham J, Cullis E L, Hasan K and Ingram J. 2003. Investigation of rising nitrate concentrations in groundwater in the Eden Valley, Cumbria: Scoping Study. Environment Agency Technical Report NC/00/24/14.

Centre for Ecology and Hydrology Atmospheric Sciences (CEH 2000). Rain ion concentration of chlorine, air pollution and trace gas fluxes research pollutant maps.

Chilton P J and Foster S S D. 1991. Control of ground-water nitrate pollution in Britain by land-use change: Nitrate contamination edited by I. Bogardi and R.D. Kuzelka; Heidelberg, Springer-Verlag p333-347.

Edmunds W M and Gaye C B 1994. Estimating the special variability of groundwater recharge in the Sahel using chloride. *Journal of Hydrology*. 156, 1-4, 47 - 59.

Environment Agency 2005. Eden and Esk Catchment Abstraction Management Strategy.

Gates J B, Edmunds W M, Ma J, and Scanlon B R 2008. Estimating groundwater recharge in a cold desert environment in northern China using chloride. *Hydrology Journal.* 16, 5, pp 893-910.

Gooddy D.C, Hughes A.G, Williams A.T, Armstrong A C, Nicholson R J and Williams J R. 2001. Field and modelling studies to assess the risk to UK groundwater from earth based stores for livestock manure. *Soil Use Management.* 17, 128-137.

Harter T, Davis H, Mathews M and Meyer R D. 2002. Shallow Groundwater quality on dairy farms with irrigated forage crops. *Journal of Contaminant Hydrology*. 55, 287-315.

Holliday D W. 1993. Geophysical log signatures in the Eden Shales (Permo-Triassic) of Cumbria and their regional significance, Proceedings of the Geological Society of Yorkshire 49, 4, 345-354.

Hooda P S, Edwards A.C, Anderson H A and Miller A. 2000. A review of water quality concerns in livestock farming areas. *Science of the Total Environment* 250: 143-167.

Ingram J A. 1978. The Permo-Triassic Sandstone Aquifers of North Cumbria, Hydrogeological Report, North West Water Authority.

Knott S D. 1994. Fault zone thickness versus displacement in the Permo-Triassic sandstones of NW England, *Journal of the Geological Society of London*, 151, 17-25.

Lord E I & Anthony S. 2000. MAGPIE (NEAP-N): A modelling framework for evaluating nitrate losses at national and catchment scales. *Soil Use Management* 16: 167–174

Macchi L. 1991. A field guide to the continental Permo-Triassic rocks of Cumbria and northwest Cheshire, Liverpool Geological Survey.

Ministry of Agriculture, Fisheries and Food, 1998. Code of Good Agricultural Practice for the Protection of Water, 'The Water Code'.

Millward D and McCormac M. 2003. Geology of the Appleby district. An explanation of the geological map Sheet 30 Appleby. British Geological Survey.

Monkhouse R A and Reeves, M J. 1977. A preliminary appraisal of the groundwater resources of the Vale of Eden, Cumbria, Technical Note, Central Water Planning Unit. Reading, No.11.

Parker J M, Chilton P J and McKittrick R. 1989. Nitrate leaching to groundwater from grassland on permeable soils BGS Report WD/89/40c.

Patrick C K. 1978. Hydrogeology. In The Geology of the Lake District F. Moseley, Ed. Yorkshire Geological Society (Occasional Publication No. 3).

Procter C and Metcalfe P, 2006. Nitrate levels and agricultural history at Greengill Head Farm. *ADAS*.

Rushton K R, 2003 Groundwater Hydrology: Conceptual and Computational Models Wiley ISBN: 0470850043.

Rushton K R, 2005. Estimating recharge for British aquifers Water and Environment Journal Volume 19, Issue 2 , Pages115 – 124 2005 J. CIWEM.

Shand P, Hargreaves R and Brewerton L J. 1997. The Natural (Baseline) Quality of Groundwaters in England and Wales. Part 4: The Triassic Sandstones of Cumbria. British Geological Survey Technical Report WD/97/54 Hydrogeology Series.

Waugh B. 1970. Petrology, provenance and silica diagenesis of the Penrith Sandstone (Lower Permian) of north-west England. *Journal of Sedimentary Petrology*. 40, 1226-1240.

Warrington G, Audley-Charles M G, Elliot R E, Evans W B, Ivimey-Cook H C, Kent P E, Robinson P L, Shotton S W and Taylor F M. 1980. A Correlation of Triassic Rocks in the British Isles. Special Report of the Geological Society of London, No 13.

Younger P L and Milne C A 1997 Hydrostratigraphy and hydrogeochemistry of the Vale of Eden, Cumbria, UK. Proceedings of the Yorkshire Geological Society, Vol.51, No.Pt 4, pp.349-366.

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APPENDICES

Appendix 1.	Borehole EV1 profile porewater hydrochemical data.
Appendix 2.	Three figures illustrating impact of unsaturated zone travel times over catchment
Appendix 3.	Report from ADAS Metcalf for land use history at Greengill Head Farm

Appendix 1. Borehole EV1 profile porewater hydrochemical data

SAMPLE ID	FIELD ID	Depth m bgl	Al	As	B	Ba	Ca	Cl	Cr	Cu	Fe	HCO3 *Field*	K	Li	Mg	Mn	Mo	Na	NH4-N	Ni	NO2-N	NO3-N	P	pH *Field*	SEC *Field*	Si	SO4	Sr	Zn
S04-00826	EV1/1	1.0	0.045	< 0.05	3.85	0.341	21.9	73.3	0.0056	0.0654	< 0.005		10.2	< 0.004	1.61	0.3	0.003	57.3	0.39	0.0056	0.054	11.9	0.16		415	5.3	16.1	0.0604	0.24
S04-00827	EV1/2	3.2	0.076	< 0.05	2.36	0.296	14.2	31.9	0.0043	0.0476	< 0.005	11.1	9.28	0.0056	0.934	0.359	< 0.003	29.5	0.132	< 0.005	0.0404	10.4	< 0.1	6.9	243	4.52	11.1	0.0384	0.194
S04-00828	EV1/3	4.4	0.052	< 0.05	0.97	0.233	10.1	25.3	< 0.002	0.0701	< 0.005	8.42	9.45	0.0164	0.678	0.265	< 0.003	22.6	0.358	0.0093	0.0185	9.51	< 0.1	6.96	183	3.83	13.2	0.0313	0.124
S04-00829	EV1/4	5.5	0.064	< 0.05	0.99	0.31	12.1	23.4	0.0023	0.0292	< 0.005	8.09	9.89	< 0.004	0.724	0.294	< 0.003	27.9	0.34	< 0.005	0.012	11.9	< 0.1	6.89	203	4.22	11.2	0.0384	0.092
S04-00830	EV1/5	6.6	0.05	< 0.05	0.83	0.311	11.3	18.6	< 0.002	0.0314	< 0.005	< 0.1	8.59	0.0163	0.502	0.34	< 0.003	19.9	0.311	0.0081	0.0081	9.51	0.14	6.64	190	4.15	12.9	0.0344	0.121
S04-00831	EV1/6	7.1	0.136	< 0.05	0.73	0.356	9.36	18.9	0.0028	0.0465	0.005	2.26	7.3	< 0.004	0.544	0.358	< 0.003	21.6	0.1	< 0.005	0.0044	9.16	< 0.1	6.19	189	4.16	13	0.0317	0.136
S04-00832	EV1/7	8.2	0.231	< 0.05	0.69	0.383	10.7	22.0	0.0024	0.0449	< 0.005	< 0.1	5.55	< 0.004	0.562	0.383	< 0.003	19	0.097	< 0.005	0.004	9.18	< 0.1	5.81	195	3.85	11.7	0.0319	0.149
S04-00833	EV1/8	8.9	0.411	< 0.05	0.92	0.326	10	29.7	0.0031	0.0586	0.0103	< 0.1	4.42	< 0.004	0.569	0.336	< 0.003	21.5	0.1	< 0.005	0.0054	6.5	< 0.1	5.52	200	4.81	12.4	0.029	0.143
S04-00834	EV1/9	9.9	0.371	< 0.05	2.25	0.475	8.95	54.4	0.0045	0.0338	0.0206		4.38	< 0.004	2.96	1.42	< 0.003	38.8	0.37	0.0084	0.013	6.33	< 0.1		289	5.9	12.5	0.07	0.153
S04-00835	EV1/10	11.2	< 0.01	< 0.05	0.73	0.527	4.68	27.3	0.0026	0.0083	< 0.005	2.86	4.66	0.017	8.54	0.268	< 0.003	14.4	0.064	0.0053	0.0109	7.25	0.33	6.44	189	5.31	11	0.0815	0.046
S04-00836	EV1/11	12.1	0.095	< 0.05	0.73	1.06	10	46.3	0.0038	0.0118	< 0.005	6.66	5.81	< 0.004	13.1	0.389	< 0.003	21.8	0.109	0.0105	0.0041	17.6	< 0.1	6.49	306	5.66	2.55	0.164	0.080
S04-00837	EV1/12	13.1	0.027	< 0.05	0.76	0.939	11.3	40.8	0.0035	0.0128	< 0.005	2.88	8.4	< 0.004	11.4	0.13	< 0.003	22.7	0.119	0.0109	0.0086	18.9	< 0.1	6.61	308	5.43	2.62	0.152	0.073
S04-00838	EV1/13	14.2	0.013	< 0.05	0.93	0.386	6.32	22.4	0.0045	0.0197	< 0.005	6.77	6.03	< 0.004	3.67	0.0578	< 0.003	19.3	0.098	< 0.005	0.0159	9.19	0.2	6.85	179	5.75	3.4	0.0494	0.064
S04-00839	EV1/14	15.0	< 0.01	< 0.05	0.96	0.396	6.65	23.6	0.0037	0.018	< 0.005	2.06	6.5	< 0.004	4.26	0.0494	< 0.003	21.3	0.19	0.0071	0.0131	9.62	0.13	6.59	194	5.42	3.55	0.0556	0.078
S04-00840	EV1/15	16.2	< 0.01	< 0.05	0.89	0.461	10.8	25.1	0.004	0.0094	< 0.005	5.38	7.23	< 0.004	5.21	0.065	< 0.003	18.8	0.475	< 0.005	0.0145	12.9	0.13	6.58	220	5.78	2.32	0.0685	0.057
S04-00841	EV1/16	17.1	0.011	< 0.05	1.3	0.605	15.9	33.4	0.0048	0.0172	< 0.005	4.73	8.83	0.0053	6.3	0.0985	< 0.003	24.3	0.614	< 0.005	0.0552	19.8	0.25	6.69	306	5.44	2.51	0.0884	0.08
S04-00842	EV1/17	19.6	0.016	< 0.05	0.97	0.581	19	28.7	0.0039	0.0286	< 0.005	3.49	6.21	< 0.004	5.95	0.0571	< 0.003	24.5	0.113	< 0.005	0.0159	19.8	< 0.1	6.56	282	5.5	1.85	0.0886	0.081
S04-00843	EV1/18	20.2	0.023	< 0.05	1.09	1.12	44.4	37.5	0.004	0.033	< 0.005	3.98	7.83	0.0143	10.1	0.157	< 0.003	28.1	0.187	0.0074	0.0786	36.7	0.31	6.71	438	5.68	2.18	0.175	0.138
S04-00844	EV1/19	21.1	< 0.01	< 0.05	0.71	0.76	29.1	27.9	0.003	0.0275	< 0.005	3.02	6.4	0.0048	7.26	0.0663	< 0.003	21.8	0.124	< 0.005	0.0155	28.1	0.19	6.63	334	5.23	1.62	0.12	0.088
S04-00845	EV1/20	22.1	< 0.01	< 0.05	0.85	0.94	39.6	34.5	0.0023	0.0256	< 0.005	2.53	6.7	< 0.004	8.81	0.0928	< 0.003	24.4	0.155	0.0061	0.0117	38.5	< 0.1	6.56	429	5.02	1.38	0.156	0.108
S04-00846	EV1/21	23.0	0.028	< 0.05	2.63	1.01	49.6	43.4	0.0036	0.113	< 0.005	< 0.1	8.85	0.179	9.44	0.478	< 0.003	35.5	0.225	0.0134	0.0575	46.7	1.8	6.34	536	6.9	3.54	0.183	0.193
S04-00847	EV1/22	24.0	< 0.01	< 0.05	0.87	0.978	52.9	34.2	0.0041	0.0197	< 0.005	2.97	8.65	< 0.004	9.95	0.125	< 0.003	28.5	0.845	0.0073	0.0102		< 0.1	6.55	545	6.05	0.86	0.192	0.090
S04-00848	EV1/23	24.9	0.019	< 0.05	1.24	1.14	52	38.4	0.0043	0.0283	< 0.005	1.76	8.16	0.0092	9.28	0.144	< 0.003	35.2	0.776	0.0072	0.0064		< 0.1	6.43	559	5.97	0.78	0.182	0.117
S04-00849	EV1/24	26.1	0.017	< 0.05	0.7	1.18	53	29.5	0.0033	0.0376	< 0.005	1.63	8.8	0.0108	8.86	0.0709	< 0.003	26.5	0.2	0.0074	0.0117		0.19	6.19	502	5.65	0.43	0.18	0.11
S04-00850	EV1/25	26.9	< 0.01	< 0.05	0.69	1.09	55.1	34.7	0.0035	0.0684	< 0.005	2.01	9.72	0.0077	9	0.0862	< 0.003	27.3	0.509	0.0083	0.0061		0.19	6.17	529	5.18	1.32	0.185	0.121
S04-00851	EV1/26	28.0	0.011	< 0.05	0.73	1.07	56.3	33.7	0.003	0.0278	< 0.005	1.04	9.5	0.0086	9.03	0.0841	< 0.003	28	0.346	0.0076	0.0117		0.11	5.56	563	6.04	0.5	0.19	0.13
S04-00852	EV1/27	28.9	< 0.01	< 0.05	0.63	0.915	43.7	31.6	0.0025	0.0291	< 0.005	1.95	7.61	0.0047	6.7	0.0469	< 0.003	24.7	0.225	0.0059	0.0284	43.6	0.14	6.3	457	5.01	0.43	0.142	0.103
S04-00853	EV1/28	30.0	< 0.01	< 0.05	0.76	0.614	28	34.4	0.0033	0.0124	< 0.005	1.88	6.52	0.0059	4.13	0.0351	< 0.003	42.3	0.332	< 0.005	0.0116	40.9	< 0.1	6.54	451	5.76	0.67	0.0876	0.119
S04-00854	EV1/29	30.9	0.016	< 0.05	0.83	0.797	37.9	35.7	0.0032	0.0127	< 0.005	1.48	7.32	0.0069	5.73	0.0531	< 0.003	42.3	0.133	< 0.005	0.0093	45	< 0.1	6.24	474	5.93	0.47	0.125	0.108
S04-00855	EV1/30	32.0	< 0.01	< 0.05	0.63	0.726	36.1	34.0	0.0029	0.0107	< 0.005	1.11	7.11	0.0112	5.55	0.0461	< 0.003	42.8	0.11	< 0.005	0.0178	49.6	0.19	5.69	497	4.87	< 0.1	0.117	0.111
S04-00856	EV1/31	33.1	< 0.01	< 0.05	0.55	0.583	24.7	23.4	0.0024	< 0.008	< 0.005	2.51	5.41	< 0.004	4.29	0.0353	< 0.003	18.4	0.068	< 0.005	0.0105	24.3	< 0.1	6.46	277	4.6	0.57	0.0867	0.084
S04-00857	EV1/32	33.9	< 0.01	< 0.05	0.65	0.646	24.7	24.4	0.0025	< 0.008	< 0.005	1.52	5.43	< 0.004	4.23	0.0427	< 0.003	18.8	0.342	< 0.005	0.0252	24.6	0.32	6.4	279	4.41	1.24	0.085	0.080
S04-00858	EV1/33	35.3	< 0.01	< 0.05	1.41	0.784	33	38.9	0.0039	0.0189	< 0.005	1.43	6.57	0.0068	5.21	0.0448	< 0.003	30	0.378	< 0.005	0.0074	35.1	0.12	6.38	393	6.01	0.38	0.107	0.100
S04-00859	EV1/34	36.1	< 0.01	< 0.05	0.97	0.771	32.9	30.7	0.0034	0.0122	< 0.005	1.24	6.79	0.0043	5.07	0.0534	< 0.003	23.5	0.439	< 0.005	0.0164	32.1	< 0.1	5.51	354	5.73	0.29	0.101	0.095
S04-00860	EV1/35	36.6	< 0.01	< 0.05	0.94	0.873	35.6	33.6	0.0046	0.0168	< 0.005	< 0.1	6.77	< 0.004	5.35	0.0688	< 0.003	27.7	0.543	< 0.005	0.0078	36.2	< 0.1	5.51	366	5.51	0.24	0.108	0.091
S04-00864	EV1/36	38.1	0.022	< 0.05	0.98	1.07	40.1	26.9	0.0031	0.0257	< 0.005	2.81	8.99	0.0095	5.92	0.069	< 0.003	26.7	0.462	< 0.005	0.0777	37.9	0.96	5.74	417	6.63	8.85	0.12	0.128
S04-00865	EV1/37	39.1	< 0.01	< 0.05	0.78	1.26	48.4	31.2	0.0036	0.0186	< 0.005	1.79	9.01	0.0069	6.68	0.0804	< 0.003	25.6	0.341	< 0.005	0.0188	47.9	0.39	6.43	493	5.98	10.6	0.139	0.109
S04-00866	EV1/38	40.0	< 0.01	< 0.05	0.57	0.991	33	31.0	0.003	0.0163	< 0.005	1.66	6.99	0.0101	4.58	0.0532	< 0.003	42.4	0.263	< 0.005	0.0282	49.1	0.43	6.11	480	5.27	8.65	0.0914	0.102
S04-00867	EV1/39	45.0	< 0.01	< 0.05	1.19	0.879	34.9	42.7	0.0047	0.169	0.0072	19.3	7.51	< 0.004	4.71	0.0295	0.003	51.1	0.51	< 0.005	0.0523	39	0.11		502	6.76	2.42	0.106	0.821
S04-00868	EV1/40	46.0	< 0.01	< 0.05	1.14	0.676	30.5	35.4	0.0048	0.0346	0.0059	< 0.1	6.33	< 0.004	4.17	0.0241	< 0.003	45.8	0.371	< 0.005	0.0747	20.9	0.2		431	6.15	1.21	0.0935	0.201
S04-00869	EV1/41	47.2	< 0.01	< 0.05	1.11	0.758	29.1	43.3	0.0047	0.0529	0.0151	5.97	6.22	< 0.004	4.07	0.022	< 0.003	47.5	0.14	< 0.005	0.051	31	0.18		471	6.61	4	0.0941	0.203
S04-00870	EV1/42	48.1	0.056	< 0.05	1.39	0.77	28.8	48.0	0.0068	0.0387	0.0598	3.72	6.09	< 0.004	4	0.0288	0.004	47.6	0.417	< 0.005	0.0333	34.6	0.12		519	6.25	0.83	0.095	0.159

Units mg/l except SEC: uS/cm and pH

Appendix 1 (cont'd)

SAMPLE ID	FIELD ID	Depth m bgl	Al	As	B	Ba	Ca	Cl	Cr	Cu	Fe	HCO3 *Field*	K	Li	Mg	Mn	Mo	Na	NH4-N	Ni	NO2-N	NO3-N	P	pH *Field*	SEC *Field*	Si	SO4	Sr	Zn
S04-00871	EV1/43	49.0	< 0.01	< 0.05	0.83	0.63	26	36.2	0.0042	0.0989	0.0142	1.53	5.41	< 0.004	3.98	0.0218	0.003	41.1	0.188	< 0.005	0.0592	32.4	0.13		436	5.83	0.23	0.0987	0.16
S04-00872	EV1/44	49.8	< 0.01	< 0.05	0.86	0.685	26.6	38.0	0.0042	0.131	< 0.005	< 0.1	5.79	< 0.004	4.72	0.0202	< 0.003	43.8	0.155	< 0.005	0.0263	33.9	< 0.1		449	5.97	0.83	0.12	0.136
S04-00873	EV1/45	51.8	< 0.01	< 0.05	0.65	0.667	22.4	38.7	0.0038	0.112	< 0.005	5.23	6.13	0.0081	5.74	0.0207	< 0.003	34.5	0.101	< 0.005	0.0546	32.4	< 0.1	6.19	381	6.45	0.86	0.127	0.091
S04-00874	EV1/46	53.0	< 0.01	< 0.05	0.89	0.563	18.4	42.3	0.0044	0.0562	< 0.005	1.96	5.82	0.0061	5.98	0.0192	< 0.003	34.9	0.181	< 0.005	0.0176	28.3	< 0.1	6.08	339	6.47	1.34	0.115	0.076
S04-00875	EV1/47	54.0	< 0.01	< 0.05	0.8	0.387	15.7	39.2	0.0044	0.0328	< 0.005	2.21	5.52	0.0064	5.65	0.0183	< 0.003	30.4	0.128	< 0.005	0.0327	24.3	< 0.1	6.1	295	6.26	1.42	0.101	0.057
S04-00876	EV1/48	55.0	< 0.01	< 0.05	0.77	0.397	14.5	40.7	0.0042	0.0821	< 0.005	1.01	5.86	0.011	7.14	0.0234	< 0.003	30.8	0.063	< 0.005	0.172	23.2	0.13	5.93	310	6.74	1.67	0.105	0.091
S04-00877	EV1/49	56.0	< 0.01	< 0.05	0.79	0.434	13	41.4	0.0059	0.0771	< 0.005	1.85	5.71	0.021	6.78	0.0134	< 0.003	31	0.066	< 0.005	0.683	21.3	0.35	6.31	307	6.79	1.84	0.0968	0.069
S04-00878	EV1/50	57.0	< 0.01	< 0.05	0.95	0.347	11.9	44.8	0.0052	0.113	< 0.005	1.26	5.36	0.0125	6.81	0.0219	< 0.003	30.8	0.082	< 0.005	0.312	21.7	0.19	6.55	299	6.87	2.44	0.0908	0.084
S04-00879	EV1/51	58.3	0.013	< 0.05	0.81	0.362	10.8	42.8	0.0053	0.0798	< 0.005	1.31	5.11	0.008	6.86	0.0106	< 0.003	30	0.074	< 0.005	0.0528	18.7	< 0.1	6.5	281	6.31	2.58	0.0838	0.063
S04-00880	EV1/52	59.0	0.019	< 0.05	1.04	0.306	10.5	42.9	0.0072	0.0557	< 0.005	2.22	4.97	0.0083	6.67	0.0081	< 0.003	31.6	0.062	< 0.005	0.0622	18.4	< 0.1	6.4	273	7.26	2.01	0.0791	0.069
S04-00881	EV1/53	60.1	0.021	< 0.05	1.07	0.366	11.4	47.3	0.0065	0.0887	< 0.005	1.17	5.3	0.0062	7.14	0.0118	< 0.003	32.4	0.171	< 0.005	0.024	18.4	< 0.1	6.4	279	6.85	2.3	0.0853	0.069
S04-00882	EV1/54	61.1	0.027	< 0.05	1.23	0.359	12.1	40.0	0.0072	0.104	0.0167	5.87	5.28	< 0.004	7.43	0.0156	< 0.003	37.1	0.119	< 0.005	0.0146	17.4	0.11		327	7.34	3.27	0.0871	0.116
S04-00883	EV1/55	62.0	0.045	< 0.05	1.12	0.329	11.8	46.3	0.0061	0.069	< 0.005	2.1	5.53	0.0084	7.27	0.0165	< 0.003	34.2	0.095	< 0.005	0.0637	18	< 0.1	6.42	291	7.62	2.83	0.0857	0.066
S04-00884	EV1/56	63.0	0.028	< 0.05	0.9	0.381	13	48.4	0.0062	0.074	< 0.005	1.4	6.06	0.0111	7.2	0.0157	< 0.003	31.4	0.056	< 0.005	0.0756	17.1	0.12	6.36	299	6.9	2.22	0.0989	0.059
S04-00885	EV1/57	64.0	0.097	< 0.05	1.44	0.356	14.5	49.0	0.0068	0.161	0.0078	2.93	6.01	0.0292	8.49	0.0215	< 0.003	42.8	0.064	< 0.005	0.768	18	0.46		378	7.75	5.08	0.105	0.149
S04-00886	EV1/58	65.0	0.073	< 0.05	1.1	0.332	12.9	41.6	0.0079	0.145	0.0052	2.7	5.08	< 0.004	7.18	0.0156	0.004	39.3	0.062	< 0.005	0.0274	18.6	< 0.1		342	7.4	3.51	0.0938	0.117
S04-00887	EV1/59	65.9	0.029	< 0.05	0.71	0.413	13.3	40.2	0.0036	0.14	< 0.005	1.79	6.48	0.0883	8.88	0.0169	< 0.003	28.2	0.048	< 0.005	0.864	19.8	0.64	6.27	289	7.08	6.04	0.0961	0.078
S04-00888	EV1/60	67.1	0.025	< 0.05	0.86	0.407	14.4	45.9	0.0064	0.118	< 0.005	1.51	6.41	0.0135	8.86	0.0198	< 0.003	32.7	0.054	< 0.005	0.0825	22.1	0.14	6.57	307	7.81	2.53	0.102	0.065
S04-00889	EV1/61	67.9	0.03	< 0.05	0.67	0.552	15.3	43.1	0.0051	0.106	< 0.005	0.98	6.63	0.0196	9.16	0.0153	< 0.003	31	0.047	< 0.005	0.207	20.5	0.29	6.41	312	7.24	2.16	0.11	0.069
S04-00890	EV1/62	71.1	0.021	< 0.05	1.33	0.368	13.3	40.4	0.0052	0.0964	< 0.005	1.14	5.95	0.0999	6.38	0.0393	< 0.003	28	0.06	< 0.005	0.626	12.7	9.97	6.75	266	7.33	11.1	0.074	0.088
S04-00891	EV1/63	71.8	0.014	< 0.05	0.86	0.442	13.8	43.4	0.0059	0.0917	< 0.005	1.02	5.29	0.0324	4.84	0.0125	< 0.003	27	0.045	< 0.005	0.0228	11.5	4.15	6.5	250	7.2	9.13	0.0635	0.072
S04-00892	EV1/64	73.1	< 0.01	< 0.05	0.83	0.677	32.2	44.2	0.005	0.0933	< 0.005	< 0.1	7.83	0.0088	7.53	0.0192	< 0.003	33.2	0.212	< 0.005	0.0103	39.2	0.39	5.68	415	7.21	1.99	0.126	0.077
S04-00893	EV1/65	76.3	< 0.01	< 0.05	1.26	0.406	11.2	43.2	0.0053	0.111	< 0.005	< 0.1	4.88	< 0.004	3.38	0.0052	< 0.003	28	0.17	< 0.005	0.0268	6.8	0.33		264	9.03	2.98	0.05	0.101
S04-00894	EV1/66	77.1	< 0.01	< 0.05	0.73	0.4	15.7	47.4	0.0043	0.0593	< 0.005	< 0.1	6.36	0.0041	4.11	0.0146	< 0.003	28.6	0.108	< 0.005	0.0156	14.5	0.15	5.26	279	7.79	4.13	0.0662	0.050
S04-00895	EV1/67	78.0	< 0.01	< 0.05	0.28	0.375	15.3	32.2	< 0.002	0.02	< 0.005	5.99	7.89	0.0312	3.55	0.421	0.004	19.6	0.291	< 0.005	0.357	13.9	0.26	7.12	231	3.69	7.59	0.0618	0.117
S04-00896	EV1/68	79.1	< 0.01	< 0.05	0.34	0.575	18.9	35.2	0.0021	0.0435	< 0.005	1.97	8.02	0.014	3.72	0.208	< 0.003	22.1	0.076	< 0.005	0.0917	18.8	< 0.1	6.67	264	6.04	5.12	0.0748	0.118
S04-00897	EV1/69	80.1	< 0.01	< 0.05	0.24	0.508	17.8	30.6	< 0.002	0.026	< 0.005	3	8.41	0.0236	3.59	0.268	< 0.003	20.1	0.082	< 0.005	0.152	18	0.1	6.69	239	5.34	6.73	0.0713	0.139
S04-00898	EV1/70	81.0	< 0.01	< 0.05	0.38	0.565	17.8	34.8	< 0.002	0.0751	< 0.005	5.62	9.14	0.107	3.92	0.144	< 0.003	21.5	0.119	< 0.005	0.594	14.7	1.33	6.98	224	4.78	10	0.0743	0.125
S04-00899	EV1/71	82.1	< 0.01	< 0.05	1.38	0.419	15.3	52.6	0.0063	0.0962	< 0.005	8.2	6.26	0.0451	3.49	0.0537	0.005	36	0.12	< 0.005	0.247	7.63	2.15		336	7.07	8.49	0.063	0.181
S04-00900	EV1/72	83.2	< 0.01	< 0.05	2.68	0.5	17.7	77.1	0.0125	0.194	0.0165	4.59	6.63	< 0.004	3.98	0.0188	0.014	57.1	0.11	< 0.005	0.0326	2.82	0.53		450	9.72	8.89	0.0732	0.315
S04-00901	EV1/73	83.7	< 0.01	< 0.05	1.8	0.499	16.2	42.2	0.0036	0.103	< 0.005	3.06	5.9	0.204	3.53	0.0264	0.004	29.1	0.195	< 0.005	0.111	4.38	4.15		273	6.96	17.7	0.0663	0.128
S04-00902	EV1/74	84.0	< 0.01	< 0.05	1.95	0.912	39.7	7.6	0.0067	0.158	0.0171	7.62	10.3	0.122	8.38	0.0292	0.004	64.2	< 0.07	< 0.005	0.009	0.05	2.97		495	6.94	277	0.166	0.184
S04-00903	EV1/75	85.1	< 0.01	< 0.05	1.19	0.732	28.3	11.7	0.0058	0.0935	0.0086	3.86	7.55	0.0296	5.78	0.0154	0.005	45.9	< 0.04	< 0.005	0.0078	1.99	0.96		351	6.36	173	0.12	0.088
S04-00904	EV1/76	86.0	< 0.01	< 0.05	0.97	0.909	33.4	7.6	0.0052	0.0996	< 0.005	3.5	7.12	0.151	6.59	0.0528	0.004	73.4	< 0.04	< 0.005	0.0049	0.21	1.3		426	4.69	316	0.148	0.125
S04-00905	EV1/77	87.0	< 0.01	< 0.05	1.61	1.03	30.1	41.8	0.0047	0.0952	< 0.005	0.71	7.83	0.7	6.15	0.0436	0.003	34.9	0.464	< 0.005	0.0494	8.98	1.07	6.75	316	6.73	107	0.129	0.080
S04-00906	EV1/78	88.0	< 0.01	< 0.05	0.54	0.703	19.7	36.5	0.0041	0.0558	< 0.005	4.11	7.02	0.0178	4.14	0.0114	< 0.003	24.6	< 0.01	< 0.005	0.0359	11.3	1.56	6.08	239	7.15	32.9	0.0911	0.075
S04-00907	EV1/79	88.9	< 0.01	< 0.05	0.42	0.831	20.4	38.1	0.0036	0.082	< 0.005	2.06	6.59	0.0104	4.27	0.0099	< 0.003	24.2	< 0.01	< 0.005	0.0655	13.7	0.62	6.61	250	6.59	20.6	0.0945	0.069
S04-00908	EV1/80	89.7	< 0.01	< 0.05	0.47	0.538	12.4	36.6	0.0039	0.0502	< 0.005	1.29	5.41	< 0.004	2.64	0.0039	< 0.003	21.6	< 0.01	< 0.005	0.004	7.48	0.41	6.77	198	7.18	9.41	0.0581	0.069

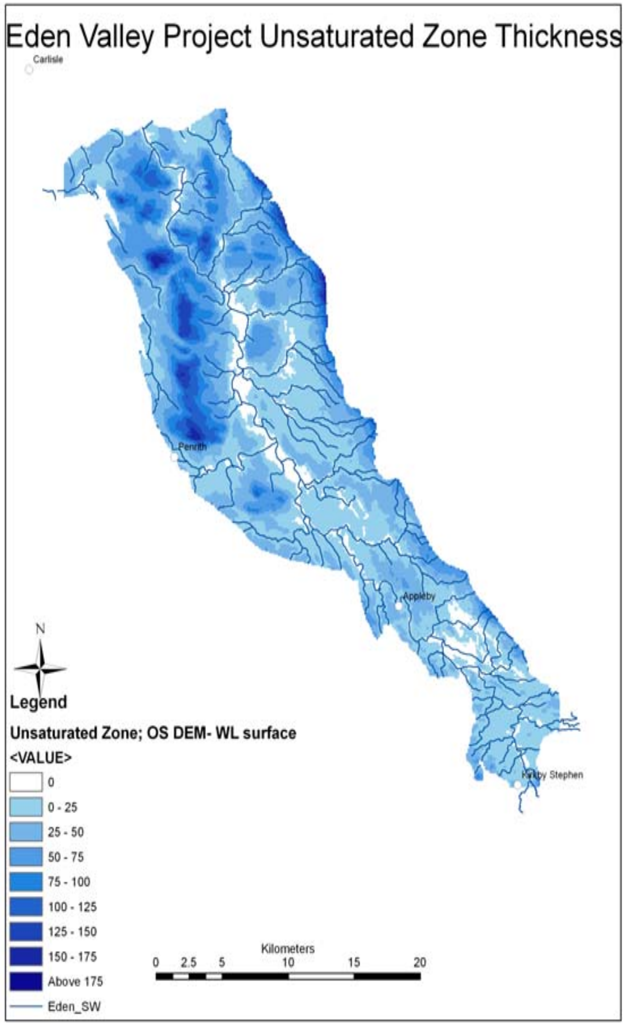
Units mg/l except SEC: uS/cm and pH

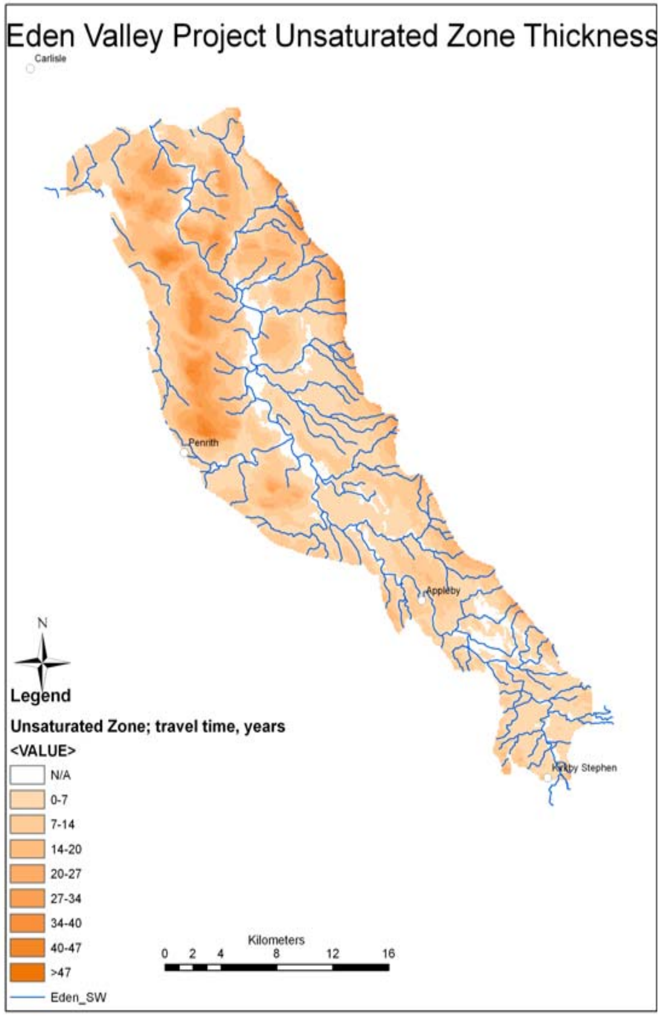
Appendix 1 (cont'd)

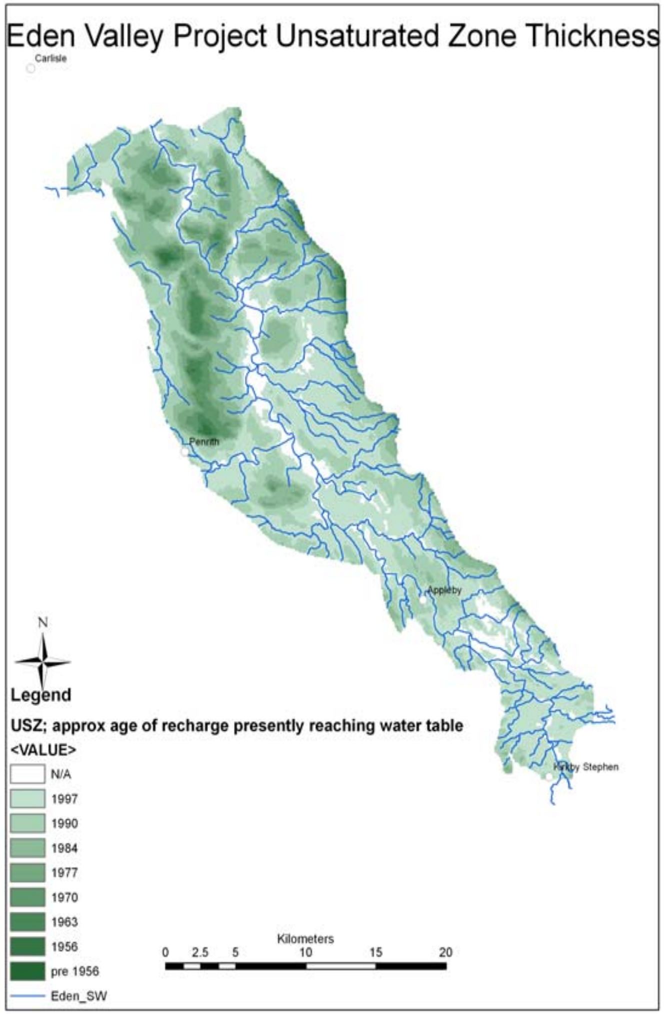
SAMPLE	FIELD	Depth	Al	As	B	Ba	Ca	Cl	Cr	Cu	Fe	HCO3	K	Li	Mg	Mn	Mo	Na	NH4-N	Ni	NO2-N	NO3-N	P	pH	SEC	Si	SO4	Sr	Zn
ID	ID	m bgl										*Field*												*Field*	*Field*				
S04-00909	EV1/81	90.5	< 0.01	< 0.05	0.78	0.529	13.2	43.2	0.0062	0.0512	< 0.005	2.44	5.52	< 0.004	2.88	0.0037	< 0.003	28.4	0.029	< 0.005	0.0146	7.44	0.13	6.64	216	7.6	7.71	0.064	0.049
S04-00910	EV1/82	92.0	< 0.01	< 0.05	0.33	5.09	181	22.8	0.0032	0.195	< 0.005	0.99	12.6	0.0516	28.5	0.345	0.003	302	< 0.01	0.0159	0.0498	5.94	2.73	6.75	799	4.67	1050	0.848	0.37
S04-00911	EV1/83	93.0	< 0.01	< 0.05	0.48	0.733	18.2	41.8	0.004	0.0617	< 0.005	1.02	5.67	0.0045	3.67	0.0074	< 0.003	23.9	< 0.01	< 0.005	0.0056	11.8	0.24	6.39	256	6.1	21.1	0.085	0.055
S04-00912	EV1/84	94.0	< 0.01	< 0.05	0.92	0.758	20	52.7	0.0066	0.0589	< 0.005	2.56	6.72	< 0.004	4.02	0.0046	< 0.003	30.1	< 0.01	< 0.005	0.0053	13.3	< 0.1	6.83	285	7.59	13.7	0.089	0.075
S04-00913	EV1/85	95.0	< 0.01	< 0.05	0.48	0.733	19.7	43.6	0.0038	0.0761	< 0.005	3.12	6.71	0.0051	4.29	0.0081	< 0.003	24.9	< 0.01	< 0.005	0.0246	12	0.2	6.77	259	6.55	21.8	0.093	0.063
S04-00914	EV1/86	95.8	< 0.01	< 0.05	0.97	0.767	18	42.3	0.0071	0.0535	< 0.005	2.14	6.63	0.0343	4.75	0.0074	< 0.003	35.7	< 0.01	< 0.005	0.148	11.9	0.15	6.34	260	7.02	29.4	0.091	0.059
S04-00915	EV1/87	96.8	< 0.01	< 0.05	1.24	0.551	14.5	10.0	0.0034	0.0939	< 0.005	< 0.1	5.14	< 0.004	4.1	0.0059	< 0.003	29.4	< 0.07	< 0.005	< 0.002	7.61	0.16		280	6.34	3.81	0.076	0.109
S04-00916	EV1/88	98.4	< 0.01	< 0.05	0.76	0.683	17.7	48.5	0.0061	0.0684	< 0.005	1.05	6.76	0.012	5.43	0.0189	< 0.003	29.3	0.023	< 0.005	0.0542	10.8	0.15	5.85		7.31	29.2	0.090	0.063
S04-00917	EV1/89	99.1	< 0.01	< 0.05	0.53	0.557	18.5	29.8	0.0041	0.0566	< 0.005	2.15	6.29	< 0.004	5.57	0.0179	< 0.003	24	< 0.01	< 0.005	0.134	3.84	0.34	6.65		6.36	84.8	0.092	0.058
S04-00923	EV1/95	105.0	0.024	< 0.05	0.39	0.401	11.4	18.3	0.0028	0.0329	< 0.005	3.34	5	0.0429	3.33	0.0177	< 0.003	20.4		< 0.005	0.0003	3.82	0.77	6.81	144	6.03	44.9	0.050	0.099
S04-00924	EV1/96	106.1	0.031	< 0.05	0.28	0.223	8.02	10.2	0.0028	0.0182	< 0.005	3.19	4.08	0.0364	2.35	0.0079	< 0.003	18.9		< 0.005	0.164	0.55	0.49	6.76	108	5.37	60.7	0.035	0.052
S04-00925	EV1/97	106.9	0.036	< 0.05	0.34	0.282	7.8	9.8	0.0022	0.0087	< 0.005	2.46	4.2	0.0276	2.26	0.0073	0.003	18.6		< 0.005	0.0057		0.44	6.61	*95.5*	6.54	70	0.034	0.053
S04-00926	EV1/98	108.0	0.052	< 0.05	0.38	0.292	19.4	23.9	0.0021	0.0447	< 0.005		6.42	0.105	3.91	0.0262	< 0.003	20.9	0.382	< 0.005	0.00883	4.26	0.7	*6.9*	*197.3*	6.23	41.2	0.076	0.131
S04-00927	EV1/99	109.0	0.016	< 0.05	0.32	0.245	12.9	11.1	0.0027	0.0161	< 0.005		4.61	0.208	2.84	0.006	< 0.003	20.4	0.014	< 0.005	0.00647	0.065	0.9	*7.04*	*175.5*	5.3	64.9	0.051	0.026
S04-00928	EV1/100	110.0	< 0.01	< 0.05	0.24	0.221	13.5	9.7	< 0.002	0.008	< 0.005		4.24	0.277	3.11	0.0054	< 0.003	20.6		< 0.005	0.0059	< 0.05	0.88	*7.08*	*178.3*	3.46	61.1	0.052	0.018
S04-00929	EV1/101	111.0	0.046	< 0.05	0.52	0.229	10.3	19.3	0.0043	0.0245	< 0.005		4.55	0.0462	2.01	0.0057	< 0.003	20		< 0.005	0.0224	0.406	0.65	*6.83*	*156.4*	5.94	31.5	0.04	0.056
S04-00932	EV1/104	114.0	0.039	< 0.05	0.74	0.414	10.9	29.2	0.0051	0.118	< 0.005	3.19	6	0.0331	1.82	0.0136	< 0.003	24.5		< 0.005	0.107	4.35	0.23	6.83	174	7.65	17.8	0.041	0.082
S04-00933	EV1/105	115.0	0.037	< 0.05	0.62	0.391	13.1	23.5	0.0038	0.0433	< 0.005	2.17	5.7	0.0232	1.96	0.0522	< 0.003	25.3		< 0.005	0.0661	6.93	0.17	6.36	173	6.08	29.2	0.047	0.138
S04-00934	EV1/106	116.2	0.031	< 0.05	0.64	0.47	15.6	23.4	0.0039	0.0671	< 0.005	2.34	6.06	0.0632	2.18	0.0261	< 0.003	27.4		< 0.005	0.0264	7.63	0.38	6.59	196	5.76	38.6	0.055	0.098
S04-00935	EV1/107	117.0	0.039	< 0.05	0.51	0.482	16.7	20.9	0.0027	0.0388	< 0.005	10.7	7.15	0.267	2.28	0.14	0.004	28.2		< 0.005	0.128	6.4	1.05	7.13	202	4.41	49.7	0.06	0.187
S04-00936	EV1/108	118.0	< 0.01	< 0.05	0.47	0.499	18.2	27.6	0.0034	0.0244	< 0.005	2.81	6.91	0.0782	2.41	0.117	< 0.003	25		< 0.005	0.158	13	0.54	6.4	216	5.6	18.5	0.065	0.232
S04-00937	EV1/109	119.0	0.044	< 0.05	0.52	0.566	20.7	29.4	0.0035	0.0239	< 0.005	4.87	8.5	0.0745	2.72	0.193	< 0.003	29.2		< 0.005	0.349	13.3	< 0.1	6.81	220	6.05	13.8	0.074	0.26

Units mg/l except SEC: uS/cm and pH

Appendix 2. Impact of unsaturated zone travel times over catchment







Appendix 3. Report from ADAS Metcalf for land use history at Greengill Head Farm

Nitrate Levels and Agricultural History at Greengill Head Farm

Chris Procter & Phil Metcalfe

1.1. History

The field has been farmed by the Thompson family for 3 generations and has been used for rough grazing. The land was bought in 1976 and gradually intensified with bracken control. Reseeding was carried out in the early 1980s. Figure. 1 shows the location of the drill site (NGR 527 322).

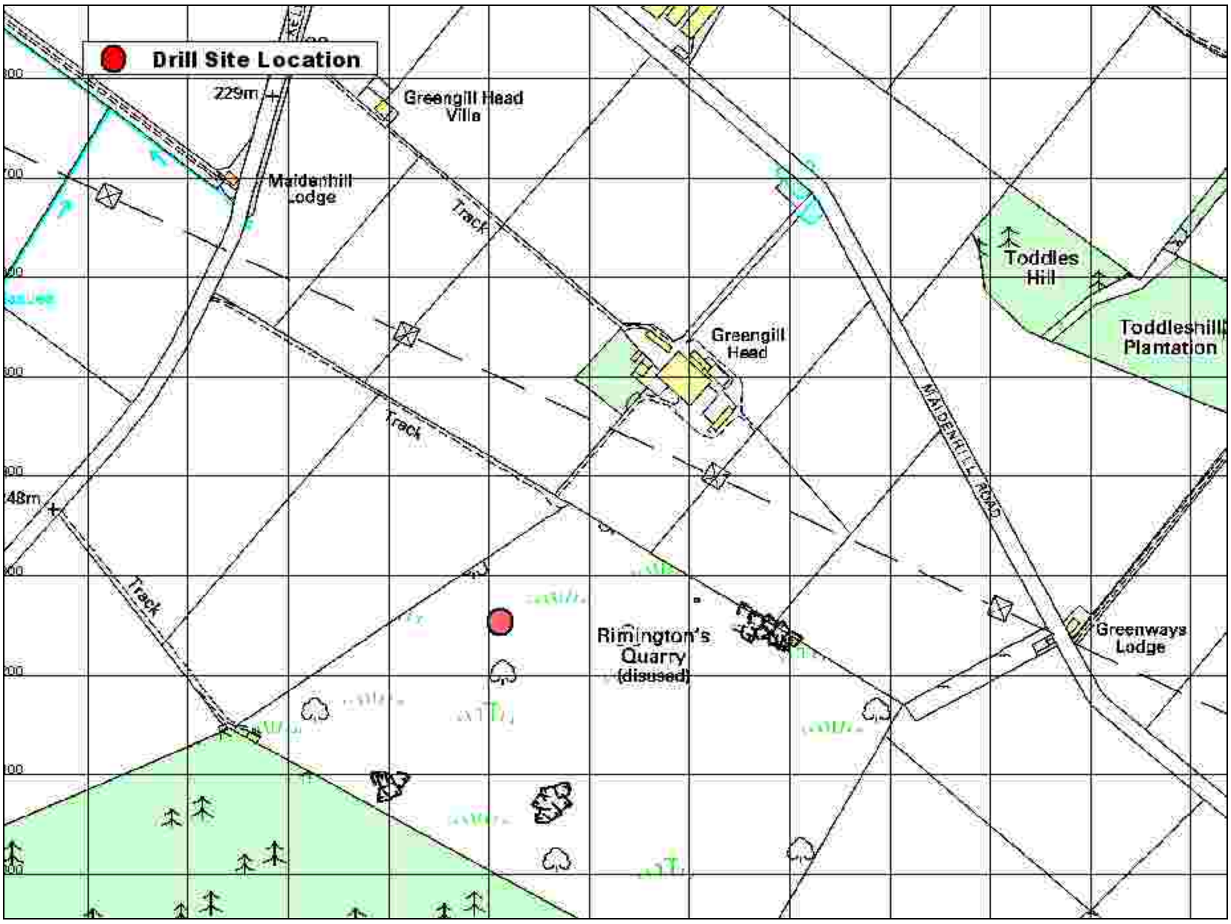


Figure. 1. The location of the drill site at Greengill Head Farm (NGR 527 322)

The completion of construction of a gas pipeline in 1982-1983 resulted in a re-profiling and levelling of the field for more intensive use. Since then the field has received slurry and chemical fertiliser on kale, rye and grassland crops.

The outbreak of Foot and Mouth in 2001 produced short term de-stocking of the farm. This also resulted in the reduction of slurry applications in 2001/2002 and a reduced chemical fertiliser use in 2001.

1.2. Nitrate and Calcium profiles

Figure. 2 shows the liming events on the field from 1974-2004. The levels of calcium in the pore water profile appear to follow the period of liming events from the earliest recorded in 1985.

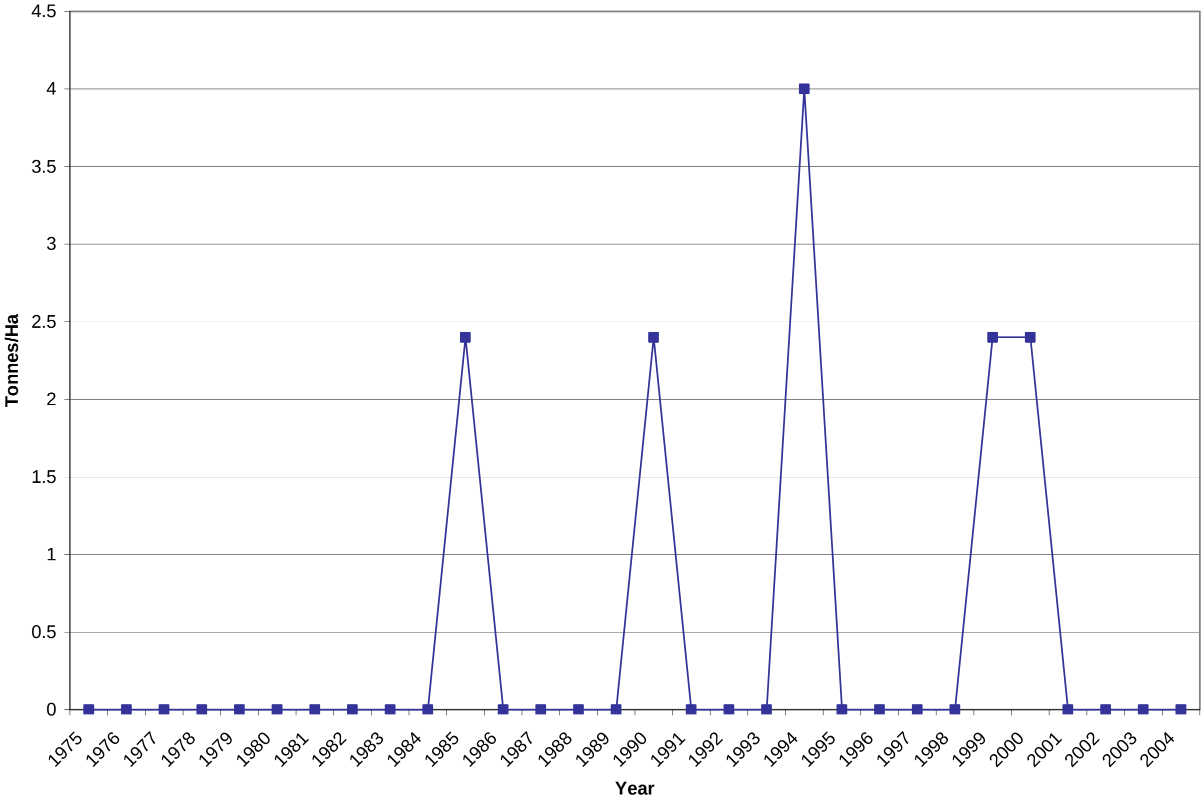


Figure. 2. Liming events at Greengill Head Farm (NGR 527 322) from 1974-2004

If there is calcium response to lime and response to a reduction of nitrogen after FMD then these do not exactly coincide with the scale for when FMD occurred. The surface of the field was re-profiled in 1983 after the gas pipeline was installed. This may have influenced the rate of infiltration near the surface. We could be seeing different rates of infiltration throughout the profile and as such the patterns not coinciding totally with the timing of Foot & Mouth.

Foot & Mouth Disease (FMD) cases in the area occurred in March 2001. The re-stocking took place by November/December 2001. All slurry up to March would have been spread in summer as part of FMD clear up, reduced as a result of no cows after March. The 2001 fertiliser applications were missed after the March application. Smaller quantities of slurry in 2002 resulted.

Figure. 3 shows the slurry applications to the field between 1974 and 2004. Very high slurry applications in the early 80s appear to correspond to a peak and the initial rise in nitrate with further peaks that correspond to Kale with slurry applications in 1997. There is no heavy slurry application event at the rise in 1990/93. In this period there was a high application in the adjacent field at a distance of 30m from the borehole position. It is possible for surface run off and infiltration from heavy applications further up the slope to drain over this distance.

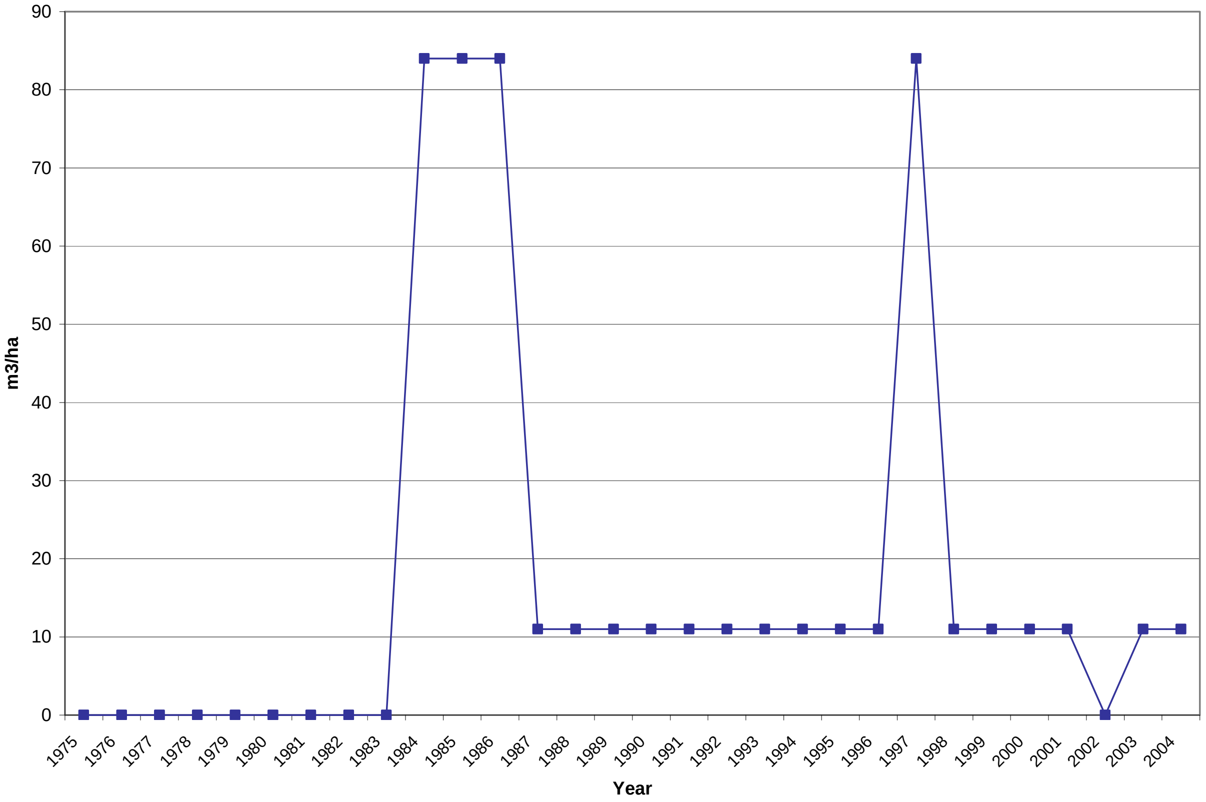


Figure. 3. Slurry applications at Greengill Head Farm (NGR 527 322) from 1974-2004

1.3. Leaching

Using the ADAS decision support tool Manner, the quantity of leaching from the applications of slurry are predicted. A January application of slurry at 82 m^3/ha applies 250 kg/ha and leaches 33kg/ha. A May application of the same amount onto grass would have minimal leaching. This would suggest that the high application events in May are not responsible for the peaks. There may be some leaching prior to full establishment.

Every year for a 12m^3/ha application in November, 11kg/ha N is leached. The light soil and low rainfall means that waste can be applied in every winter month. A convenient field close to the farm such as the one under consideration will receive repeated applications.

1.4. Chemical Fertilisers

Chemical fertiliser is applied at an overall farm rate of around 300 kg/ha. The field where the borehole was drilled tends to receive slightly less than the average. Figure 4 shows the application rate between 1974 and 2004. This level of fertiliser has been used on this field since it was brought into intensive grassland after the pipeline was put in 1982. In the years from 1976 the pasture was unimproved. Chemical fertiliser was used in increasing amounts. Detailed information on nitrogen fertiliser applied in selected years has been supplied by Mr Thompson. This information is presented in Table. 1. This shows monthly applications starting in March with the last application in July or mid August.

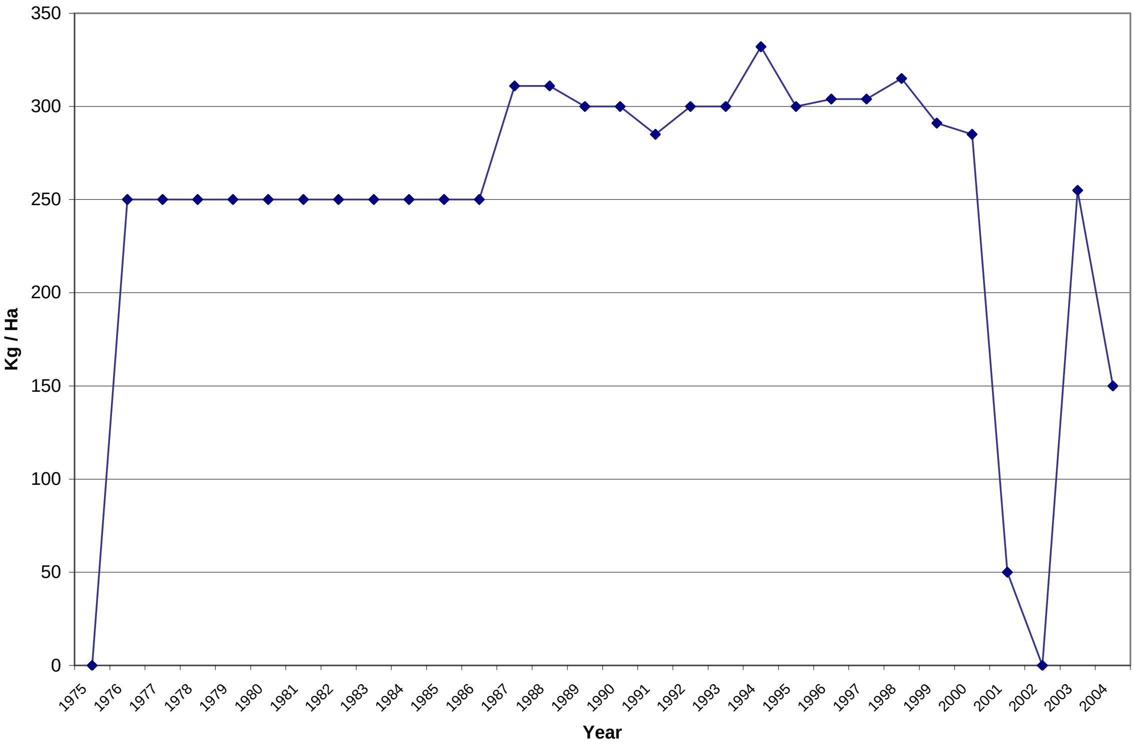


Figure. 4. Chemical Fertiliser application (Kg/Ha) at Greengill Head Farm (NGR 527 322) from 1974-2004

Table. 1. Fertiliser and Slurry Applications at Greengill Head Farm (NGR 527 322) from 1974-2004

Year	Dairy Cattle	Waste	Waste m^3/ha	Month	Fertiliser	Kg/ha	Month
1975	nil	nil	nil	N/A		nil	N/A
1976	120	nil	nil	nil		250 kg/ha *	March -Sept
1977	120	nil	nil	nil		250 kg/ha	March -Sept
1978	120	nil	nil	nil		250 kg/ha	March -Sept
1979	120	nil	nil	nil		250 kg/ha	March -Sept
1980	120	nil	nil	nil		250 kg/ha	March -Sept
1981	120	nil	nil	nil		250 kg/ha	March -Sept
1982	120	nil	nil	nil		250 kg/ha	March -Sept
1983	120	nil	nil	nil		250 kg/ha	March -Sept
1984	120	Slurry Application	67-84m3/ha	May		250 kg/ha	March -Sept
1985	120	Slurry Application	67-84m3/ha	May	Lime 2.4 t/ha	250 kg/ha	March -Sept
1986	120	Slurry Application	67-84m3/ha	May		250 kg/ha	March -Aug
1987	120	Slurry Application	11m3/h	June		311kg/ha	March -Aug
1988	120	Slurry Application	11m3/h	January		311kg/ha	March -July
1989	120	Slurry Application	11m3/h	January		300kg/ha	March -Aug
1990	120	Slurry Application	11m3/h	January	Lime 2.4 t/ha	300kg/ha	Dec lime
1991	120	Slurry Application	11m3/h	January		285kg/ha	March -July
1992	120	Slurry Application	11m3/h	January		300kg/ha	March -Aug
1993	120	Slurry Application	11m3/h	January		300kg/ha	March -Aug
1994	120	Slurry Application	11m3/h	January	Mg lime 4t/ha	332kg/ha	March -Aug
1995	120	Slurry Application	11m3/h	January		300kg/ha	March -Aug
1996	120	Slurry Application	11m3/h	January		304kg/ha	March -July
1997	120	Slurry Application	67-84m3/ha	May		304kg/ha	March -July
1998	120	Slurry Application	11m3/h	January		315kg/ha	March -Aug
1999	120	Slurry Application	11m3/h	January	Lime 2.4 t/ha	291kg/ha	March -Aug
2000	120	Slurry Application	11m3/h	January	Lime 2.4 t/ha	285kg/ha	March -Aug
2001	120	Slurry Application	11m3/h	January		50-100kg/ha	March
2002	nil	Slurry Application	nil	N/A			Feb-Aug
2003	120	Slurry Application	11m3/h	January		255kg/ha	Feb-Aug
2004	120	Slurry Application	11m3/h	January		150 kg/ha	March – July