

Investigation of Rising Nitrate Concentrations In Groundwater In The Eden Valley, Cumbria:

4. Estimating Recharge Rates Through Glacial Till Using An Applied Tracer Technique

Groundwater Systems and Water Quality
Commissioned Report OR/09/059

Environment Agency Science Group
Project SC030113



A joint programme of research by the British Geological Survey and the Environment Agency with additional support from United Utilities Plc.

BRITISH GEOLOGICAL SURVEY
Commissioned Report OR/09/059
ENVIRONMENT AGENCY
Science Group Project SC030113

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Cover illustration

Shallow Till sampling at test site in the Eden Valley west from near Penrith

Key words

Nitrate, Penrith Sandstone, Cumbria, recharge, tracer, hydrogeology, Till, UK aquifer.

Bibliographic Reference

Butcher, A., Griffiths, K., Lapworth, D., Humpage A., Burke, S. 2009. Investigation of Rising Nitrate Concentration in Groundwater in the Eden Valley, Cumbria: Estimating Recharge Rates Through Glacial Till Using an Applied Tracer Technique.

British Geological Survey Commissioned Report No. OR/09/059.

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

4. Estimating Recharge Rates Through Glacial Till Using An Applied Tracer Technique

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Environment Agency Science Group, Solihull 2009
British Geological Survey, Keyworth, Nottingham 2009

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ACKNOWLEDGEMENTS

This work would not have been possible without the support of the Thompson family, land owners at Greengill Head Farm, who allowed access to establish tracer plots and drill at their farm and for detailing land use history. The staff of the laboratories of the British Geological Survey are thanked for undertaking the chemical and aquifer properties analyses. We are also grateful to members of the Project Steering Group for support and advice and George Darling and Ann Williams who were consulted during the planning stages of this study and who undertook technical reviews of the methodology.

The Project Board for this Work Package consisted of Dr Sean Burke (EA – Science Group), Andrew Butcher (BGS) Adrian Lawrence (BGS), John Ingram (EA – North West Region), Keith Seymour (EA – North West Region), Mike Eggboro (EA – Executive), Dr Rob Ward (EA – Science Group), Alwyn Hart (EA – Science Group), Mr Tim Besien (EA Executive), Phil Merrin (United Utilities), Mike Marks (DEFRA), Chris Procter (ADAS), Paul Buckels (Well Well Well UK Ltd), Mr Peter Easton (Zenith Consultants, for Well Well Well UK Ltd).

EXECUTIVE SUMMARY

This component Work Package of the Eden Valley Groundwater Nitrate Project was undertaken with the objective of determining the velocity of recharge through Glacial Till. Glacial Till overlies the sandstone aquifer in much of the study area and depending on its thickness and composition, it is thought could exert a significant control on the amount of recharge entering the sandstone.

Tracer tests were undertaken at research plots established at the edges of the Till. The results will be used to assess the impact on recharge caused by the presence of lower permeability Till compared to areas where sandstone outcrops.

Accepting that there are inherent uncertainties and limitations associated with the various methods for estimating recharge, it was proposed to use a direct method that could be undertaken within the proposed project timescale of two years. The method used was to measure the rate of movement of a peak concentration of applied tracer within the pore water profile of the Till (and depending on drilling capability, the top part of the sandstone).

The tracers applied were deuterium and bromide which were irrigated onto small research plots. The plots were left uncovered for duration of c. 400 days. Five plots were established, three at the edges of intensive pasture fields, one adjacent to a previous deep borehole site and one on fallow land.

A percussion drilling rig was then used to extract undisturbed cores through the Till. The shallow boreholes were drilled in April 2007. The thickness of Till encountered on drilling ranged from c. 0.9m to 4.2m.

The cores were sealed and transported to BGS Aquifer Properties Laboratories where following logging and photography samples were taken every 20cm along the cores and porewaters were extracted using a centrifuge. Extracted porewaters were then analysed in the BGS Environmental Indicators Laboratories for deuterium and in the Hydrochemical Analysis Laboratories for bromide.

The pore water chemistry results indicated that elevated deuterium and bromide had penetrated to between 1 and 2 m depth, equivalent to a downward velocity of 0.85 to 1.7 m/y probably depending on the amount and composition of Till present and the nature of cultivation. The correspondence between deuterium and bromide profiles was very good in all profiles. The coefficient of determination, R^2 , in three profiles was between 0.66 and 0.84.

Where Till was thicker it was rather more difficult to determine the 'peak' of tracer present particularly with the bromide tracer, although this appears to be at a depth of approximately 0.7m, equivalent to a downward velocity of 0.6 m/y. Till appears to disrupt the vertical flow of tracer through to the sandstone aquifer below. Hence there should be enhanced run-off associated with the thicker Till.

This contrasts with some conclusions from preceding Work Packages in this study where the rate of water movement through the unsaturated zone in the sandstone underlying any superficial deposits is between 3.5 - 3.85 m/y at an adjoining plot where the average recharge rate is in the range 424-468 mm/y.

There is an interesting distinction between profiles of nitrate and chloride. Where Till is thin these demonstrate a general correspondence. However, where Till is thicker or in the fallow plot, chloride profiles follow trends in other profiles (a concentration effect) whilst nitrate profiles remain very low.

1. INTRODUCTION

1.1 Project objectives

The objectives of the project ‘Investigation of Rising Nitrate Concentrations in Groundwater in the Eden Valley’ are:

- i) to identify the causes of rising nitrate concentrations in groundwater in the Permo-Triassic sandstone aquifer of the Eden Valley area in Cumbria.
- ii) to gain a better understanding of the groundwater and surface water flow system, including the sources of the nitrate contamination and the processes controlling nitrate movement
- iii) consider possible management options for reversing this trend.

The main objective of this work package (Work Package 4 ‘Estimating Recharge Rates Through Glacial Till Using An Applied Tracer Technique’) is to provide an approximate timescale for the passage of recharge through the thin Till (typically less than 2m) and hence through to the underlying Permo-Triassic sandstone aquifer where these sandstones are not exposed at the surface in the Eden Valley (Figure 1).

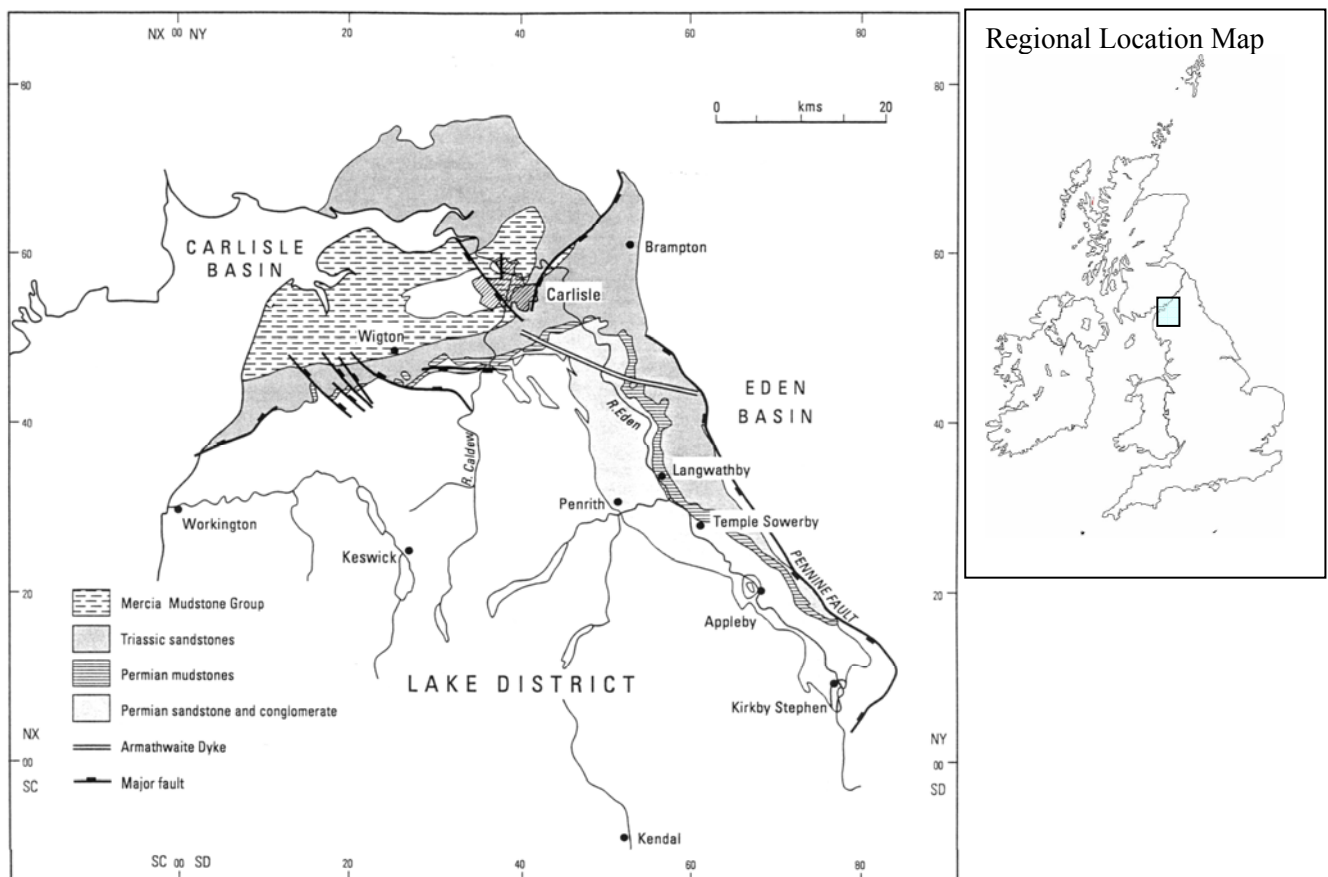


Figure 1. Location Map

1.2 Background

At the outset of this EA-BGS funded research project it was assumed that the presence of Till cover would reduce and delay recharge to the underlying aquifer. Various recharge scenarios were also investigated in a scoping study using numerical modelling (Butcher et al 2003, 2006). Where the superficial cover is thin and especially where it is permeable, recharge may be similar to the rate on exposed sandstone. 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 is to be addressed by this Work Package.

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 1997, Finch et al 1997).

In a preceding investigation of the broader project, recharge rates to the sandstone aquifer have been estimated at c. 450 mm/y where the sandstones are exposed at the surface (i.e. Till-free). These estimates were based on two techniques, a soil moisture water balance approach and the use of historical tracers (nitrate and chloride derived from normal agricultural fertilisation practices) to date the pore water in the unsaturated zone. Rates of water movement (velocity) through the unsaturated zone were estimated to be 3.5 – 3.8 m/y.

In this part of the broader study, use of applied tracers (deuterium and bromide) were proposed to estimate recharge rates to the sandstone aquifer where the sandstone is overlain by thin or relatively permeable Till deposits. Deuterium can replace the normal hydrogen in water molecules to form heavy water (D₂O), which is about 10.6% denser than normal water however when mixed with other water this is not considered to be significant in terms of vertical tracer velocity.

The reason for restricting these tests to where the Till deposits are thin or relatively permeable is because:

- These deposits are widespread and account for c. 70% of the Quaternary cover.
- It was anticipated that the vertical displacement of the applied tracer, over a 1 – 2 year period (which fitted within the timescales of the project) would be sufficient to permit a reasonable estimate of recharge rates to be made.
- The use of applied tracers, where the superficial cover is poorly permeable and relatively thick, is likely to produce results difficult to interpret, because of complex flow paths. These flow paths could include laterally, via more permeable horizons and vertically, (e.g. via fractures in the Till).

In order to assist in site selection, a review of the distribution, composition and thickness of Superficial Deposits in the Eden Valley was undertaken based on Arthuton and Wadge (1981), Burgess and Holliday, (1979), Delaney (2003) and Johnson (1985).

1.2.1 Distribution and Thickness of Superficial Deposits

In the Eden Valley more than 75% of the Permo-Triassic sandstone aquifer is covered by Quaternary Superficial Deposits. Their significance (based on lithology and thickness) on recharge is indicated (Figure 2 and Appendix 1).

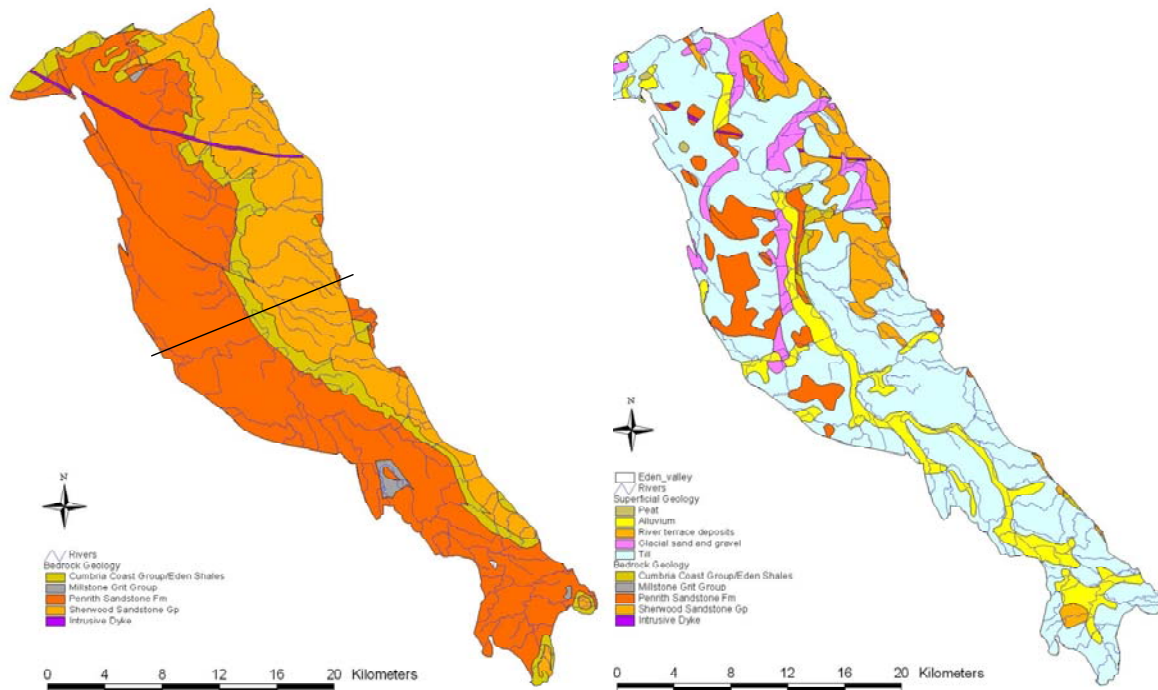


Figure 2. Bedrock and superficial geology, Eden Valley

South of Penrith, the Eden valley is dominated by Glacial Till with relatively small areas of post-glacial Holocene fluvial deposits, these being river terraces and alluvium adjacent to the modern course of the River Eden. There are also small peat basins mapped.

North of Penrith, the proportions of the deposits change. Till is largely thin or absent in many areas and bedrock is exposed, whilst along the River Eden extensively glacial outwash deposits of sand and gravel are recorded, above the level of the Holocene terraces and alluvium. Some larger peat-filled basins are also present.

1.2.2 Characteristics of main Superficial Deposits

Till

The most extensive deposit in the study area, borehole logs and sections reveal that the Glacial Till is typically a red-brown, stiff, silty sandy clay to a friable clayey sand with pockets and lenses of medium and fine sand and gravel and cobble grade clasts, typically of limestone, Permo-Triassic sandstone and volcanic dolerite. Sand bodies within the Till may exceed 5-6m in thickness, and laminated clays and silts may also be present within the Till, perhaps indicating a complex history of Till emplacement within the Eden valley. In the upper Eden valley, much of the Till is formed into high mounds with a preferred long axis and is often described as ‘drumlinoid’.

Glacio-fluvial Outwash

These deposits are characterised by stratified, well-sorted sand and gravel deposits that post-date the Glacial Till deposition. Their greatest extent in the Eden valley occurs north of Penrith, where a variety of typically glacio-fluvial landforms can be recognised including long, linear, ridge-forming eskers, valley marginal hummocky-surfaced kame terraces and glacio-fluvial sheet deposits which the river Eden has subsequently dissected. Thicknesses are highly variable, and can reach 40m, although 10-20m is more typical.

River Terrace Deposits

These post-date the glacio-fluvial and glacio-lacustrine deposits and are associated with the modern rivers and streams. The terraces consist mainly of sand and gravel, and a single terrace surface ranges in height between 5-9 m above present river levels. This variation may reflect the importance of locally fluctuating base levels associated with breaching of morainic dams, rather than regional base-level variation.

Alluvium

Associated with all the major streams and rivers, these deposits for the most part are composed of fine sand and gravel south of Penrith, and brown sandy loam north of Penrith, where the alluvial tract in the Eden valley becomes almost 1km wide. Organic silt and peat may be present in abandoned channels.

1.3 Site Selection

The sites were to be selected in discussion with researchers at the University of Newcastle upon Tyne. Criteria included:

- Access to field plot over two-year period. With field plots to be secure and possibly fenced off (to prevent field plot markers being destroyed/moved).
- The surface geology to include exposed sandstone (control site); thin Till (<1 m) over sandstone (2 – 3 sites).
- Thicker till site to be investigated e.g. drumlins (1 site). Some auguring to confirm shallow geology prior to tracer tests would be required.
- Surface slope should not be too steep.

Several sites in the Appleby area were investigated but most of these were considered either to be covered with thicker till or there were no agreements in place with the landowners. In the event, the farmer/landowner at a previous research site offered 4-5 plots within different fields at the edge of a thin Till cover. This offer circumvented the need to establish new agreements with other landowners and was accepted.

In the study area to the northwest of Penrith, thin (<2 m) till deposits are the most widespread of these superficial deposits (Lawley et al 2007, Figures 3 & 4).

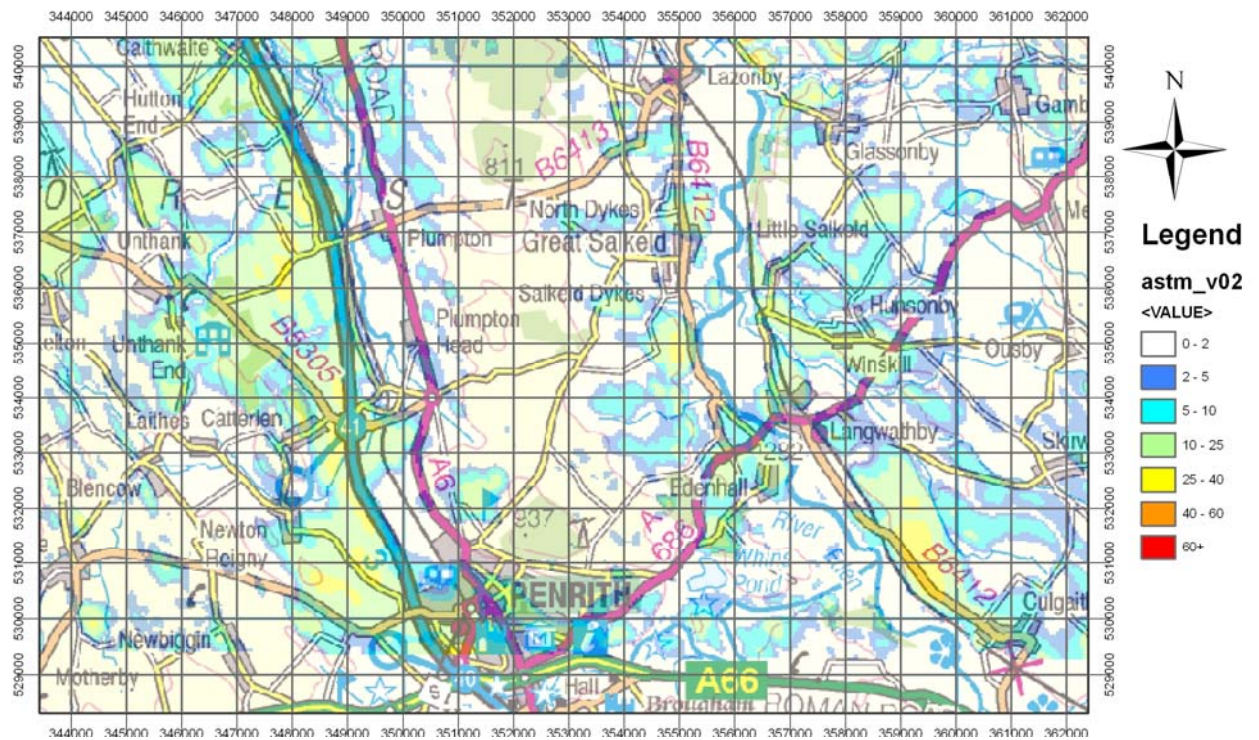


Figure 3. Advanced Superficial Thickness Model (ASTM) of Penrith area.

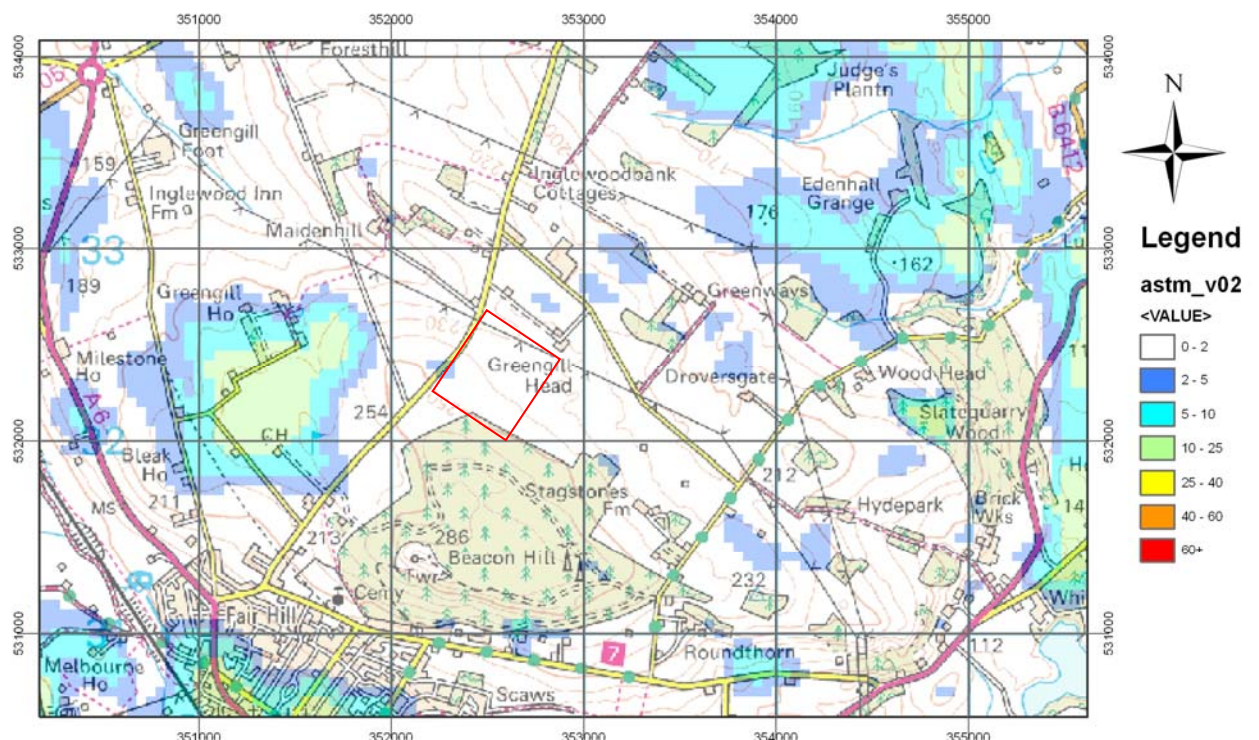


Figure 4. Advanced Superficial Thickness Model (ASTM) of study area.

1.4 Work Plan

Deuterium was used as the applied tracer because:

- The deuterium can be measured directly from the solid sample without the need to extract the pore water if sample recovery is poor.
- Relatively small samples are required for analysis, potentially providing better definition of the tracer peak.
- It is a conservative tracer.
- There are low background concentrations, so applied tracer quantities need not be excessive.

Previous Work

A tracer test carried out at the 'Fleam Dyke lysimeter' in Cambridge on the Middle Chalk (Darling, & Bath, 1988) applied D₂O at the rate 120g m⁻² (equivalent to ²H at 13.3g l⁻¹). The tracer was dissolved in water and applied at the rate of 1 litre per m². The distribution of isotope values in the upper few metres of soil and unsaturated zone showed that the mechanism of infiltration was not simple piston-like downward displacement.

Barraclough et al (1994), applied ¹⁵NO₃, ²H and Cl⁻ to the surface in the unsaturated zone of the British Upper Chalk. Sampling from rock cores followed over a 4 year period. Some lateral flow was evident from cores taken outside the plot.

Eden Valley Tracer Test Design

Rainfall in the Eden Valley is higher than at Fleam Dyke, Cambridgeshire (c. 900 mm/y compared with c. 500 mm/y) and so dilution would be expected to be greater in the Eden Valley. Even so, the peak tracer concentrations would still be considerably higher than background concentrations. Therefore it was decided to apply a similar quantity of the tracer per unit area to that used at Fleam Dyke.

The maximum concentrations of the tracer (ignoring background ²H in the water added to the tracer) were estimated to be c 1.25 g l⁻¹ (as ²H). However, it was anticipated that peak concentrations would be lower, in the sandstone pore waters, because of (a) mixing with water in the soil zone and (b) in mass balance terms there would be some losses of the tracer by evapotranspiration. Maximum or peak tracer concentration in the sandstone pore waters were considered to be well in excess of detection limits. Some thought was given to whether a background concentration of tracer should be determined prior to applying tracer. It was concluded that this could be determined from an additional control site during sampling.

2. METHODS

2.1 Tracer Method for Estimating Recharge

2.1.1 Field programme

The size of the field tracer plots was 2 x 2 m (Figure 5), therefore the quantities of tracer required per test is 480 g (D_2O) or about 50 g as 2H .

The tracers (D_2O and Br) were dissolved in 20 l of water (equivalent to 5 mm over the field plot) and a further 20 l of water was added to wash the tracer into the surface layers. This is equivalent to 2.5% of annual recharge. The plot was subdivided into a grid to help apply the tracer evenly and so that subsequent sampling within the plot could be undertaken systematically. The locations of the plots were recorded to allow repeat sampling in following years (Figures 6 & 7).

The tracer should have been applied in late autumn when the soil moisture deficit is close to zero (and when recharge can occur) to help reduce losses of the tracer by evapotranspiration. Actually it was applied in February 2006 and it was sampled in April 2007 after 420 days.

A small tracked ‘Dando Terrier’ core drill was used to recover tracer at four locations within the plots (and one control location). An adjacent core (to observe if lateral movement is significant)) was scheduled but abandoned due to difficulties in withdrawing the core barrel next to one plot. The shallow boreholes were drilled to a maximum total depth of 4.2m. Percussion coring was selected as the preferred sampling method to ensure minimum contamination of the pore waters in the unconsolidated core (Figures 8-13).

Cores were recovered within plastic liners, sealed and returned to BGS laboratories where they were sub-sampled and centrifuged to remove porewaters. These were analysed for deuterium, bromide and other dissolved constituents in the porewater. The boreholes were back-filled with a bentonite mixture to ground level.

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).



Figure 5. Typical plot EVT1 following tracer application



Figure 6. Tracer sites located at research farm



Figure 7. Tracer sites located at research farm with Till extent identified (in light blue)

2.1.2 Laboratory programme

The core was geologically logged at the BGS Physical Properties Laboratories in Wallingford using BS5930: Code of Practice for site investigations, (British Standards Institution 1999). Lithology, colour, percentage core recovery and other features were noted.

Samples of core for porewater 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 sampled, 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 and then samples were split for subsequent analyses. The samples were stored in a refrigerator and analysed at the Hydrochemical Analysis Laboratories and Environmental Indicators Laboratories at BGS Wallingford.

Water chemistry

Porewater concentrations of Br, Cl, F, NO₃-N, and SO₄ were determined by ion chromatography using a Dionex system with AutoAnalyzer and Dionex PeakNetTM data capture software. The samples were filtered through a 0.45µm filter but were not acidified.

A proportion of the samples were acidified by 1% nitric acid and stored for potential analysis using Inductively Coupled Plasma Optical Emission Spectrography (ICP OES).

Samples were prepared for δ²H analysis by reacting 10 microlitres of water with zinc shot at 450°C. The resulting hydrogen gas was measured for its ²H/¹H ratio on a VG Optima dual-inlet mass spectrometer. Measurements are expressed with respect to VSMOW (Vienna Standard Mean Ocean Water). Measurement precision is better than ±2 ‰.



Figure 8. EVT2 site at application of tracer. Plots positions recorded against wall.



Figure 9. Unloading drilling rig at EVT1 drillsite



Figure 10. EVT1 drillsite, looking east over Eden Valley towards Pennines.



Figure 11. EVT2 drillsite looking east over Eden Valley towards Pennine uplands.



Figure 12. Core barrel EVT2 site drilling.



Figure 13. Core barrel containing Till core.

3. RESULTS

3.1 Core Drilling and Testing

Core recovery was generally good (c. 95%); the core consisted of soil in the upper 20-50cm followed by dark red Till with some red-grey mottled Till. A relatively sharp contact with weathered coarse red sand at the base of all of the cores (Figures. 14-16). Core recovery was excellent using the percussion drilling method but there were difficulties in retrieving the core barrel from depths exceeding 2m when the superficial deposits were more cohesive. In both cases the core barrel was released by hand-excavating a small hole on the outside edge of the barrel taking care to minimise disruption to the plots mindful that re-drilling was an option at a later stage.

3.2 Water Quality

3.2.1 Water types

The porewater analyses for selected ions are presented in Table 1; full analyses are presented in Appendix 2. Ionic balances were not determined in all cases. Porewater analyses from the soil zone are not included.

Table 1. Till porewater analyses for major and selected minor ions

Symbol	Ion	Units	Min	Max	Median	Mean	No.
Ca	calcium	mg/l	1.7	57.0	9.8	17.6	50
Mg	magnesium	mg/l	0.6	15.6	2.8	3.49	50
Na	sodium	mg/l	9.4	28.3	18.2	17.8	50
K	potassium	mg/l	0.64	28.6	2.7	4.7	50
Cl	chloride	mg/l	13.8	70.7	32.8	35.6	50
SO ₄	sulphate	mg/l	1.5	48.2	8.7	11.2	50
HCO ₃	bicarbonate	mg/l	<5.0	81			50*
NO ₃	nitrate as NO ₃	mg/l	0.21	219	47.4	11.4	50
Fe	iron	mg/l	<0.005	6.75	0.07	0.6	41
Mn	manganese	mg/l	0.01	1.4	0.06	0.2	50

* includes values at detection limit of <5 mg/l

The porewaters in the Till zone are of a mixed water type, with low HCO₃ concentrations although a rigorous analysis of major ion chemistry in the cores was of a lesser priority than of the tracers.

3.2.2 Solute porewater depth profiles

Porewater concentration – depth profiles for the applied deuterium and bromide tracers are indicated in Figures 17 and 18. Nitrate and chloride (derived from natural sources, chemical fertilisers and animal slurry) in the cores through the Till (Figure 19) are also of interest.

A comparison between the concentrations in different cores on farmed land (EV1-3) and the contrast with the profile from a control plot (EVT4) where no tracer or agricultural inputs is marked.



Figure 14. Cores from Plot 1 (EVT1 and EVT1a)



Figure 15. Cores from Plot 3 (EVT3)

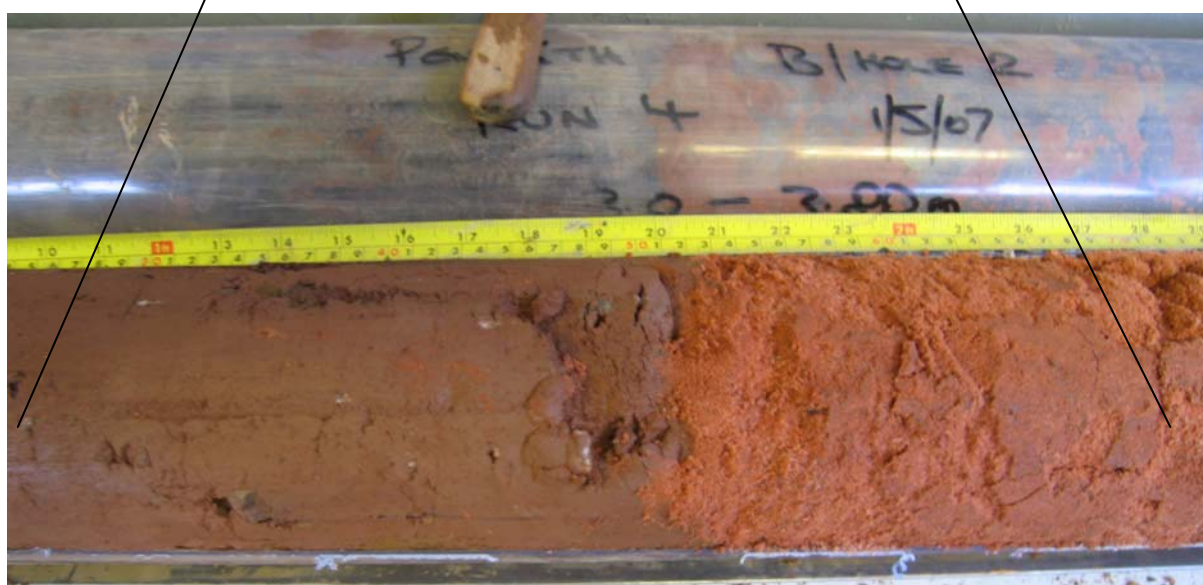


Figure 16. Cores from Plot 2 (EVT2) and close-up of Till/sandstone contact



Figure 17. Deuterium (D^2O) profiles from tracer plots (EVT1-4)

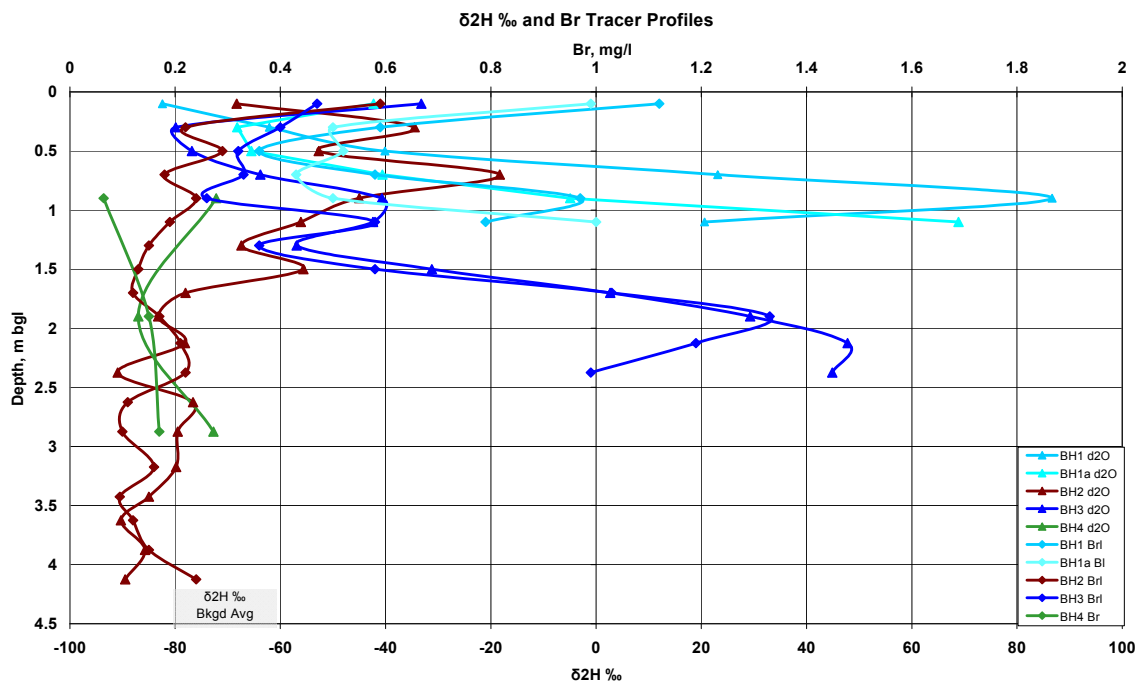


Figure 18. Deuterium (D^2O) and bromide tracer profiles from tracer plots (EVT1-4)

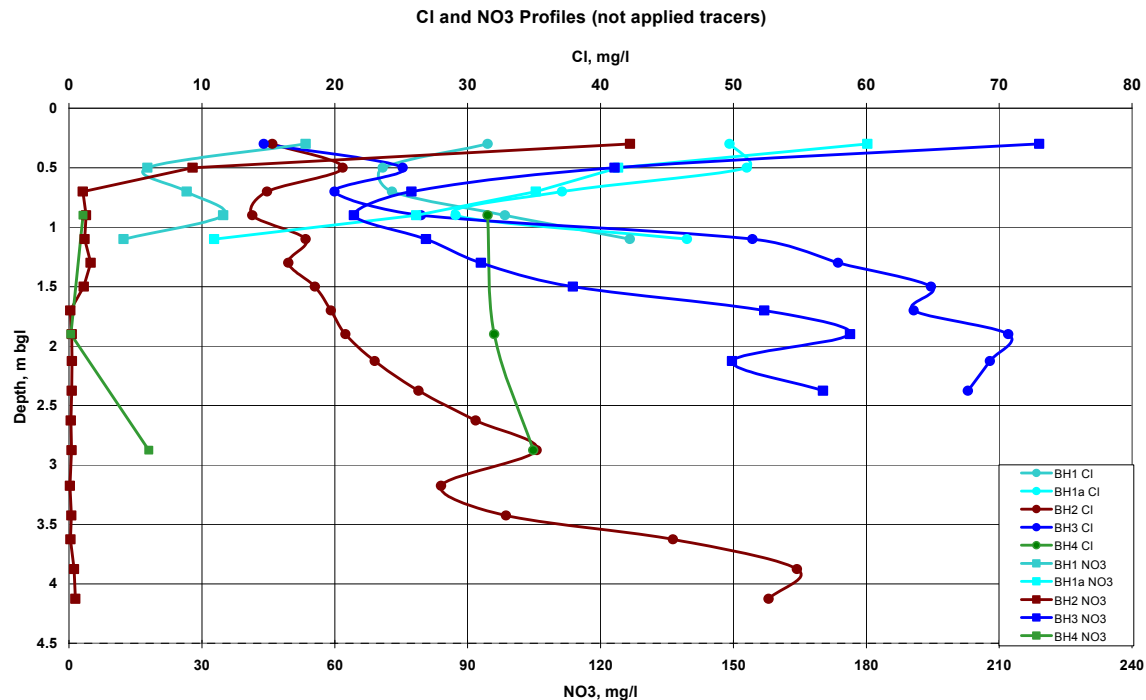


Figure 19. Nitrate (as NO_3) and chloride (Cl) profiles from plots (EVT1-4)

The pore water chemistry results (Figures 17 and 18) indicate that elevated deuterium and bromide had penetrated to between 1 and 2 m depth, equivalent to downward velocity of 0.85 to 1.7 m/y. Background concentrations for deuterium $\delta^2\text{H}$ are in the range -60 to -80 ‰. Background concentrations of bromide of c. 0.1 mg/l in the fallow plot (EVT4) are consistent with average profile determinations conducted on the adjacent EV1 borehole site (Butcher et al 2008). In the profiles where Till was thicker it was rather more difficult to determine the ‘peak’ of tracer present (particularly with the bromide tracer) although this appears to be at a depth of approximately 0.7m, equivalent to a downward velocity of 0.6 m/y.

The profiles of nitrate and chloride (Figure 19) exhibit porewater concentrations ranging from c. 14 mg/l to 70 mg/l for chloride and 0 to c. 220 mg/l for nitrate (as NO_3). Below a depth of one meter below the surface in the profiles (and thus below the main soil horizon) the maximum concentrations are 70 mg/l and 175 mg/l respectively. In both cases these are at a depth of approximately 2 m below the surface in the profile EVT3. Note that these concentrations are not from applied tracers.

In general the profiles for nitrate and chloride follow a similar general trend in profiles EVT1/1a and EVT3 but are quite different in profiles EVT2 and EVT4.

The coefficient of determination, R^2 , for applied tracers deuterium and bromide in the profiles ranges from 0.125 for borehole EVT2 to 0.84 for borehole EVT3 (Figure 20).

The coefficient of determination, R^2 , for chloride and nitrate in the profiles ranges from 0.02 for borehole EVT1 to 0.50 for borehole EVT3 (Figure 21).

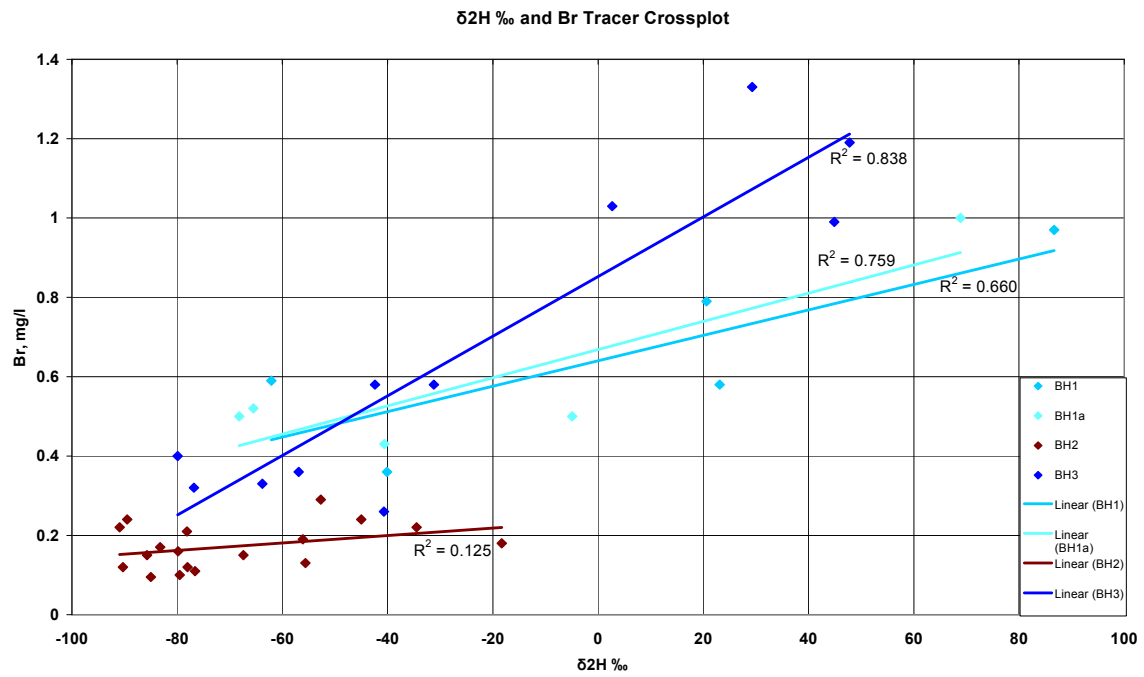


Figure 20. Deuterium (D^2O) and bromide (Br) tracer crossplots from tracer profiles (EVT1-3)

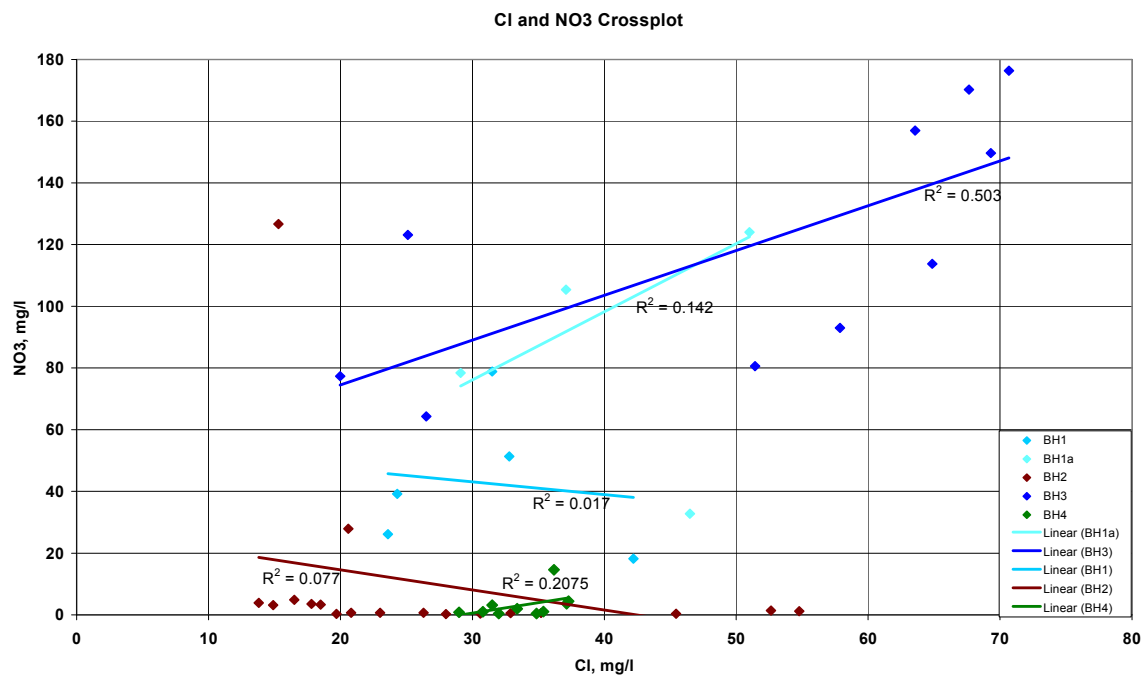


Figure 21. Nitrate (as NO_3) and chloride (Cl) crossplot from profiles (EVT1-3)

4. DISCUSSION

The pore water chemistry results indicated that elevated deuterium and bromide had penetrated to depths of between 1 and 2 m, equivalent to downward velocity of 0.85 to 1.7 m/y. This is dependent on the amount and composition of Till present and probably the nature of cultivation. The deeper penetration was found at site EV3T where the composition of the soil was thicker and more freely draining and where Till appeared to contain a greater proportion of sand. The plot is on a lower field where deeper and more regular ploughing and grass re-seeding has taken place (pers comm. Richard and Peter Thompson; farmers). The coefficient of determination, R^2 , for applied tracers deuterium and bromide in these profiles is between 0.66 and 0.84.

Where Till was thicker in EVT2 the tracer peak appeared to be at a depth of approximately 0.7m, equivalent to a downward velocity of 0.6 m/y. As mentioned above, it was rather more difficult to determine the 'peak' of tracer present (particularly with the bromide tracer). The nature of the Till was different (more clay rich and hence cohesive) to that in plot EV3T. The coefficient of determination, R^2 for applied tracers deuterium and bromide in the profile EVT2 is 0.125; much less than above.

There is an interesting distinction between profiles of nitrate and chloride (Figure 18). Where Till is thin as in plots EVT1 and EVT3 these (accepting different ranges) demonstrate a general correspondence (note coefficient of determination, R^2 for EVT3 is 0.5). However, where Till is thicker or in the fallow plot, chloride profiles follow trends in other profiles (a concentration effect) whilst nitrate profiles remain very low. Profiles are quite complex and difficult to interpret to a depth of about metre

The results of soil moisture-water balance modelling on an adjacent plot were presented in Butcher et al (2008). 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 and Penrith Cemetery raingauges. A FAO/EA approach considered only 'grazed pasture' crop type.

Runoff estimated by the model for both the conventional and the FAO methods were found to be 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.

Some conclusions from preceding Work Packages in this study were that the rate of water movement through the unsaturated zone in the sandstone underlying any superficial deposits is c. 3.5-3.85 m/y and that the average recharge rate is probably in the range 424-468 mm/y.

The apparent lack of penetration of the tracers where Till is thicker however suggests that runoff must be greater over the Till and at the Till edges.

The results suggests that there should be enhanced run-off associated with the thicker (>2m thick) Glacial Till.

Site selection, establishment of tracer plots and subsequent core drilling was eased significantly due to familiarity with the farm where these were located. The development of an Advanced Superficial Thickness Model (ASTM) during the project and covering the study area will help with site selection for any future studies.

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APPENDICES

Appendix 1. Map output from superficial deposits thickness model (Lawley et al 2005).

Appendix 2. Borehole EVT1-4 profile porewater hydrochemical data.

Appendix 1. Map output from superficial deposits thickness model V1 (Lawley et al 2005).

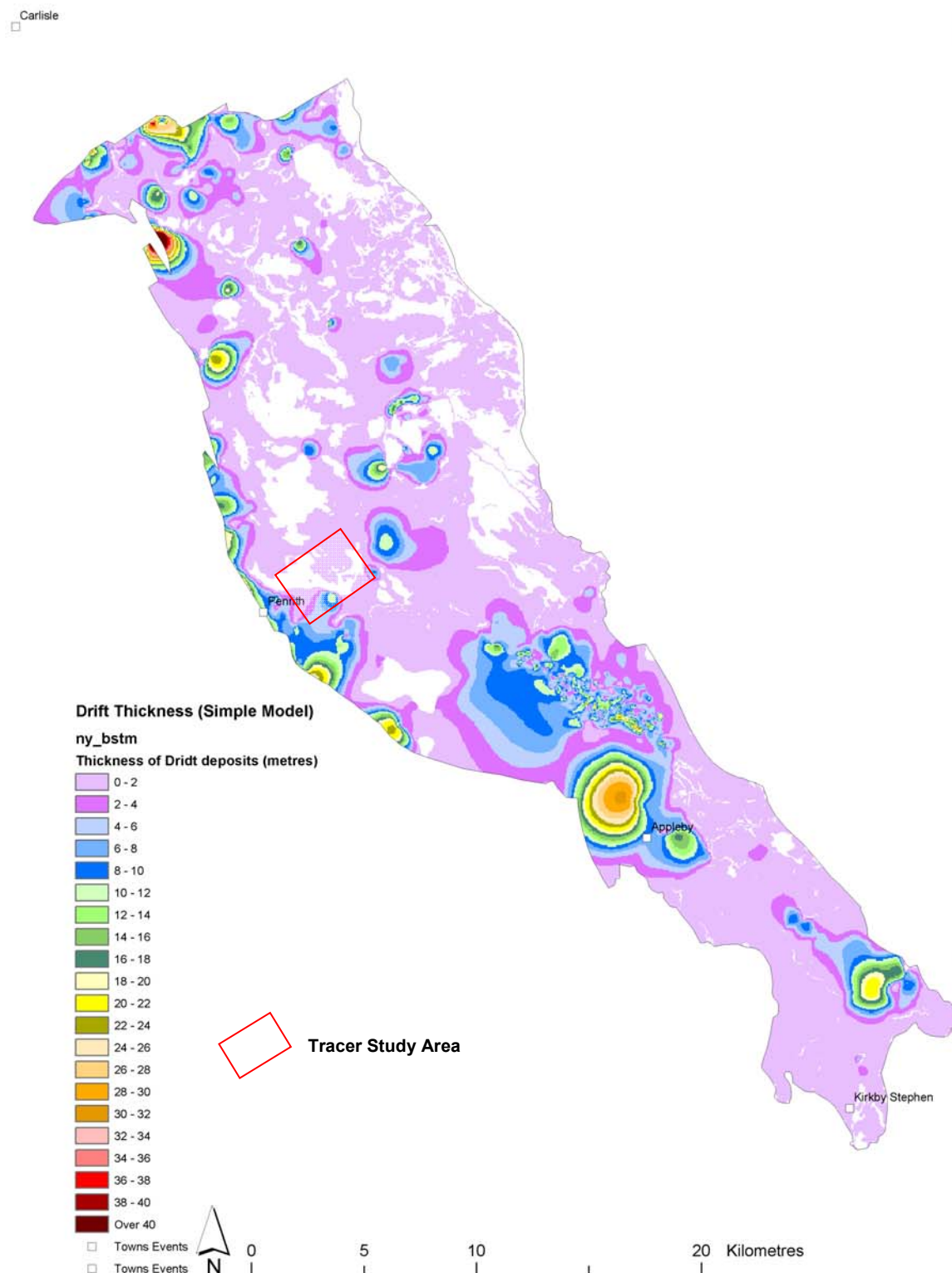


Figure A1. Basic Superficial Thickness Model BSTM (v1) of Eden Valley

Appendix 2. Boreholes EVT1-4 profile porewater hydrochemical data.

SAMPLE ID	FIELD ID	Depth m bgl	Al	B	Ba	Br	Ca	Cl	Cu	d2H	DOC	F	Fe	HCO3 Lab	K	Mg	Mn	Na	NO2-N	NO3-NO3	P04	Si	SO4	Sr	Zn
S07-00504	EV4/T1	0.3	<0.01	0.239	0.267	0.59	26.1	31.5	0.525	-62.1	33.2	0.390	0.168	19	2.53	8.51	0.025	16.3		78.83	0.14	4.33	10.1	0.119	0.07
S07-00505	EV4/T1	0.5	0.034	< 0.05	0.175	0.36	25.6	23.6	0.279	-40.1	14.5	0.249	0.098	52	0.76	4.44	0.017	11.3		26.13		2.96	11.1	0.117	0.08
S07-00506	EV4/T1	0.7	0.022	< 0.05	0.29	0.58	36.6	24.3	0.195	23.1	9.06	0.213	0.02	81	0.72	3.01	0.006	9.77		39.19		2.18	8.67	0.144	0.05
S07-00507	EV4/T1	0.9	0.031	< 0.05	0.156	0.97	32.2	32.8	0.15	86.7	4.12	0.289	0.008	31	1.85	2.74	0.045	12.3		51.37		1.85	8.26	0.119	0.05
S07-00508	EV4/T1	1.1	0.036	< 0.05	0.124	0.79	20.8	42.2	0.171	20.6	16.9	0.350	0.224	10	3.4	2.46	0.030	15.3		18.16	0.25	5.57	13.7	0.0999	0.02
S07-00510	EV4/T1a	0.3	0.043	< 0.05	0.569	0.5	48.6	49.7	0.288	-68.2	16.7	0.313	0.025	11	2.2	15.6	0.012	22.6		180.24		3.65	5.95	0.225	0.08
S07-00511	EV4/T1a	0.5	0.026	< 0.05	0.537	0.52	38.3	51.0	0.264	-65.5	7.44	0.278	0.039	10	1.62	10.9	0.009	17.1		124.00		2.83	5.4	0.172	0.06
S07-00512	EV4/T1a	0.7	0.307	< 0.05	0.332	0.43	36.1	37.1	0.18	-40.6	5.12	0.316	0.052	16.5	3.51	8.92	0.022	10.7		105.40		2.63	7.95	0.201	0.06
S07-00513	EV4/T1a	0.9	0.024	< 0.05	0.249	0.5	32.4	29.1	0.0922	-4.9	4.92	0.245	0.043	17.4	2.47	5.14	0.011	9.96		78.39		2.1	8.43	0.166	0.04
S07-00514	EV4/T1a	1.1	0.021	< 0.05	0.189	1	30.6	46.5	0.156	68.9	11.5	0.590	0.056	10	3.09	3.34	0.012	19		32.77		5.22	31.2	0.134	0.03
S07-00517	EV5/T2	0.5	0.943	< 0.05	0.0551	0.29	14.1	20.6	0.123	-52.7	11.9	0.170	3.400	5	0.91	1.41	0.154	10.6		27.90		2.01	6.09	0.0624	0.02
S07-00518	EV5/T2	0.7	0.085	< 0.05	0.0457	0.18	7.38	14.9	0.0445	-18.3	6.04	0.253	0.329	8.7	0.5	0.55	0.016	9.42		3.10		1.32	8.22	0.0262	0.01
S07-00519	EV5/T2	0.9	0.023	< 0.05	0.0463	0.24	5.14	13.8	0.0698	-45	3.5	0.186	0.038	7.6	0.64	0.72	0.006	10.6		3.85		2.08	8.05	0.0177	0.03
S07-00520	EV5/T2	1.1	0.237	< 0.05	0.0725	0.19	2.55	17.8	0.0329	-56.1	2.9	0.264	0.116	10	1	1.14	0.012	14.2		3.54		5.32	11	0.0121	0.04
S07-00521	EV5/T2	1.3	0.025	< 0.05	0.0498	0.15	3.39	16.5	0.0804	-67.4	3.7	0.251	0.029	10	1.14	1.15	0.013	13.8		4.87		5.91	10.9	0.0155	0.04
S07-00522	EV5/T2	1.5	0.07	< 0.05	0.0559	0.13	3.09	18.5	0.0722	-55.6	3.75	0.282	0.095	10	1.12	1.07	0.021	13.1		3.32		7.99	9.31	0.0152	0.04
S07-00523	EV5/T2	1.7	1.85	< 0.05	0.056	0.12	2.69	19.7	0.0878	-78	1.95	0.301	0.83	10	1.35	1.21	0.105	13.3		0.30		12.3	9.63	0.0128	0.06
S07-00524	EV5/T2	1.9	0.04	< 0.05	0.0552	0.17	2.49	20.8	0.0493	-83.2	3.55	0.623	0.135	10	1.03	0.73	0.095	15.4		0.62		9.26	9.99	0.0108	0.01
S07-00525	EV5/T2	2.125	0.067	< 0.05	0.0298	0.21	2.64	23	0.0782	-78.1	5	0.410	0.213	10	0.88	0.94	0.256	16		0.66		11.4	9.37	0.0118	0.02
S07-00526	EV5/T2	2.375	0.388	< 0.05	0.0715	0.22	3.69	26.3	0.059	-90.9	5.4	0.578	0.381	10	0.91	0.95	0.159	17.7		0.62		11.5	5.55	0.0131	0.02
S07-00527	EV5/T2	2.635	0.012	< 0.05	0.0769	0.11	3.15	30.6	0.0512	-76.6		0.816	0.027	10	1.09	0.92	0.117	20.8		0.40		11.2	8.72	0.0126	0.01
S07-00528	EV5/T2	2.875	<0.01	< 0.05	0.0705	0.1	4.47	35.2	0.0451	-79.5		0.707	0.021	10	1.13	1.42	0.050	20.7		0.58		12.4	10.1	0.018	0.01
S07-00529	EV5/T2	3.175	0.054	< 0.05	0.032	0.16	3.51	28	0.0659	-79.8		0.364	0.049	10	1.3	1.4	0.322	16.7		0.21		9.6	12.1	0.0157	0.04
S07-00530	EV5/T2	3.425	<0.01	< 0.05	0.091	0.095	5.68	32.9	0.0565	-85		0.969	0.01	10	0.92	1.55	0.033	20		0.52		10.9	9.44	0.0208	0.01
S07-00531	EV5/T2	3.625	<0.01	< 0.05	0.0538	0.12	6.19	45.5	0.125	-90.3		1.356	0.005	10	1.23	1.81	0.057	22.8		0.34		11.2	8.05	0.0219	0.01
S07-00532	EV5/T2	3.875	0.022	< 0.05	0.086	0.15	7.68	54.8	0.117	-85.7		1.391	0.006	5	1.72	2.11	0.068	28.3		1.15		12.2	6.98	0.0263	0.02
S07-00533	EV5/T2	4.125	0.04	< 0.05	0.108	0.24	8.48	52.6	0.0983	-89.5		1.076	0.005	5	2.31	2.2	0.057	25.9		1.42		13.4	5.57	0.0279	0.02
S07-00535	EV6/T3	0.3	0.036	< 0.05	0.576	0.4	31.2	14.7	0.498	47.8		0.188	0.065	5	28.6	11.6	0.025	17.1		219.04		4.11	5.75	0.143	0.06
S07-00536	EV6/T3	0.5	<0.01	< 0.05	0.356	0.32	25.2	25.1	0.202	44.9		0.262	0.005	5	6.81	5.66	0.143	21.7		123.16		3.28	10.4	0.124	0.04
S07-00537	EV6/T3	0.7	0.031	< 0.05	0.249	0.33	14.6	20	0.197	-63.8		0.227	0.162	5	4.46	4.26	0.062	17.6		77.32		3.79	7.86	0.0674	0.04
S07-00538	EV6/T3	0.9	0.017	< 0.05	0.12	0.26	13.7	26.5	0.238	-40.7		0.383	0.028	5	14.2	2.82	0.018	19.2		64.35		3.26	13.1	0.0672	0.03
S07-00539	EV6/T3	1.1	<0.01	< 0.05	0.364	0.58	27.9	51.4	0.172	-42.4		0.261	0.005	5.5	15	3.19	0.019	18.7		80.60		2.15	9.63	0.163	0.04
S07-00540	EV6/T3	1.3	< 0.01	< 0.05	0.378	0.36	32.2	57.9	0.13	-56.9		0.257	0.005	5	12	4.33	0.151	22.1		93.00		2.58	8.34	0.179	0.04
S07-00541	EV6/T3	1.5	<0.01	< 0.05	0.493	0.58	38.8	64.9	0.133	-31.2		0.279	0.010	5	13.1	5.14	0.076	23.8		113.77		2.59	6.45	0.219	0.04
S07-00542	EV6/T3	1.7	<0.01	< 0.05	0.637	1.03	45.9	63.6	0.0808	2.7		0.258	0.005	5	17.1	5.18	0.059	21.3		156.95		1.96	4.48	0.285	0.04
S07-00543	EV6/T3	1.9	<0.01	< 0.05	0.69	1.33	56.8	70.7	0.108	29.3		0.307	0.005	5	13.1	3.6	0.027	23.5		176.35		2.19	4.19	0.385	0.04
S07-00544	EV6/T3	2.125	< 0.01	< 0.05	0.623	1.19	52.9	69.3	0.131	-3.5		0.266	0.005	5	11.1	4.43	0.219	22.1		149.69		2.62	5.71	0.344	0.05
S07-00545	EV6/T3	2.375	<0.01	< 0.05	0.647	0.99	53.8	67.6	0.0957	-2.5		0.257	0.005	5	10.8	4.97	0.153	20.3		170.19		2.64	4.11	0.339	0.04
S07-00548	EV7/T4	0.5	0.346	< 0.05	0.067	0.22	10.7	35.4	0.295			0.230	0.289	5	3	2.52	0.322	20		1.02		6.66	26.5	0.0556	0.12
S07-00549	EV7/T4	0.7	0.279	< 0.05	0.116	0.09	9.63	30.8	0.261			0.170	0.149	5	3.88	3.92	0.488	19.8		0.97		9.42	43.5	0.0565	0.15
S07-00550	EV7/T4	0.9	0.311	< 0.05	0.154	0.064	8.93	31.5	0.2	-72.2		0.381	0.078	5.9	5.4	5.85	0.852	19		3.14		13.3	48.2	0.0557	0.20
S07-00551	EV7/T4	1.1	0.224	< 0.05	0.232	0.083	4.37	37.3	0.299			0.654	0.025	5	5.28	3.82	0.841	21		4.40		18.5	37.6	0.0303	0.27
S07-00552	EV7/T4	1.3	0.055	< 0.05	0.116	0.092	4.97	37.1	0.192			0.479	0.148	5	4.63	2.55	0.634	20		3.59		20.9	17.6	0.0283	0.20
S07-00553	EV7/T4	1.5	0.272	< 0.05	0.13	0.11	2.32	33.4	0.138			0.300	0.685	5	3.43	1.13	0.398	16.9		1.95		28.2	1.88	0.015	0.12
S07-00554	EV7/T4	1.7	0.739	< 0.05	0.122	0.106	1.74	34.9	0.0945			0.330	1.530	5	2.81	0.63	0.255	16.3		0.39		25.2	1.56	0.0134	0.11
S07-00555	EV7/T4	1.9	0.4	< 0.05	0.12	0.15	1.86	32	0.102	-87		0.372	6.270	5	2.22	0.63	0.479	15.4		0.40		17	5.85	0.013	0.11
S07-00556	EV7/T4	2.125	0.643	< 0.05	0.132	0.138	2.17	29	0.131			0.280	6.750	5	2.71	0.84	1.27	13.6		0.84		15	1.53	0.016	0.09
S07-00557	EV7/T4	2.375	0.032	< 0.05	0.0717	0.16	6.86	34.5	0.0676			0.562	0.026	5	3.31	2.87	1.4	22.9		19.31		16.1	23.3	0.0588	0.09
S07-00558	EV7/T4	2.635	<0.01	< 0.05	0.0691	0.162	9.9	38.8	0.0576			0.446	0.027	5	3.56	3.82	0.393	21.7		22.98		17.3	30.2	0.0671	0.10
S07-00559	EV7/T4	2.875	0.093	< 0.05	0.0804	0.17	11.1	34.9	0.0364	-72.7		0.519	0.144	5	3.45	4.23	0.119	22.4		18.02		17.2	31.9	0.0717	0.07

Units mg/l except d2H, ‰.

