

# CONTAMINANT ATTENUATION THROUGH GLACIAL DRIFT OVERLYING THE CHALK AQUIFER IN SOUTHERN EAST ANGLIA, UK

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**Abstract.** The Chalk is the major aquifer in the UK. Parts of the Chalk are covered in places by glacial drift deposits, which can have a significant influence on recharge and contaminant movement, particularly where dominated by low-permeability lithologies such as the boulder clay (Till) sheet of East Anglia. Fracturing in Till has been widely observed and its potential for providing a route for rapid contaminant movement identified. A groundwater sampling programme has been undertaken and two cored boreholes drilled to investigate the degree of attenuation effected by the Till cover. Results from CFC and nitrate sampling show the Chalk groundwater beneath the interfluves is old and has negligible nitrate concentrations. Groundwaters beneath the valley and Till edge have a component of modern water and generally high nitrate concentrations. Evidence for denitrification is also found. Data from gas samplers shows modern air deep in the unsaturated zone suggesting a by-pass route for recharge. The Till layer attenuates nitrate concentrations in groundwater by restricting the downward movement of recharging rainwater and promoting denitrification both in terms of redox conditions and the by increasing the time of exposure to these conditions.

## 1. Introduction

The Chalk is the major aquifer in the UK, providing 15% of the water supply nationally and up to 35% regionally in the south and east. It is a soft microporous and fractured calcium carbonate aquifer with high intergranular porosity (25-45%) but low intergranular hydraulic conductivity as a result of small pore-neck size. The fracture component has low porosity (0.1-1%) but can increase the hydraulic conductivity by up to three orders of magnitude<sup>[1]</sup>. In the unsaturated zone of the Chalk of Southern England, recharge has an apparent downward velocity of  $\sim 1 \text{ m/a}$ <sup>[2]</sup>, probably achieved rather discontinuously by relatively immobile porewater flooding into fractures when tensions permit<sup>[3]</sup>. However, faster 'preferential' flow through fractures may be important especially for transport of trace contaminants such as pesticides<sup>[4]</sup>.

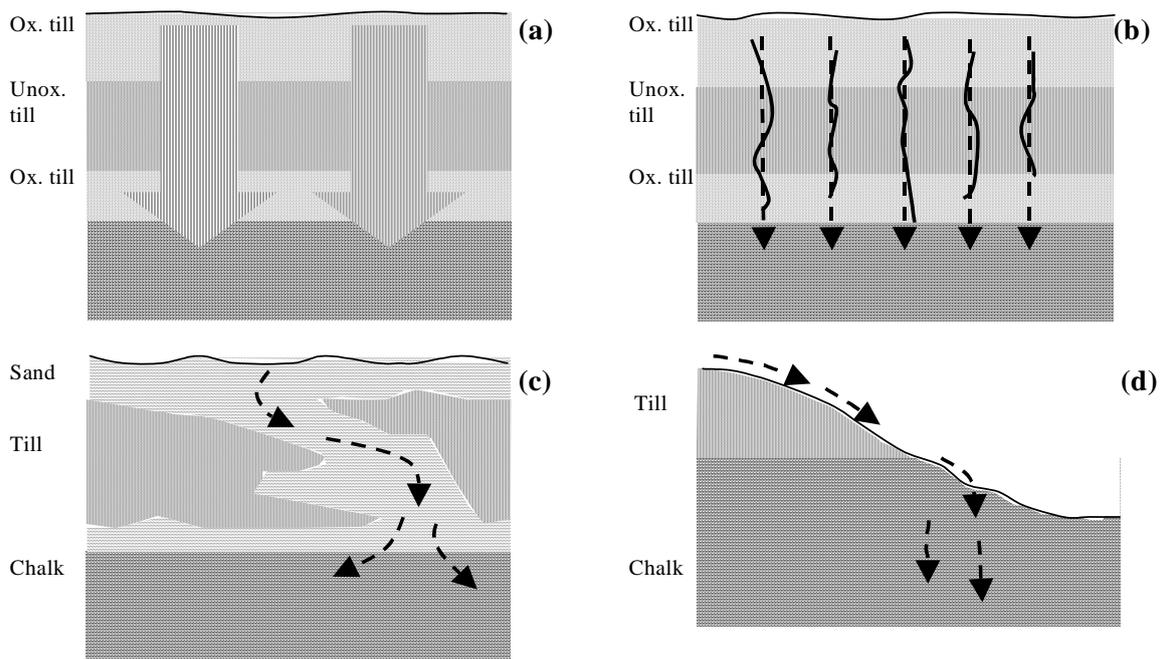
The Chalk aquifer is a highly complex natural system<sup>[5,6]</sup> and consequently is very difficult to measure or sample in a systematic manner in either the saturated or unsaturated zones. Recharge can be localized due to the highly inhomogeneous nature of the shallow weathered Chalk<sup>[7]</sup>. Major aquifers in the UK are partially covered by Drift, which can have a significant influence on contaminant movement, particularly where dominated by low-permeability lithologies such as clay. The extensive Till (boulder clay) sheet of East Anglia, characterised by a thick sequence of low-permeability deposits overlying the important Chalk aquifer, is one such example and the focus of this study. The complexity of drift cover in Britain, coupled with a wide variety of depositional environments, means that a large number of hydrogeological settings or 'domains' exist. Clearly these need to be characterised and their influence on recharge assessed.

The predominant route taken by contaminants in low-permeability drift-covered areas remains far from well-established. In Till for example it could be more or less direct, via intergranular movement (Scenario 1, Fig 1a). Oxidised Till is likely to have a higher permeability than unoxidised Till. Previously it had generally been considered that Till is unlikely to possess

significant fracture permeability. However, in recent years, fracturing in Till has been widely observed and its potential for providing a route for rapid contaminant movement recognized<sup>[7,8]</sup> (Scenario 2, Fig 1b). Other routes for contaminant movement to aquifers overlain by Drift are possible and include permeable lenses within the Till (Scenario 3, Fig 1c) or direct entry at the edge of the Till (Scenario 4, Fig 1d). It is also possible that no significant contaminant movement or attenuation occurs.

Earlier investigation of the East Anglian Till<sup>[9]</sup> left unexplored several aspects of the effect of Drift cover. The biggest questions left unresolved were: (i) the residence times of the various groundwater components, (ii) the degree of importance of fracture-related bypass flow and (iii) the mechanism of attenuation of dissolved nitrate. Through measuring CFCs in groundwaters and in the gaseous phase as an indicator of residence time, and determination of nitrate and the products of denitrification, this study attempts to address some of these questions.

The overall objective of this paper is to understand the effects of the extensive Drift (superficial deposits) cover overlying the Chalk aquifer on contaminant attenuation, specifically nitrate. This requires an identification of the key Chalk hydrogeological environments, an understanding of water movement and measurement of nitrate and likely products of denitrification. Although the drift cover may not have particularly significant resource implications, it is an important consideration when attempting to model or predict the movement of water and contaminants through the Chalk.



*Figure 1. Scenarios for contaminant movement to Chalk through till. (a) Scenario 1: dispersed contaminant movement occurs through till pores, (b) Scenario 2: contaminant movement occurs through till fractures, (c) Scenario 3: contaminant movement occurs through permeable lenses in the till, (d) Scenario 4: contaminant movement occurs at the edge of the till outcrop.*

## **2. Geology, hydrogeology and site descriptions**

### **2.1. Geology**

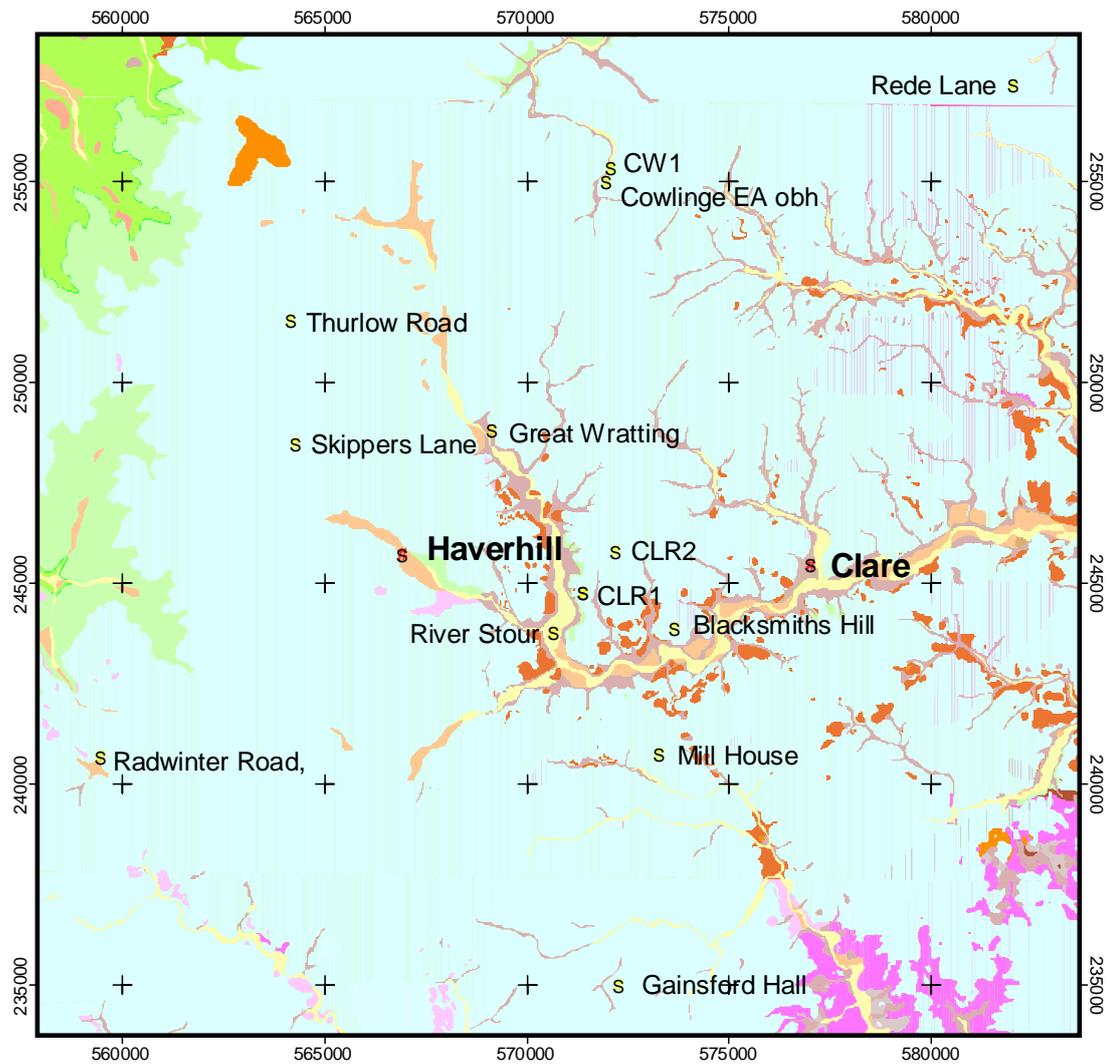
The Lowestoft Till (Quaternary) is sometimes referred to as the Chalky Boulder Clay. This Till covers much of the N Essex—S Suffolk district in a plateau-forming sheet commonly between 30 and 50 m in thickness<sup>[10]</sup>, which locally varies with the elevation of the ground. The Drift/Chalk interface is largely a planar feature with a regional dip to the south-east. The valley of the River Stour, the most significant watercourse in the district, is considered part of a glacial buried valley, which has cut down into the planar surface of the Chalk.

The Lowestoft Till is characteristically an unstratified bluish-grey silty sandy clay with pebbles where it is unoxidised<sup>[11]</sup>. A weathered, oxidised zone of brown and orange-brown in colour between 0.2 and 2 m thick is commonly developed beneath the soil and an oxidised zone is often present at the base of the sequence. Fractures with oxidised surfaces are occasionally found in the Till. The pebble erratics are usually some 50-75 mm in diameter and consist largely of well-rounded Chalk clasts, but also include sub-angular flints. The Till was deposited during the Middle Pleistocene glaciation, which was also the source of much of the other drift cover in the general area.

The thick Till domain is probably the most important for contaminant attenuation. Consequently this domain was used for the field study, looking at two distinct sub-domains: the centre and edge of the Till sheet respectively. The required site characteristics included a homogeneous Till sequence between roughly 15 and 30 metres thick overlying Chalk. Two sites were identified: Cowlinge, on an interfluvium several km from any exposed Chalk, and Clare on the edge of the Stour Valley approximately 100 m from the exposed Chalk (Fig. 2).

### **2.2. Hydrogeology**

The principal aquifer in the region is the Chalk which is extensively developed for water supplies<sup>[10]</sup>. As can be seen from the schematic cross-section (Fig. 3), hydraulic conditions at the two sites differ. In the centre of the Till sheet the groundwater is confined, with a piezometric surface within the Till. Towards the edge, the water level falls to the extent that there is unsaturated Chalk beneath the Till. The regional hydraulic gradient is towards the south-east. The River Stour is likely to be in hydraulic continuity with groundwater. Contours on the potentiometric surface<sup>[10]</sup> show highs of over 70 mAOD beneath the Till plateau, indicating some recharge to the Chalk through the thick Till sequence (Fig. 3). Annual fluctuation of the potentiometric surface where the Chalk is confined by the Till is about 2 m in a hydrograph to the east (NGR TL 846 410) of the drill site, which compares with about 9 m in a hydrograph from the exposed Chalk to the north-west (NGR TL 594 591). The end of the recession and recovery periods on the confined hydrograph<sup>[10]</sup> coincides closely with the times on the exposed Chalk hydrograph. This suggests that there is little if any time lag in the recovery beneath Drift compared to the exposed Chalk environment.



- s Boreholes with CFC data
- s Main towns

	<b>Alluvium</b>		<b>Till</b>
	<b>Head</b>		<b>Glacial Sand and Gravel</b>
	<b>River Terrace Deposits</b>		<b>Upper Chalk</b>

Figure 2. Location of sampling sites.

The Chalk is a dual-porosity aquifer that relies on fractures and jointing for much of its transmissivity. The upper 10-20 m of the Chalk, particularly where it is exposed, may be poorly-jointed putty-chalk, and have a reduced permeability. Storage of water takes place mostly in the intergranular matrix of the Chalk, which has high porosity but low hydraulic conductivity.

Beneath the Till the Chalk groundwater carbonate hardness rises to 260-350 mg/L and non-carbonate hardness to 300-400 mg/L<sup>[10]</sup>. This compares to a non-carbonate hardness of 50–

100 mg/L in exposed Chalk. The chloride ion concentration increases to over 100 mg/L (Fig 4) and sulphate also shows high concentrations where the Till cover is thickest. This compares to a concentration of 15-50 mg/L Cl in the exposed Chalk. Whilst these highs might generally reflect reduced recharge they also coincide with highs in the groundwater surface which are indicative of recharge through the Till. These highs in the groundwater surface may partly relate to low transmissivity in the Chalk in these areas.

The boulder clay itself has a low intergranular permeability. However, fractures and sand lenses in the clay may enhance the overall permeability, although the extent and properties of these is not well known. The boulder clay in this area probably reduces recharge to the Chalk and also reduces the vulnerability of the Chalk aquifer to contamination. Furthermore, clay minerals (especially smectitic clays) within the boulder clay have the ability to attenuate contaminants by sorption and cation exchange<sup>[12]</sup>.

Beds of sand and gravel within the Till can be unsaturated, but most are partially or fully saturated. These perched water tables typically have limited storage indicative of their isolated nature. Groundwater derived from sands and gravels within the Till and beneath the Till, where they overly low-permeability bedrock, is characterised by high non-carbonate hardness (calcium sulphate and magnesium sulphate). Total dissolved solids (TDS) concentrations often exceed 700 mg/L and chloride ion concentrations are mostly between 60 and 110 mg/L<sup>[10]</sup>.

### 2.3. *Sampling sites*

At Boyton End, near the town of Clare, Suffolk, a borehole number CLR1 was drilled to a total depth of 31 m, through 21.4 m of Till and into the unsaturated and saturated Chalk (NGR 7142 4477) in the Till edge domain (Fig. 3). The borehole was constructed with a groundwater piezometer and six gas piezometers.

Near the village of Cowlinge (also Suffolk), a second borehole CW1 was drilled to a total depth of 80 m, through 35.8 m of Till into the saturated Chalk. A further 9 sites were identified in the area for groundwater sampling and are shown in Fig. 2. Table I shows the depth of the drift cover at each of these sites.

Table I. Till depth at each of the groundwater sampling locations

<b>Till Depth</b>	
m	
CLR1	21
Blacksmith Hill	20
Mill House	31
Great Wrattling	2.4
Gainsford Hall	40
Rede Lane	50
Radwinter Road	32
Skippers Lane	29
Thurlow Road	10
CW1	36
Cowlinge EA obh	29

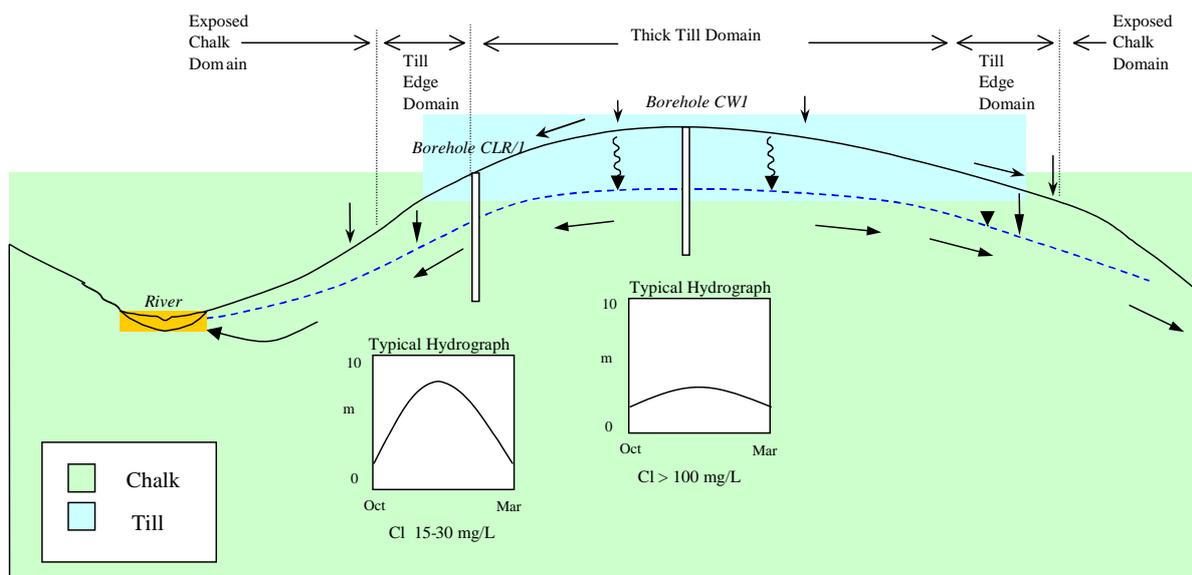


Figure 3. Schematic cross-section.

### 3. Sampling and analysis

#### 3.1. Chlorofluorocarbons (CFCs)

Pumped groundwaters were sampled by the bottle-in-can method<sup>[13]</sup>. Unsaturated zone gases were sampled using evacuated glass bulbs. Analysis was carried out using a purge-and-trap system (cooling to  $-50^{\circ}\text{C}$  and desorbing at  $100^{\circ}\text{C}$ ) coupled to a GC with electron capture detection. For dissolved CFCs detection limits of roughly  $0.02\text{ pmol/L}$  and  $0.13\text{ pmol/L}$  were possible using  $35\text{ mL}$  of water for CFC-11 and CFC-12 respectively. This is equivalent to 0.3 and 4 % of modern water respectively. Calibration was carried out by using an air standard prepared at the University College Galway Atmospheric Research Station in Mace Head, Ireland.

#### 3.2. Nitrate

Filtered, unacidified aliquots of groundwater were collected in Nalgene bottles. Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) was determined using standard colorimetric methods.

#### 3.3. Nitrous oxide

Pumped groundwater samples were collected in evacuated glass bulbs with known headspace volumes. Nitrous oxide ( $\text{N}_2\text{O}$ ) was analysed using a Porapak-Q column with nitrogen carrier gas and an electron capture detector. A certified gas standard was run with the samples to calibrate the results.

#### 3.4. Nitrogen/argon ratio

Samples for  $\text{N}_2/\text{Ar}$  measurement were prepared by gas-pipetting an aliquot of headspace gas (see  $\text{N}_2\text{O}$  above) into a 'finger'-type vessel containing approximately  $0.5\text{ g}$  of copper flakes. Atmospheric air was sampled in the same way to produce 'air spikes' against which to calibrate the results. The sealed fingers were then heated at  $450^{\circ}\text{C}$  for 15 min in order that all  $\text{O}_2$  could be removed by the copper. After cooling, the fingers were attached to a VG Optima Mass Spectrometer and analysed by ratio measurement of the mass 28 ( $\text{N}_2$ ) and 40 ( $\text{Ar}$ )

peaks<sup>[14]</sup>. This allows analysis on a dynamic (i.e. constant flow) mass spectrometer, which is an improvement on static mass spectrometry because of the absence of ‘cracking’ effects in the ion source. A higher precision is therefore possible. Ratios of N<sub>2</sub>/Ar were calculated by reference to the results obtained for air samples. Precision is ±0.2%.

## 4. Results and discussion

### 4.1. Regional concentrations

A summary of the percentage of modern water as determined by the CFC data is given in Table II. The percentage of modern water in the groundwater samples varies from 5-97 % based on the CFC-11 measurement and from 6-97% based on the CFC-12 measurement. In the majority of cases the percentage of modern water determined by CFC-12 is greater than that determined by CFC-11. Where the percentage of modern water determined by CFC-12 is less than CFC-11 then the values are generally low (i.e. both CFCs indicate a small fraction of modern water) or the two values are very close (note the relative fractions of modern water determined by the two CFCs in the River Stour). At one Till-edge site (Great Wrattling) there was evidence of CFC pollution, possibly associated with leakage from cold storage facilities at the adjacent pork-processing plant.

Table II. Summary of % of modern water present in samples as determined by CFC-11 and CFC-12.

	CFC-11			CFC-12			(F12-F11)/F12
	% modern	Stdev	CV (%)	% modern	Stdev	CV (%)	
CLR1	79	7	9	97	15	16	0.19
Blacksmith Hill	77	10	13	82	15	19	0.06
Mill House	35	30	85	82	28	34	0.57
Great Wrattling	>modern			>modern			
River Stour	97			94			-0.03
Gainsford Hall	5			15			0.67
Rede Lane	10			58			0.83
Radwinter Road	10			9			-0.08
Skippers Lane	6			66			0.90
Thurlow Road	12			8			-0.52
CW1	24			33			0.28
Cowlinge EA obh 11				6			-0.71

Nitrate, nitrous oxide and the N<sub>2</sub>/Ar ratio for the sampled groundwaters are given in Table III. The majority of the sites sampled contain nitrate-N concentrations below the 0.2 mg/L limit of detection. In general terms nitrate concentrations are highest where the Till layer is thinnest, with the one exception of the Thurlow Road Site.

Table III. Summary of nitrate (as nitrogen) nitrous oxide concentrations in selected groundwaters together with the N<sub>2</sub>/Ar ratio.

	NO <sub>3</sub> -N	N <sub>2</sub> O	N <sub>2</sub> /Ar		
	mg/L	µg/L	Mean	Stdev	CV (%)
CLR1	39.6		46.2	3.5	7.6
Blacksmith Hill	8.3	26	44.5	2.2	4.8
Mill House	<0.2	1100	42.0	1.7	4.1
Great Wrattling	4.5	34	44.6		
River Stour	8.7				
Gainsford Hall	<0.2		39.2		
Rede Lane	<0.2		39.9		
Radwinter Road	<0.2				
Skippers Lane	<0.2		38.8		
Thurlow Road	<0.2		44.5		
CW1	<0.2		49.4		
Cowlinge EA obh	<0.2		46.1		

Where significantly lower fractions of CFC-11 relative to CFC-12 are present it is probable that environmental conditions are more reducing (as the CFC-11 is degraded under reducing conditions) which might coincide with denitrification. Site CW1 contains relatively more CFC-12 than CFC-11 and has N<sub>2</sub>/Ar ratios significantly above the background value of ~ 40, based on equilibration at 10°C plus minor excess air. Both suggest that some denitrification is taking place. At the Mill House site, there is considerable variation in the fraction of modern water as indicated by CFC-11 and CFC-12 (Fig 4), with the suggestion that CFC-11 has been degraded under reducing conditions. Data from the N<sub>2</sub>/Ar measurement however shows little N<sub>2</sub> enhancement although the concentration of N<sub>2</sub>O in the water is very high. It is suggested therefore that denitrification is occurring at this site but that conditions are not suitable for the formation of nitrogen gas (i.e., a suitable microbial population is not present). A similar observation has previously been made for a site underlying a cattle slurry storage lagoon<sup>[15]</sup>.

With the exception of the River Stour, Great Wrattling and CLR1, groundwater is composed of between 6 and 80% modern water. Where the Till depth is greater than 5 metres this suggests that some preferential water movement is taking place.

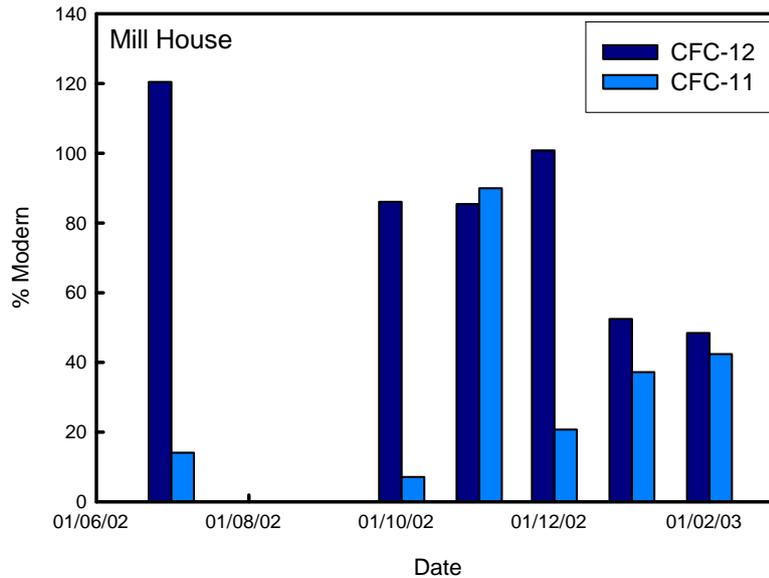


Figure 4. Concentrations of CFC-11 and CFC-12 at the Mill House site sampled over 7 months from July 2002.

#### 4.2. Modelling Gas Movement at CLR1

The variation with depth in CFC-12 concentration in the gas samplers positioned in borehole CLR1 are given in Fig 5. The dotted line also shows the time lag for CFC-12 passing through a 26.8-metre unsaturated zone, calculated with the model of Cook and Solomon<sup>[16]</sup>. Gas- and liquid-filled porosities of 0.05 and 0.3 were used respectively, along with gas- and liquid phase tortuosities of 0.05 and 0.5. A liquid phase velocity of 0.3 m/a was used in the simulation. Other parameters for the properties of CFC-12 are given elsewhere<sup>[16]</sup>. The dashed line shows the time lag for CFC-12 passing through a three layer version of the Cook and Solomon model so as to simulate the unsaturated zone geology at this site. Layer one uses gas- and liquid filled porosities of 0.04 and 0.2; layer two 0.05 and 0.03; and layer three 0.3 and 0.05 respectively. Layer one uses gas- and liquid- phase tortuosities of 0.03 and 0.03; 0.1 and 0.2 in layer 2; and 0.05 and 0.5 in layer 3. The liquid phase velocity used was 0.1 m/a.

The small reduction in gaseous phase concentration in the unoxidised Till combined with the large step in concentration in the oxidised Till proved too difficult to model with this 1-D model. Highest concentrations, of the order of 100% modern, are seen at the top of the profile in the oxidised Till as would be expected. Lowest concentrations are found towards the bottom of the unoxidised Till. It could be argued that this should in reality be zero (i.e. pre-CFC usage) and that the presence of a proportion of modern air is an artifact of the installation process, even though great care was taken to evacuate any modern air from the system following sampler installation. The high moisture content and relatively high liquid phase velocity common in the Chalk mean advection in the liquid phase is much greater than diffusion in the gas phase and as such, time lags are all approximately equal to the water residence times. The gas concentration at 20 metres indicates atmospheric penetration of the Till layer to this depth takes some 20 years. This is in sharp contrast to the <1 year for penetration of a Chalk unsaturated zone of similar thickness suggested by gas tracer tests<sup>[17]</sup>. These results infer that fracturing in the unsaturated zone of the Chalk has an important influence on gas concentrations. The higher than predicted CFC-12 concentrations in the unoxidised Till and rise in CFC-12 values in the unsaturated Chalk beneath the Till likely

reflect the existence of groundwater recharge round the Till edge bringing more modern water (and air) into the system together with fluctuations in the water table. At 20 metres, the observed data contains roughly 15% modern air when compared with the model.

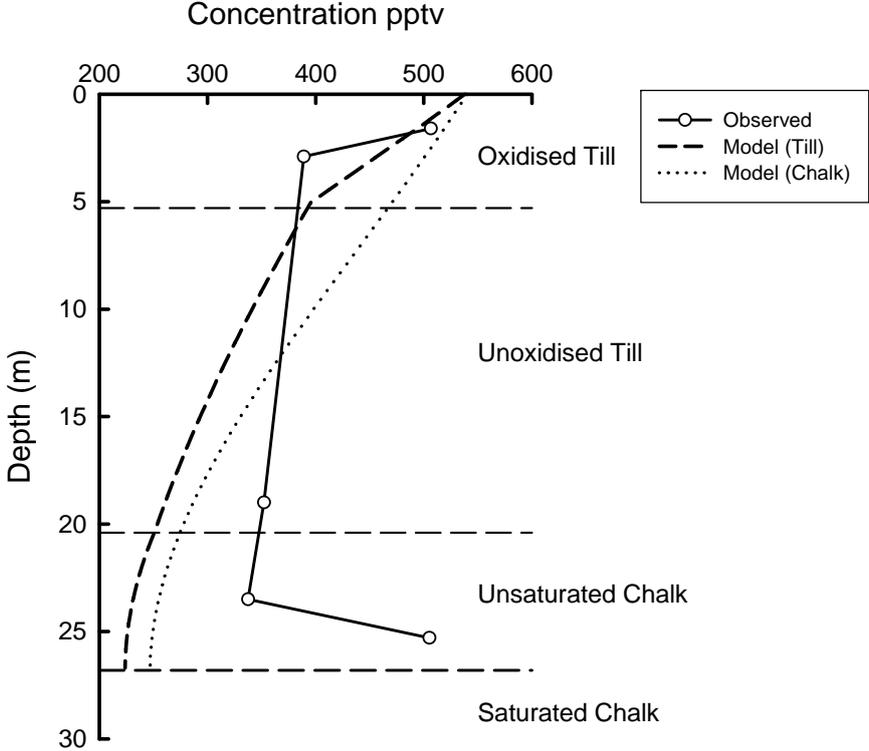


Figure 5. Variation in CFC-12 in gas samplers positioned in borehole CLR1 and two simulated profiles using the model of Cook and Solomon (1995).

### 4.3. Conceptual Model Development

The groundwaters show considerable variability both in water type and in apparent residence time. However, a pattern can be discerned (Fig. 6) which suggests that two groundwaters of different origins are present. The first type includes the Chalk groundwaters from the interfluvium at distances greater than 1 km from the edge of the till sheet. These have low nitrate (<0.2 mg/l N) and appear to be relatively old waters (proportion of modern water <15% as indicated by CFC measurements). The second water type occurs within the main river valleys and beneath the edge of the till sheet. These groundwaters, which have high nitrate concentrations, are of modern origin (proportion of modern water >70% according to CFCs) and are largely derived from rainfall of the last few decades

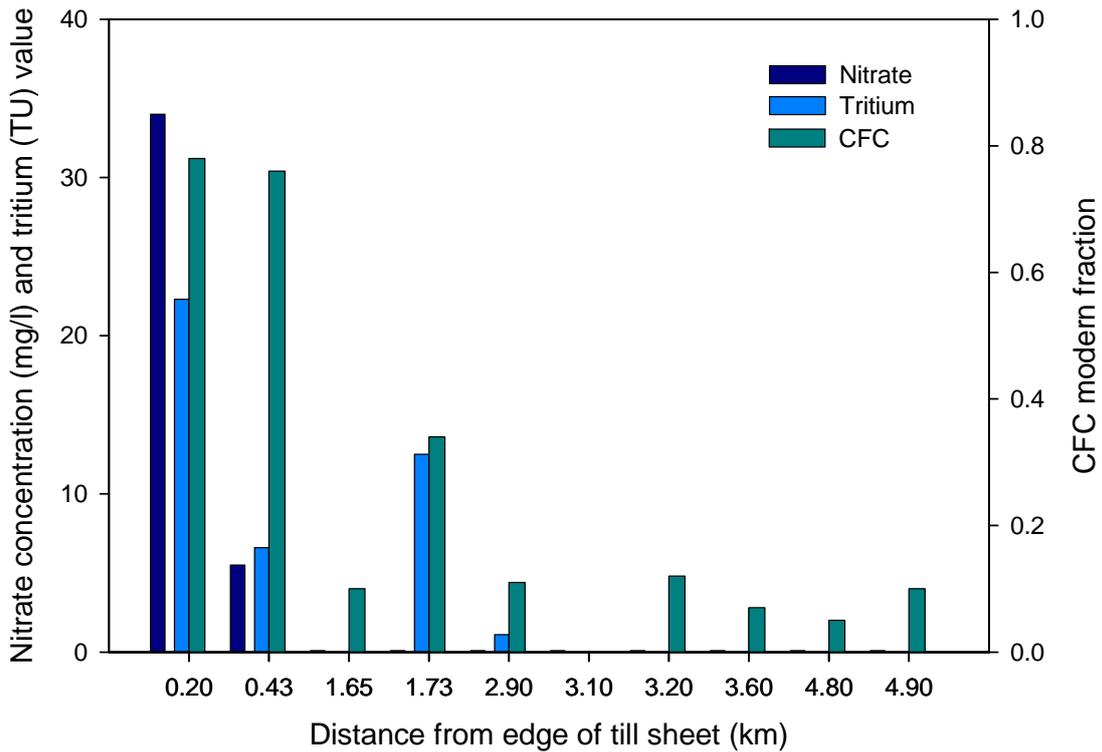


Figure 6. Variation in Chalk groundwater  $NO_3$ ,  $^3H$  and CFC-12 concentrations with distance from edge of till sheet.

It is postulated that there are also two distinct groundwater flow systems in the Chalk aquifer and more than one recharge mechanisms (Fig. 7). One groundwater system is represented by the relatively old groundwaters present beneath the interfluves. Here, the aquifer is confined (or semi-confined) and recharge occurs mainly as slow leakage through the till. Discharge from this aquifer system is limited by the low transmissivity of the Chalk and occurs as lateral flow into the more transmissive Chalk of the river valleys. Rapid infiltration to the Chalk occurs at the margins of the till sheet because fracturing in the till is better developed. The bulk of recharge beneath the interfluves occurs as slow ‘piston flow’, allowing time for diffusional exchange to occur between infiltration and till porewaters.

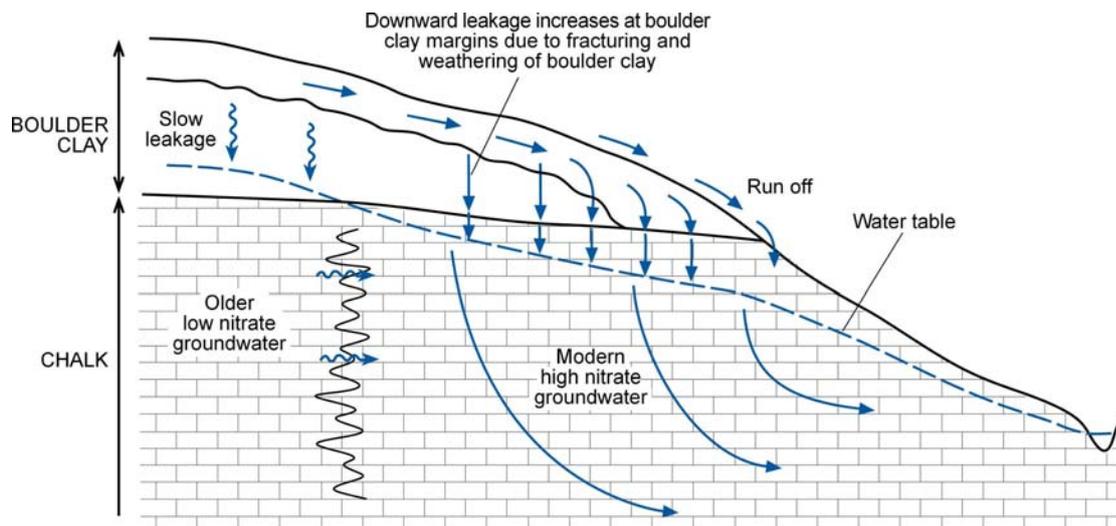


Figure 7. Conceptual model showing enhanced recharge to the Chalk occurs where fracturing and weathering develops at the edge of the till sheet.

## 5. Conclusions

The conceptual model of the Chalk-till system developed as a result of this study indicates that the till has a major impact on recharge. The Chalk groundwaters beneath the valley and till edge are very different; they have a large component of modern water and generally high nitrate concentrations. The groundwaters beneath the interfluvium do have a small modern component; CFC concentrations in these groundwaters suggest that this could be up to 15%. Data from the gas samplers when compared with a 1-D transport model seem to support this. These results show that the Till layer attenuates nitrate concentrations in groundwater by restricting the downward movement of recharging rainwater and promoting denitrification both in terms of redox conditions and time of exposure to them. Some water movement clearly occurs via preferential 'by-pass' flow paths.

## 6. References

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