BRITISH GEOLOGICAL SURVEY
Natural Environment Research Council

and ADAS

TECHNICAL REPORT WD/00/09
Hydrogeology Series

Technical Report WD/00/09

Impact of Farm Waste Stores on Groundwater Quality – FINAL REPORT

D C Gooddy[1], A G Hughes[1], A C Armstrong[2],
A T Williams[1], K J Griffiths[1], R A Nicholson[3],
J W Williams[3], H K Jones[1] and P J Chilton[1]

[1]British Geological Survey, Wallingford
[2]ADAS Gleadthorpe, Nottinghamshire
[3]ADAS Boxworth, Cambridgeshire

This report was prepared for
Ministry of Agriculture Fisheries and Food

Bibliographic Reference

D C Gooddy, A G Hughes, A C Armstrong,
A T Williams, K J Griffiths, R A Nicholson,
J W Williams, H K Jones and P J Chilton (2000)
Impact of Farm Waste Stores on
Groundwater Quality –
FINAL REPORT
British Geological Survey Report WD/00/09

British Geological Survey Keyworth, Nottinghamshire

Contents

List of Figures

List of Tables

Acknowledgements

The authors gratefully acknowledge the help and assistance of Peter Williams, Kerry Dodd and Janice Trafford for analytical work carried out on this project. George Darling is gratefully acknowledged for nitrogen isotope analysis and assistance with interpretation of the unsaturated zone gas data. The authors would also like to thank Tony Moore for microbial analysis and Roy Cross for collecting lagoon samples.

Executive Summary

This report details the findings of a three year study into the impacts of farm waste stores on groundwater quality. This is a joint project between the British Geological Survey and ADAS and began in April 1997. Funding has been from the Ministry of Agriculture, Fisheries and Food, Environment, Fisheries and International Science Division, under contract number WA0517 as part of their ongoing research and development programme into farm wastes.

Unlined earth-banked farm slurry stores pose a particular threat to groundwater since recent research suggests that the waste and its constituents is able to leach from the bottom of these stores. After investigating a potential 68 sites, we have undertaken a detailed field programme at 3 sites on the Chalk and 5 sites on the Permo-Triassic Sandstone, the two principal aquifers in the UK, beneath unlined slurry stores. Seven of the sites (2 Chalk and 5 Permo-Triassic) concentrated on unlined cattle slurry lagoons whilst one site examined the effects of a turkey manure store.

Boreholes were drilled at an angle of 45° so as to obtain material from directly beneath the stores at several of the sites. In addition, a vertical hole was often drilled adjacent to the slurry stores so as to assess the degree of lateral spreading. Vertical boreholes were also drilled through the centre of the turkey litter store since the management of solid manure heaps left a period of the year where the storage area was free from waste. Cores from the boreholes were centrifuged so as to extract the interstitial waters and selected samples were taken for microbial examination. At one Sandstone site and one Chalk site, specially designed gas samplers were installed beneath the slurry lagoons to investigate the aquifer gas composition.

Cores taken from beneath the two cattle slurry store Chalk sites showed visual staining from slurry material along fracture faces in the rock. In addition, porewaters from all of the Chalk sites and one of the Sandstone sites showed distinct coloration. These samples showed very high concentrations of nitrate, ammonia, organic carbon, potassium and chloride. The cores taken from beneath two cattle slurry lagoons situated on Chalk exhibited different chemical characteristics with the inference that the least contaminated of these two had formed a sealed base. Gas samplers installed at this Chalk site showed very high rates of denitrification. The physical and chemical properties of the different aquifers were also shown to impact on contaminant movement and attenuation.

Microbial studies showed contamination from clostridia in all of the sites studied, however this contamination extended to a depth of 18 m in the two Chalk sites beneath cattle slurry lagoons. *Cryptosporidia* was found in cattle slurry from five sites, whereas *E.coli* O175 was found in cattle slurry from just one of the six sites tested for these pathogens. Neither *Cryptosporidia* nor *E.coli* O157 was found in any of the rock samples taken for microbiological examination. This may however relate to the small sample size and limits of detection rather than their absence.

Taking data obtained from the field site investigation, we attempted to model mathematically the impact on local groundwater concentrations as a result of a leaking farm waste store. Modelling studies showed that concentrations in theoretical nearby production boreholes would be expected to rise only very slightly, typically by 0.5 mg/L for nitrate.

Two maps assessing the risk to the principal aquifers in England and Wales have been generated by overlaying the volume of slurry stored in a given region over the aquifer outline and combining this with either the HOST classification system of soils or the geological drift map. These maps identify the Chalk outcrop of the Dorset and small parts of the Permo-Triassic Sandstone in the West Midlands as the regions most at risk from farm waste stores. Areas with a shallow water table are also considered to be at higher risk to groundwater contamination from unlined slurry lagoons.

1. INTRODUCTION

1.1 Background

1.1.1 Groundwater in England and Wales

Groundwater provides over 30% of all water abstracted for public water supplies in England and Wales (DETR 1997), 8% in Northern Ireland and 5% in Scotland (Bell et al, 1997). The regional differences reflect the distribution of aquifers and the more favourable geological conditions for surface water resource development in Northern Ireland and Scotland. It should be noted that in upland Britain while the proportion of the total supply derived from groundwater is low, the number of individual sources involved is large.

Over 80% of the total public supply in south-east England is derived from groundwater, while in the Severn and Trent basins, eastern England, the Thames Valley and the Wessex region the figure is between 30 and 50%. Extensive blending of groundwater and surface water further increases the extent of groundwater use. Industry and the agricultural community rely on groundwater in many areas and it is the predominant source for private water supplies. The total abstraction of groundwater in the UK, including that used by industry and agriculture, is some 2400 million m^3/year. About 85% is pumped from the two major aquifers, the Chalk and the Permo-Triassic sandstones which provide 60% and 25% respectively.

1.1.2 Farm waste stores

Storage of farm wastes presents a serious potential risk of surface water pollution usually following structural or operator failure. In the past, serious pollution incidents to surface waters have led to prosecutions by the Environment Agency (EA). There has not been the same concern about potential pollution to groundwater perhaps in part because 'out of sight is out of mind' and because of the greater dilution and less immediate impact expected in groundwater systems. Groundwater source catchments are more difficult to define than the surface water equivalents as they cannot be as easily delineated by topography. Information from the EA's groundwater protection zone database shows that 875 of the 2,200 sources so far defined have a total catchment area exceeding 11,000 km^2. It therefore seems likely that as much as 15% of the land area of England and Wales may comprise catchment of an important potable groundwater supply source.

The main types of store in use in the UK can be classified as follows:

Table 1.1 Types of stores common in the UK

Slurry	Solid Manure
Cylindrical above ground tank	Concrete pad – with tank
Weeping wall store	Field Heap
Unlined earth-banked lagoon	Roofed store with concrete base
Lined earth-banked lagoon	
Below-ground concrete tank	

The majority of structures generally only pose a risk of water pollution because of structural or operator failure. In the case of unlined earth-banked slurry lagoons which were unregulated before 1991, and field heaps of solid manure, there is a potential risk that they have been built on relatively permeable sites and that leakage of pollutants through the base and walls will occur and cause pollution of groundwater. The study has therefore concentrated on these types of store.

The 1991 Control of Pollution (Silage, Slurry and Agricultural Fuel Oil) Regulations introduced for the first time minimum requirements for the sizing and siting of new or substantially modified slurry storage structures and laid down minimum constructional standards based on BS 5502 (Buildings and Structures for Agriculture) and mandatory notification to the EA before being brought into use. Impermeability required for earth-banked structures is not defined in these regulations, however CIRIA Report 126 (1992) recommends that for new unlined earth banked structures permeability should not exceed 10^{-9} m/s. This rules out all but impermeable clay sites with at least 1 m depth of suitable material as appropriate for installation of an unlined structure of this type. Slurry stores built before 1991 were not subject to these controls and there are still a number of earth banked stores constructed before that date which remain in use. Storage of solid manure in the field is not subject to these regulations but is covered in the MAFF Code of Good Agricultural Practice for the Protection of Water (MAFF, 1998). An ADAS study suggests that there could be as many as 11,500 unlined farm waste stores in England and Wales (Nicholson and Brewer, 1997) some of which are likely to be located above aquifers and/or in the catchment of a potable groundwater supply.

1.1.3 Potential Groundwater Contaminants

Slurry stores are designed to contain liquid and solid wastes, however, due to leakage they will almost invariably impose a higher hydraulic loading than pollutants solely entering at the top of the soil zone. One impact is the potentially large nitrogen (ammonium and nitrate) load. In addition, faecal matter contains very large numbers of non-pathogenic bacteria but may also contain helminth eggs, protozoa, bacteria and viruses which are capable of causing infectious diseases. Virulent pathogens such as *Escherichia coli* O157 are also known to be present in cattle (Hancock et al, 1994) and are thought to contaminate between 1 and 15% of UK cattle herds, depending on region (Jones, 1999). While most microbial contaminants die off in passage through the soil, they may enter the subsurface directly via farm waste stores which by-pass the soil zone. Where by-passing of the sub-soil occurs, the role of the unsaturated zone is especially important. Thus the unsaturated zone offers an effective barrier for pathogen removal. Like the soil profile, the unsaturated zone exhibits aerobic conditions. As aerobic degradation is more effective than anaerobic decomposition for many organic compounds, this will favour pollutant removal as part of a natural biological process. However, soil and unsaturated zones can be overloaded. Furthermore, microorganisms may percolate most soils and rock pores, except in fine-grained strata where pore diameters are small (Harvey et al, 1995). Cryptosporidium oocysts are larger than the typical 1μm pore size of the Chalk aquifer but they are within the pore size range of arenaceous aquifers like the Permo-Triassic sandstones. Oocysts are almost certainly smaller than the fracture and micro-fracture/bedding plane aperture systems which dominate groundwater transmission in most important UK aquifers. It should be noted that the effects of fractures can be even more important in the unsaturated zone than below the water table, because significant by-pass flow can occur along vertical fractures activated after major recharge events. This by-pass flow, especially in the Chalk, can be very fast compared to typical intergranular flow rates.

It is unclear how important these impacts currently are or the timescale over which their future impact is likely to be felt. This is set against a background of a determined attempt by MAFF and others to limit future nitrate leaching to groundwater and to minimize the possibility of pathogens entering the public water supply. This is also recognised by the European Union under Directive 91/676/EEC concerning protection of waters against pollution caused by nitrate from agricultural sources, Directive 80/68/EEC on the protection of groundwater from pollution by dangerous substances, and the EU Drinking Water Directive 80/778/EEC (currently under review). All of these Directives are scheduled for integration into the Water Framework Directive which hopes to achieve 'good status' for all groundwaters and surface waters by 2010 at the latest.

1.1.4 Protection of Groundwater

A technical and policy framework for groundwater protection in England and Wales is provided by the EA Policy and Practice for the Protection of Groundwater (NRA, 1992). The methodologies employed comprise: A classification of groundwater vulnerability and a national set of maps showing areas of high, intermediate and low vulnerability to contamination. A programme of mapping at 1:100,000 scale has been under way in England and Wales since 1992. Complete national coverage on 53 maps has now been published. The maps all classify groundwater on the basis of intrinsic aquifer vulnerability. This addresses characteristics that determine vulnerability, rather than behaviour of specific contaminants.

Source protection zones defined by the travel time of potential pollutants from within the overall source catchment areas are superimposed on the zones defined on groundwater vulnerability criteria. The programme of defining protection zones around supply sources in England and Wales also commenced in 1992, and of the 2,500 or so licensed public groundwater supplies yielding 0.25 ML/d or more, some 2,200 now have delineated zones. However, due to the inherent uncertainties in the data used in groundwater catchment delineation techniques, there is generally a margin of error, sometimes significant, in the resultant zones. A matrix of policy statements, relating to activities at the land surface and to the control of groundwater abstraction allows the EA to exercise consistently its statutory powers. At the same time users and other interested parties can assess what practices are likely to be unacceptable in a given zone.

The groundwater vulnerability mapping and protection zone programmes undertaken by the environmental regulators provide a basis for assessing which British public groundwater supply catchments are likely to be most susceptible to contamination but there are some limitations. Although the vulnerability maps use soil leaching potential as a criterion, they do not take account of the other most important attenuating property: depth to water table. For a contaminant like Cryptosporidium this factor, which extends recharge travel time, could be significant, given its potential for retention in the unsaturated zone. By-pass features that may allow the rapid passage of water from the land surface to the water table, are not taken into account in the vulnerability classification.

1.2 Previous Research

A study carried out by Barrington et al (1991) on below ground concrete tank stores revealed that extensive leakage could occur from these stores, especially during times of high water table, if they had been poorly installed with no special precautions to seal the joints between the floor and the walls. However, provided no defects arise in the floor slab, either through design or general usage, above ground concrete structures should present minimal risk of groundwater pollution.

Structures with an impermeable synthetic liner should also present minimum risk of groundwater pollution provided the liner remains intact both during installation and for the duration of its active life time. Ritter and Chirnside (1983) showed that failure of a clay liner in a lagoon overlying a highly permeable soil caused serious groundwater contamination.

There is conflicting evidence with regard to the risks from unlined cattle slurry lagoons. Monitoring around large-scale structures (Miller et al, 1984; Rowsell et al, 1985) in Canada has sometimes shown no adverse effects on groundwater, even when constructed on sandy material. This has often been attributed to the self-sealing effects of slurry. Monitoring of slurry constituents in groundwater beneath lagoons in the United States has lead several researchers (Oliver et al, 1974; Robinson, 1973; and Sewell et al, 1975) to conclude that the infiltration rate of lagoon contents decreases with time, although there is little consensus as to the rate or degree of this decrease. In a laboratory study, Rowsell et al (1985) found the infiltration rate of a sandy loam, a loam and a clay soil decreased with time to a value of 10^{-8} m/s or less within 30 days at a hydraulic head of 1 m. This study showed slurries to have a significant self-sealing effect by causing physical blockage of pores.

Culley and Phillips (1989) studied 3 unlined lagoons in the US on a range of soil types to conclude that effective sealing did not occur within a five year period. A recent study in Japan (Kanazawa et al, 1999) showed evidence of groundwater pollution 75 m away from an unlined slurry lagoon just four days after the lagoon was first filled. Contamination of nearby groundwater persisted for the 85 day duration of the study. In a UK study beneath an unlined store on the Upper Chalk of Southern England, microbiological and other slurry contamination was found to depths of at least 30 m after 18 years of use (Gooddy et al, 1998a). From the same store, slurry components and bacterial contamination were found 80 m down groundwater gradient in an observation borehole with a water table more than 50 m deep (Withers et al, 1998). It was deduced that the contamination in the observation borehole must have occurred by rapid transport of slurry and its constituents through fractures in the unsaturated and saturated zones. Any loss of self sealing and subsequent leakage were attributed to disruption of the self-sealing layer during emptying of the lagoon by dragline. Other studies have identified drying of exposed subsoil or embankment soil during the recession of liquid levels (Ciravalo et al, 1979), and repeated freezing and thawing as factors causing loss of self-sealing.

1.3 Objectives

The objectives of this study were to establish whether farm waste slurry stores posed a significant threat to groundwater and to suggest ways in which the pollution risk could be minimised. This was to be achieved by:

(i) Determining the chemical and microbiological concentrations of slurry constituents in the unsaturated zone beneath farm waste stores most likely to threaten groundwater

(ii) Estimating the likely pollutant load to groundwater of such waste stores and their overall contribution to groundwater pollution.

(iii) Identifying any mechanisms that might ameliorate such pollution during transport in the groundwater.

(iv) Estimating the timescale of any significant deterioration in groundwater quality.

(v) Estimating the number and geographic distribution of such sites in England and Wales and superimposing these on a map of the UK aquifers to define the most susceptible locations.

The study focuses on Britain's two major aquifers, the Chalk and the Permo-Triassic Sandstone. As described earlier, these are the major aquifers in the UK supplying nearly 90% of groundwater in England and Wales. Since all stores constructed after 1991 should have an impermeable base, the decision was made to focus field studies on unlined stores where possible, since it was considered that these pose the greatest threat of contamination to groundwater.

1.4 Scientific Approach

The project has combined data from field studies undertaken in years one and two of the project with hydrogeological modelling of contaminant movement at the catchment scale. Using the combined expertise of the British Geological Survey and ADAS, risk mapping at a national scale has been undertaken through overlaying estimated cattle numbers on a geological map of the UK.

As part of the field study, cored boreholes were constructed at each site close to existing farm waste stores. Where necessary these were drilled at an angle as close to 45° as possible to give access to the rock directly underneath the store. Porewaters were extracted by centrifugation and analysed for a wide range of pollutants and other indicators. Selected inclined boreholes from the first year of the investigation contained specially designed gas samplers. These were sampled to characterize the subsurface atmosphere (O_2, CO_2, CH_4) and to see if denitrification is significant (N_2, N_2O N_2/Ar). Core material was also examined for coliforms, faecal enterococci, *Clostridia*, *E.coli* and for the pathogens *Salmonella*, *E.coli* O157:H7, *Cryptosporidium parvum* and *Campylobacter*.

Modelling has been aimed at assessing the potential risk to groundwater sources caused by slurry pits on both a regional and local scale. To do this a variety of modelling techniques have been used. The main emphasis has been on trying to quantify the effect of the solutes within the slurry on groundwater abstractions within the area. No work has been done on particulate transport which poses its own special problems. Also the way in which the slurry pits are managed has not been examined in detail.

Vulnerability mapping on a national scale was carried out by using a GIS to overlay layers containing information on aquifer outcrop, drift cover and soil HOST classification. The resultant vulnerability map was combined with data on farm waste store density to identify areas at highest risk of groundwater pollution from farm wastes.

2. METHODS

2.1 Site Selection

During the course of the project, several lists of potential sites for investigation were supplied to BGS by ADAS. These sites had been identified by ADAS consultants in the field as unlined earth-banked stores with the right construction configurations to make them of potential use for further investigation by drilling and sampling. Farmers were generally very reluctant to become involved in the project despite assurances that sites would not be identified.

A further major consideration for the selection of sites for investigation was the geology underlying the stores. The project was orientated towards the major British aquifers, especially the Chalk and Permo-Triassic (Sherwood) sandstones. Other rock types could be considered but only if they constituted a locally important aquifer. It was desirable for the aquifer to be at or very near to surface outcrop at the store site. Large (thick) coverings of superficial deposits may have a significant effect on the fate of any slurry etc. leaking from a store down to the bedrock aquifer.

Each potential site submitted to BGS was checked for the bedrock type underlying the store along with details (if any) of superficial deposits at the site. In the first instance, only the two major aquifers above were deemed suitable and no account has been taken of any "minor" aquifers at this stage. The geology checking procedure took the form of locating the site on the BGS 1:50000 geological map (or where not available, the 1:63360 scale map) and determining the bedrock at that point. If the site occurred on an aquifer of interest, the presence of any superficial deposits was determined. The next stage of checking of sites passing this initial sift was by reference to the BGS Hydrogeology Group borehole records. The location of any borehole or well in the vicinity was determined and the geological logs of those sites were examined. This provided (with interpolation if necessary) the most accurate prediction of the geology at the sites of interest.

2.2 Borehole Construction

As all of the slurry stores were still active, it was necessary to construct inclined boreholes (generally at an angle of 45°) so as to obtain material from directly underneath the lagoon. For all but one of the sites, continuous core was obtained throughout the unsaturated zone by rotary coring using air as the lubricating fluid. At the Chalk Site 3, core was obtained through a percussion drilling process where no lubricating fluid was required.

2.3 Sample Handling and Porewater Sampling

Porewater was extracted from both the Chalk and the Sherwood Sandstone core material as soon as possible after drilling. This was carried out on the core by using the high speed centrifuge 'drainage' method (Kinniburgh and Miles, 1983). Briefly, core is crushed in a polythene bag to produce fragments of roughly 5 mm diameter before placing into the buckets of a fixed angle rotor refrigerated centrifuge. Specially made Delrin liners with collection cups and pre-filters hold the rock fragments in the centrifuge rotor. The samples are centrifuged at 14000 rpm (a driving force of roughly 2.0MPa) for 35 minutes. The resulting porewater is then split into three fractions; one filtered and acidified for cations; one filtered and unacidified for anions; the other unfiltered and unacidified for dissolved organic carbon.

2.4 Chemical Analysis

All analyses were carried out in the BGS laboratories at Wallingford. Filtered acidified porewaters are analysed using an ARL 34000C Inductively Coupled Plasma-Optical Emission Spectrometer

(ICP-OES) which is calibrated for the following 28 elements: Na, K, Ca, Mg, B, Li, P_{total}, SO_4, Si, Sr, Be, Ba, Sc, Y, Mn, Co, Fe_{total}, Zn, V, Cd, La, Cu, Zr, Cr, Ni, Mo, Al, and Pb. All analyses are blank corrected and detection limits defined as 6 times the standard deviation of the blank.

Selected acidified, filtered samples (where sufficient sample is available) from each borehole were also analysed for Li, Be, Al, Cr, Co, Ni, Cu, Zn, Ga, Ge, Rb, Y, Zr, Mo, Cd, Sb, Cs, Ba, La, Tl, Pb, Bi and U, using a VG Plasma Quad Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Internal standards of In and Pt (at 50 $\mu g\ L^{-1}$) are used to compensate for any instrument drift and matrix effects caused by the relatively high TDS likely in some of the samples. Calibration is carried out for each element using aqueous standards in the range 1-100 $\mu g\ L^{-1}$. Standard reference materials, SLRS2 (National Research Council, Canada) and 1643c (National Bureau of Standards, USA) are used to check the accuracy of the calibrations. Instrument configuration is detailed in Gooddy et al (1995).

Nitrate-nitrogen (NO_3-N), ammonium-nitrogen (NH_4-N), molybdate-reactive phosphorus (MRP) and Cl are determined using standard Auto Analyser II colorimetric methods (Kinniburgh and Miles, 1983) on the filtered, unacidified water fraction. To overcome interference problems with the likely yellow/brown colour of some of the porewaters (Gooddy et al, 1995), samples are run with and without the colour reagent for Cl analysis and the difference between the two taken as the actual concentration. NO_3-N is determined by the cadmium column reduction method since the likely high organic carbon content of the samples can cause suppression of the baseline when the hydrazine/copper reduction method was used. pH is measured with a glass micro electrode and bicarbonate (HCO_3) determined with an automated Radiometer titrator. Specific electrical conductance (SEC) is measured using a Radiometer conductivity probe and corrected to 25°C. Dissolved organic carbon (DOC) is measured on the unacidified, unfiltered sample with a Skalar CA 10 TOC analyser.

2.5 Unsaturated Zone Gas Samplers

The gas samplers were made from short lengths of plastic waste pipe perforated with 10 mm diameter holes at 30-40 mm centres and packed with glass wool to prevent ingress of the sand screen material. Sampler length and diameter were 300 mm and 43 mm, respectively, for the deeper samplers and 200 mm and 35 mm, respectively, for the shallow samplers. These samplers were installed at the required depth and surrounded with coarse sand. Each section was isolated from its neighbour using a thick bentonite seal. The samplers were connected to the surface by 6 mm colour-coded nylon tubing. Each tube has a toggle valve at the top to prevent contamination by the atmospheric gases. Samples were taken after an acclimation period of about 6 months (Kinniburgh et al., 1998).

2.6 Microbiological Examinations

Core material from the boreholes was selected at approximately 5 m vertical intervals, comminuted and suspensions in maximum recovery diluent were prepared using a wrist action shaker for 15 minutes. The suspensions were examined for the following microorganisms:

- Coliforms by plate count (based on BS5763 part 2 1991)
- Faecal enterococci by plate count (based on BS5763 part 10 1993)
- *Salmonella* presence/absence by enrichment and plating (based on BS5763 part 6 1993)
- *Escherichia coli* by plate count method (based on BS4285 3.8 1988)
- *Clostridia* by anaerobic plate count (based on BS5763 part 1 1991)
- *E. coli 0157:H7* presence/absence test using immunomagnetic separation

- Detection and enumeration of *Cryptosporidium* oocysts by concentration and specific staining (based on ISBN 0 11 75228 1)

- *Campylobacter* presence/absence by selective enrichment using Park Sanders broth and selective plating using Nutritive Blood Gelatine agar and Modified Charcoal Cefoperazone Deoxycholate agar.

2.7 Modelling Approaches

A range of models and techniques have been used to assess the likely effect of farm waste pits on groundwater abstractions. Further details are in Williams et al (2000). The first technique is essentially a mass balance approach which is based on the principle of conservation of mass. All the pollutant introduced to the groundwater is assumed to find its way to the abstraction point. The calculated concentration at the abstraction point is an average of the concentrations in the contributing water. This technique gives an indication of the long-term effect of the slurry pits but gives no indication of the time scale of the effect and so cannot be used to show the effect of changes in leakage from the pits (for instance if the pits were to be lined).

In order to estimate the possible flux from a waste store a model was developed which incorporates a simple waste store management model with a variable unsaturated zone. The permeability of the unsaturated zone is assumed to be reduced by the effect of the slurry, and the Richard's equation is solved to estimate the flux through the store under a range of effective permeabilities.

Numerical groundwater flow modelling was used in several ways. Firstly a model representing the situation in the vicinity of a slurry pit was developed. This was done to assess the possible impact of a slurry pit on a farm abstraction borehole. The model was based on one of the sites investigated during the drilling programme but was necessarily simplified. This is because it was not possible to measure the hydraulic conductivity of the aquifer material or to accurately assess the hydrogeological boundary conditions. Also estimates had to made for the recharge rate.

A further model was developed which represented the catchment of a larger abstraction borehole. This was developed to be used in conjunction with a transport model to give an indication of the timescales appropriate to changes in concentrations caused by the slurry pits.

2.7.1 Data used for modelling

The basic chemical data used for this modelling work was obtained from the field investigations carried out as the main part of the project. Table 2.1 shows the concentrations of various ions measured in the pore waters beneath two of the sites investigated, one on Chalk and the other on sandstone.

Table 2.1 Mean concentrations of porewaters (entire profile) for two of the sites investigated (figure is mg/L).

	pH	Cl	HCO_3	SO_4	DOC	NO_3-N	NH_4-N	Na	K	Ca	Mg
Chalk Site 2	7.6	732	459	497	130	201	96	200	1007	937	29
Sandstone Site 3	7.2	454	79	126	2900	0.5	256	122	673	545	119

The physical parameters, hydraulic conductivity and porosity, required for the numerical models were obtained from Allen et al (1997) and the values used are summarised in Table 2.2. This table also gives the values of other parameters required for the transport simulations. These values are based on those used for previous work with this model on predicting nitrate concentrations in abstraction boreholes in Yorkshire (Chilton et al, 1997, 1999). Some sensitivity analysis has been carried out to assess the effect of poor parameterisation on the conclusions of this work.

Table 2.2 Physical properties used during modelling work

Property	Permo-Triassic sandstone	Chalk
Transmissivity (m^2/d)	100-500	100-500
Hydraulic conductivity (m/d)	0.5-10	0.001-10
Porosity (%)	10-30	25-45
Fracture porosity (%)		1
Block size (m)		1
Diffusivity (m^2/s)		10^{-9}

2.7.2 *Unsaturated zone modelling*

A simple model was used to examine the balance of water in a slurry lagoon subject to downward seepage, and also to variable inputs. This model predicts the state of the water level (W) in a slurry pit as a function of a simple balance:

$$W = Rain - Evaporation - Seepage + Additions \qquad (1)$$

where all the components are added as units of depth per unit area. The model is shown schematically in Figure 2.1.

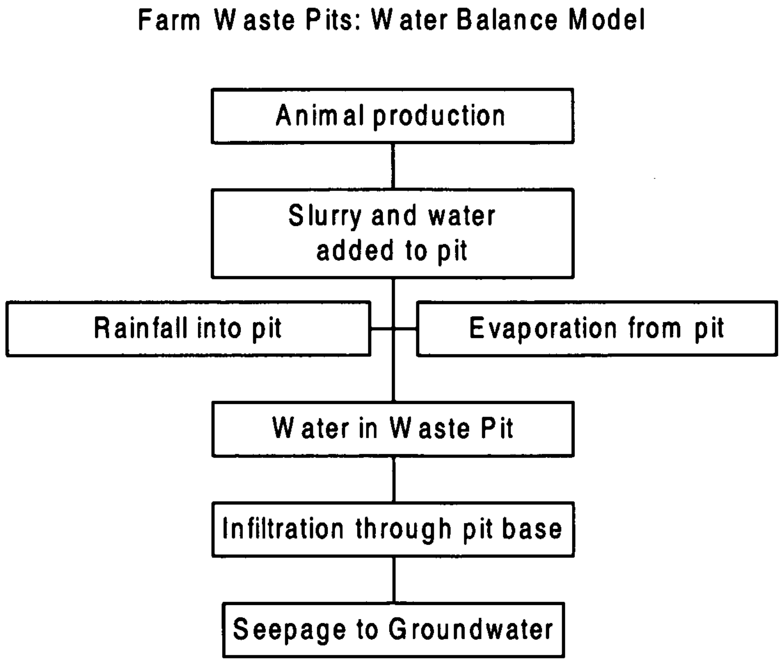


Figure 2.1 Farm waste pits water balance model

Rainfall and evaporation values were provided as from climatic data from the ADAS Boxworth site. Using a daily time step, the amount of fluid in the store accumulates due to the addition of more material from the farm. Seepage was calculated as unsaturated flow through the base of the pit using the Richards' equation. This required a description of the material profile beneath the pit base. It was assumed that the profiles could be based on the description of the unmodified geological material underneath, given by Allen et al (1997).

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial Z}\left(K(\theta)\frac{\partial H}{\partial Z}\right) \tag{2}$$

where:

$\partial\theta/\partial t$ is the rate of change of water content of the soil
$K(\theta)$ is the hydraulic conductivity of the soil. a function of the water content, θ, and
$\partial H/\partial Z$ is the hydraulic gradient.

This model then predicted the fluxes through the bottom of the pit, and through the base of the soil profile, over a period of years. It was used with a variety of soil profile descriptions to identify the importance of the surface sealing layer, and to estimate the fluxes of water that would travel to the groundwater.

Median values for the Permo-Triassic were used, with a K_{sat} of 0.56 m/d and a porosity of 26%. Values for the Chalk were more difficult to estimate, because of the observation that hydraulic conductivity measured in boreholes is at least an order of magnitude greater than that measured in the matrix. The conductivity in the chalk matrix is extremely low, with an average of 6.3×10^{-4} m/day. The presence of fracture systems which provide the majority of the flow paths increases the "effective" conductivity in a way that is far from homogenous. For the purposes of the present study, we adopt a value that is an order of magnitude greater than the matrix mean, i.e. 6.3×10^{-3} m/day.

Values for the conductivity of the contaminated layers at the base of the pit were more difficult to estimate. Studies by Owens (no date) showed "that slurry had a highly significant and dramatic sealing effect on soils" reducing the mean hydraulic conductivity by an order of 94-98%. This level of sealing has been noted by other workers (e.g. Barrington et al,1987). Owens also reported no differences in the sealing effect between types of slurry. It was thus considered that a suitable case for modelling would be that of a layer 0.2 m thick with the K_{sat} reduced to 1% of its original value, and a further layer, 0.3 m thick, reduced to 10% of its original value.

In order to investigate the effects, four soil scenarios were created, based on different degrees of sealing. These involved different configurations of the sealing effect. Three or four layers were identified, with their conductivities one, two or three orders of magnitude smaller than that of the unsealed geological material.

The main assumption in this modelling is that the slurry causes a reduction in permeability in the formation directly below it, which inhibits the flow of fluid out of the store. This is a reasonable assumption to make and is based on laboratory experiments. It is not certain how thick the 'sealed' layer is, and this has been tested in the modelling. It is also assumed that flow below the waste pit is vertically downward. The other major assumption is of the rate at which liquid is added to the store. For the purposes of this model, it was assumed that the pit was designed to hold 6 months worth of slurry in a pit 2m deep – and so that daily rate of addition was 0.01m/day. This assumption is based on the known geometry of most waste stores and the feeling that if the store filled up any quicker than this then a larger (areally) waste store would be constructed. It is not thought that the waste store is likely to be much higher than 2 m.

2.7.3 *Mass balance approach*

This simple initial approach to the problem is designed to give an indication of the long term effect of leakage from slurry pits on abstracted water quality. The relevant equations are given below:

$$M_{pit} = C_{pit} \times A_{pit} \times R \tag{3}$$

$$M_{background} = C_{background} \times A_{background} \times R \tag{4}$$

$$C_{well} = \frac{M_{pit} + M_{background}}{Q_{well}} \tag{5}$$

where:

M = Mass loading of contaminant (kg/d)
A = Area (m^2)
R = Recharge rate (m/d)
C = Concentration (kg/m^3)
Q = Abstraction rate of the well (m^3/d)

The subscripts refer to the slurry pit, the well and the catchment area of the well excluding the slurry pit. The catchment area of the well is calculated from:

$$A_{well} = \frac{Q_{well}}{R} \tag{6}$$

Thus:

$$A_{background} = A_{well} - A_{pit} \tag{7}$$

This method is based on the assumption that the water removed at an abstraction point is a mixture of all the water recharging the aquifer within its capture zone. The capture zone in this case is defined simplistically as being that area of land which provides the same volume of recharge as is abstracted at the point of interest. No account is taken of the time taken for the water to arrive at the abstraction.

The recharge through the slurry pit is assumed to be at the same rate as that in the surrounding area, but is associated with a higher concentration (500 mg/L as opposed to 5 mg/L). Thus the mass of nitrate applied to the catchment can be calculated by calculating the mass of nitrate leaching from the slurry pit combined with the mass leaching from the surrounding area. This mass of nitrate will be abstracted at the borehole and the concentration of the abstracted water can therefore be calculated.

2.7.4 *Farm scale modelling*

The mass balance modelling suggested that the main concern with the leachate from slurry pits would be on small abstractions in the immediate vicinity of the pits. To consider this problem a finite difference numerical flow model was created to represent conditions at one of the sites investigated during the field work. The site chosen is on the Chalk aquifer in southern England and was chosen as hydrogeological details of the site were known.

The model was created using the MODFLOW code (McDonald and Harbaugh, 1988) which simulates 3-dimensional flow in a saturated aquifer. Boundary conditions, which surround the modelled region, can be fixed head, fixed flow or head-dependant flow. Recharge is applied to the top of the saturated zone. The initial assessment was carried out with a single layer, steady-state model. Particle tracking with MODPATH (Pollock, 1989) was used to define the capture zone of a small abstraction well in the vicinity of the farm.

The model grid is shown in Figure 2.2. As can be seen an expanding mesh was used to allow the well to be accurately represented. Two of the model boundaries are no-flow boundaries, representing natural groundwater divides and the other two are flow-dependant head boundaries representing the river which passes close to the farm site. Details of the hydrogeological parameters used are given in Table 2.3. The modelled region is 4 km by 5 km.

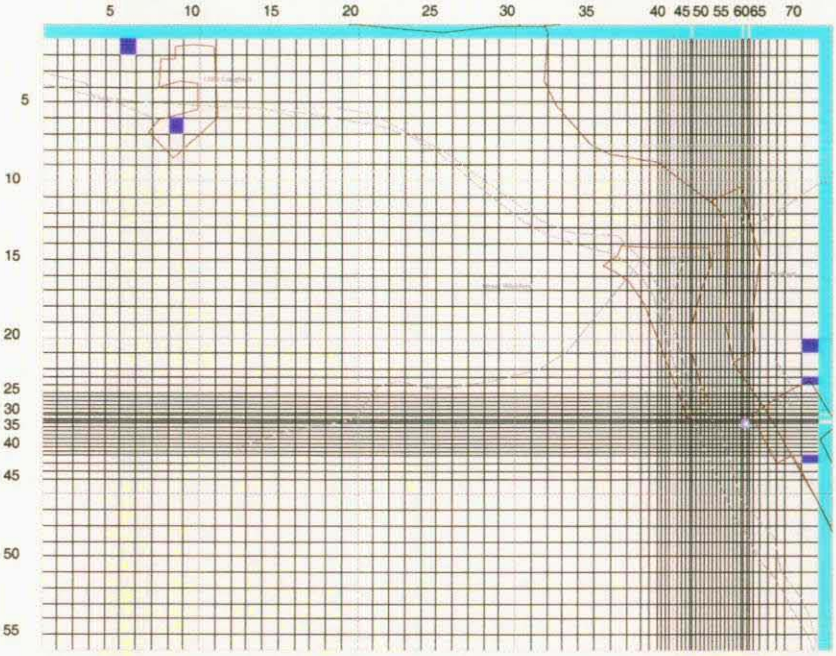


Figure 2.2 **Model grid used in site scale modelling.**

The objective of this part of the modelling was to assess the possible risk to pollution of a small farm water supply from a slurry pit on the site. The assumptions made are those required to make the problem tractable without collecting any extra data from the site. The local hydrogeology is simplified and it is assumed that the recharge rate over the area is uniform. This is probably not correct as much of the immediate vicinity of the farm may be paved, thus altering the recharge pattern. However as the model only considers the water from when it reaches the water table, having passed through the unsaturated zone, this assumption may be justified. It is also assumed that the well in the model fully penetrates the aquifer.

As with the mass balance approach, there is an assumption that the leachate from the slurry pit has a concentration similar to that measured in the field trials and that no retardation or geochemical reactions take place during the transport in the aquifer.

Table 2.3 Site and generic based model aquifer properties, recharge and boundary conditions

Parameter	Site-based model	Generic Model
Recharge rate	275 mm pa = 0.0007 m/d	35 mm/pa = 0.0001 m/d
Transmissivity	Zone 1 (along valley): 300 m^2/d Zone 2 (interfluve): 175 m^3/d	Only one zone of 60 m^2/d
Saturated thickness	60 m	60 m
Hydraulic conductivity	Zone 1:$K_{x,y}$ 5 m/d, K_z 0.5 m/d Zone 2:$K_{x,y}$ 2.9 m/d, K_z 0.29 m/d	$K_{x,y}$ 1 m/d, K_z 0.1 m/d
Boundary conditions	Drain along northern and eastern boundary, stage from 65 to 55 m	Drain at eastern boundary, constant stage of 60 m
Aquifer type	Unconfined	Unconfined

2.7.5 *Generic modelling*

This model is a smaller version of the site model and was designed to assess the worst case scenario. The parameters for this modelling were chosen so as to give a worst case in terms of the width of the capture zone of the abstraction well. This was done so that the influence of the slurry pit on the abstraction could be modelled with more ease. As in the case of the site specific modelling, the abstraction borehole is assumed to be fully penetrating and the slurry pit is assumed to be in the capture zone of the well.

The generic regional model was primarily used to provide streamtube data for input to the MAP modelling work described below. The hydrogeology was chosen to give the 'worst-case' situation for leachate from a waste store reaching the abstraction point. This was undertaken by modelling an area with low recharge rate and low hydraulic gradient which gives a wide capture zone. Particle tracking to the well was then used to give streamtube inputs for use with the MAP modelling package.

The work undertaken for the site based model as described in the section above revealed that the width of the capture zone for a borehole pumping at 10 m^3/d was less than 10 m for the gradients and recharge rates likely to be encountered in a typical chalk aquifer. It would therefore be extremely unlikely that this capture zone would intercept the pollutants from a waste store. It is therefore necessary to construct a model which will produce a capture zone with as large an area as possible. A model was therefore created to enable this work to be carried out and required a recharge of 0.1 mm/d and a hydraulic conductivity of 1 m/d. These are low values for the chalk and represent a worse case. Particle tracking was used with the flow model to give data for input to the MAP modelling (see below) and also to give estimates of the travel times within the aquifer system.

The methodology used for particle tracking to obtain the appropriate data for MAP is described below:

a) Release particles from around the borehole and use reverse tracking to identify the well capture zone.
b) Forward track particles from each grid cell (or imported from larger grid cells, depending on the number of particles required to cover capture zone area) within the area indicated to be the capture zone by (a). Refine area of the slurry pit to an appropriate size.

c) Using particle options, select the option to change the colour of the particles to the colour of the boundary capturing them. Particles not being captured by the well can be identified and eliminated using the output data file.
d) From the sum of the areas represented by each particle the total area of the capture zone can be calculated.

2.7.6 *Multiple Analytical Pathway (MAP) modelling*

The MAP model has been developed to deal with the specific problems of solute transport to a borehole in a single or dual-porosity aquifer, although the model is very general in its application. It models flow and transport along a series of streamtubes from the ground surface through to output features, such as boreholes, where predictions of concentration are required. As the name suggests, the model is based on analytical solutions. The form of analytical solutions that have been adopted for the MAP model is that of Laplace transforms (Barker, 1982). Implementation of the method is based on numerical inversion of the Laplace transform solutions. The solutions are for transport (not flow) through the unsaturated zone and sections of the streamtubes through the aquifer. Conditions of flow and transport parameters are assumed constant within each streamtube section. When a streamtube passes into a different aquifer or aquifer region with different properties, the streamtube is split into different sections.

The flow system must be steady state and is modelled separately from the solute transport to reveal the streamtubes and their connections to surface zones, via regions of unsaturated zone, and to output features such as boreholes where concentration variations are to be simulated.

The flow in the unsaturated zone is assumed to be vertical and is represented by a characteristic time, which represents a flow velocity and a thickness. It is possible to incorporate some ‘bypass flow’ in MAP but this feature has not been used in this work. In the saturated zone the aquifer is characterised in the single porosity case by an effective porosity and in the case of dual-porosity by the fracture porosity, the matrix porosity and the diffusion coefficient. The water in the abstraction borehole is assumed to be fully mixed.

The aim of this part of the modelling is to estimate the effect of leachate from a farm waste store within an abstraction well catchment on concentrations in the abstracted water. This has been done with the outputs of the various models described above and also with a pre-existing groundwater model, developed to predict the effect of land-use change on long-term nitrate concentrations.

MAP requires information on all the components of water transport from the surface to the abstraction point. This includes travel time through the unsaturated zone, concentration of nitrate in the recharge as a function of time, path lengths and travel times through the saturated zone. Also required is an assessment of the likely number of waste stores in a catchment and the volume of leachate released by each store.

The particle tracking used to give travel times within the generic model aquifer was also used to give the input data for the streamtubes for MAP. This involved assigning a high nitrate concentration to a particle (and associated area) representing the slurry pit and a lower, background nitrate concentration to the particles representing the rest of the capture zone.

At the time of modelling MAP only had the capacity to process less than 50 streamtubes (although the code is now being adapted to allow for an increased number). If each 100 x 100 metre grid cell within the capture zone was assigned as a streamtube surface element (i.e. particle release point) then this produced more than 50 streamtubes. Therefore particle release points were imported from larger scale grids. For hypothetical model 1, a 200 x 200 m spacing was used, whilst for model 2, a 500 x 500 m spacing was imported. Around the area of the slurry pit the particle release spacing (which determines surface element areas) was reduced in order to represent the limited spatial extent of the farm waste store.

Existing models developed to predict the long-term effect of land use change on nitrate concentrations at abstraction wells have been used to indicate the possible influence of waste stores on measured nitrate concentrations. These models, developed for a sandstone site and a Chalk site, were adapted to show the difference in modelled nitrate concentrations if the effect of waste stores were included. The calibrated models were not changed in any of their parameters except for the addition of pathlines representing waste stores.

The waste stores were given an area of 225 m^2 and a leakage rate of 10 times the local recharge rate. This is an over estimate based on the unsaturated zone modelling work, but was chosen to give a 'worst-case' estimate of the scale of the problem. Waste stores were distributed randomly in the modelled catchments at a density of $0.5/km^2$. This figure was chosen as the upper end of assessments made by ADAS of waste store density. The leachate from the waste stores was given a concentration of 500 mg/L-N in contrast with the general agricultural inputs which varied from 3 mg/L in 1940 to 17 mg/L in 1990. The stores were assumed to come into existence in 1940 and model runs were made to show how their existence might affect concentrations at the abstraction well into the future and also the effect of removing all the stores in 2000.

2.8 Vulnerability and Risk Mapping

Simple vulnerability mapping was carried out to assess, on a regional scale, the areas most likely to be vulnerable to groundwater pollution from farm wastes. Two approaches were taken to assess groundwater vulnerability to pollution from farm wastes: the HOST soil classification approach, and the drift mapping approach. These are both described in more detail below. In reality, these two separate approaches to groundwater vulnerability mapping are very simplistic. Both of the approaches are physically based, and do not take into account chemical attenuation of contaminants. Nor do they take into account factors such as drift thickness or depth to groundwater.

The results of the two approaches were then compared to assess the degree to which they differed, and try to explain why differences occurred. Checking of the results was carried out by examination of more detailed geological mapping and also comparison with the recently available digital groundwater vulnerability mapping for England and Wales (NRA/EA, 1994-1998).

2.8.1 Selection of geology

Chalk and Permo-Triassic outcrops were taken from the digital 1:625 000 geology map. All Chalk was selected. All Permian or Triassic sandstones, breccias or conglomerates plus the Magnesian Limestone were selected. The geology data were combined into a single dataset, and the internal polygons removed to simplify the linework.

2.8.2 HOST approach

- The HOST classification system is based on a number of conceptual models that describe dominant pathways of water movement through the soil and, where appropriate, the substrate (Boorman et al., 1995). The aim of the approach is to identify where rain hitting the ground surface would have an influence on stream and springflow in the short term, and where it may have more of a long term influence. The two extreme response models are quoted as being:

- there is little restriction to vertical drainage. The time elapsing between rain falling and leaving a catchment is long, and the rain therefore has little or no influence on the short term

- the system is concerned with lateral flow i.e. non-vulnerable soils have to be interpreted as those which encourage lateral flow and hence don't permit much vertical flow;

- leading on from this, soils that permit lateral flow of water may protect the underlying aquifer, but may contribute to groundwater recharge elsewhere in the catchment.

In addition, the soil properties are averaged over a 1 km grid.

As a check on the classification, soils that were classified by HOST as vulnerable were checked against soils classed as having low leaching capacity ie non-vulnerable, on the groundwater vulnerability maps; most of the vulnerable soils correctly fell outside this category. Where there were discrepancies, this is most likely to be due to the fact that the HOST classification is purely physically based, and does not take into account the possibility of adsorption of chemical contaminants by the soil. Leaching potential does take this into account. The problem is most likely to occur with HOST classes 3, 7 and 8, which may have high leaching potential (personal communication, Bob Palmer, SSLRC).

When the opposite check was carried out, large areas were found to have a HOST classification of not vulnerable whilst having a high soil leaching potential. This suggests that the HOST classes chosen as not vulnerable may not be correct, and some may provide less protection to groundwater than anticipated. The problem may also be partly a result of the soil mapping used to ascribe the HOST classes being of a different accuracy or scale to that used for the vulnerability mapping.

2.8.3 Drift mapping approach

In the drift mapping approach, areas of outcrop covered by permeable drift were considered to be vulnerable, and areas with impermeable drift were considered to be conferred some protection by the drift. Table 2.5 shows the drift types mapped at 1:625, 000 scale.

Table 2.5 Drift classes on the 1:625 000 drift map of the UK

	Drift type	Classification
1	Peat	Impermeable
2	Alluvium (including River Terrace Deposits in Scotland)	Permeable/Impermeable
3	Brickearth, mainly loess	Impermeable
4	River Terrace deposits (mainly sand and gravel)	Permeable
5	Lacustrine clays, silts and sands	Impermeable
6	Boulder clay and morainic drift	Impermeable
7	Blown sand	Permeable
8	Landslip	Impermeable
9	Clay with flints	Impermeable
10	Glacial sand and gravel	Permeable
11	Sand and gravel of uncertain age or origin	Permeable
12	Crag	Permeable
13	Raised Beach and marine deposits	Permeable

Thus the following drift types were selected as a "permeable drift" set:

- Blown sand

- Alluvium

response of the catchment (in terms of stream or springflow), but low flows would be maintained by the slow passage of water through the ground

- vertical drainage is restricted such that the dominant pathway for movement of water is lateral. The response to rainfall at the catchment outlet is rapid, and little water is retained within the catchment to support flow between rainfall events.

- These are the two extremes, and a number of intermediate models are required. The models have three physical settings:

- a soil on a permeable substrate in which there is a deep aquifer or groundwater (i.e. at >2 m depth)

- a soil on permeable substrate in which there is normally a shallow water table (i.e.within 2 m depth)

- a soil (or soil and substrate) below which there is no significant aquifer or groundwater.

Within the three physical situations are variations that allow for different soil properties (e.g. a peaty top layer), and wetness regimes (e.g. as indicated by the presence of gleying), that give rise to a total of 11 models. The 11 models are further sub-divided into 29 HOST classes, based on other properties or the geology of the substrate.

In all cases, the basic concern is at what depth does lateral water movement become a significant factor; i.e. the HOST system is concerned principally with the lateral movement of water to surface water courses, rather than its vertical movement to the groundwater table.

The HOST classes considered to be vulnerable are shown in Table 2.4. All these classes are considered to allow some or most of the rainfall to reach the water table.

Table 2.4 HOST classes defined as vulnerable

HOST class	Presence of groundwater	Presence of impermeable layer
1 to 6 (model A)	Aquifer or groundwater normally present and at depth > 2m	No impermeable or gleyed layer within 1 m
13 (model B)	Aquifer or groundwater normally present and at depth > 2m	Impermeable layer within 1 m or gleyed layer at 0.4 to 1 m
14 (model C)	Aquifer or groundwater normally present and at depth > 2m	Gleyed layer within 0.4 m
7 & 8 (model E)	Aquifer or groundwater normally present and at depth < 2m	No impermeable or gleyed layer within 1 m
10 (model F with IAC >= 12.5)[†]	Aquifer or groundwater normally present and at depth < 2m	Gleyed layer within 0.4 m

[†] Integrated air capacity

The remaining classes are considered to offer some protection to groundwater: these are the classes for which there is no significant aquifer or groundwater beneath the soil and substrate, or which have a raw peaty top soil.

The main drawbacks with this approach are that:

- it deals with models rather than the raw data i.e. relies on interpreted data

- River terrace deposits
- Raised beach deposits
- Glacial sand and gravel
- Sand and gravel of uncertain origin
- Crag

Areas with no drift cover were also selected.

It should be noted that there are drawbacks with the 1:625 000 drift cover, mainly that it is incomplete, being derived from old mapping which did not always include drift cover. However, the areas that are known to have the worst problems (for example Wales and the Pennines) are not areas underlain by the Permo-Triassic sandstones or Chalk, and this may not therefore pose a significant problem. Where required, the drift mapping was checked against the low permeability drift stipple on the published 1:100 000 vulnerability maps (NRA/EA, 1994-98) or the 1:50 000 geology maps. Other than the classification of alluvium (see below), there were not found to be any major problems with the 1:625 000 drift mapping for the purposes of this work.

It should be noted that the mapping shows the deposits at the surface, and does not take into account their thickness. Therefore, if they are thin or of varying lithologies, they may be more vulnerable than they appear.

Furthermore there is no differentiation on the 1:625,000 drift map between river alluvium and coastal/estuarine alluvium, and all alluvium is grouped and classified as permeable cover. However, there are likely to be significant differences in the groundwater protection offered by these different types of alluvium: the former is more likely to be composed of layers and lenses of variable permeability materials, and is also frequently in contact with sands and gravels. The latter are more argillaceous deposits, and, when of sufficient thickness, reduce the vulnerability of the underlying aquifer (NRA/EA 1994-98). As a result of this, the low permeability stipple that had been developed as part of the EA's vulnerability mapping (NRA/EA, 1994-98) was used to modify the alluvium class and sub-divide it into permeable and impermeable classes.

2.8.4 Assessing Risk

The vulnerability maps identify those locations that are vulnerable to pollution. However, it is also necessary to identify those locations where that vulnerability is converted to risk by the presence of high densities of slurry lagoons. This information was derived from the MAFF agricultural census, which was used to identify the location of animal numbers. Census data on cattle numbers (beef and dairy) and pigs were available for the 1995 census, and were used as the basis for this study. From these numbers, the estimated annual production rate of slurry was calculated and storage method used was based on the estimates presented by Nicholson & Brewer (1997) per ADAS Business Centre. These were converted to number of slurry lagoons by assuming a typical volume of 1500 m^3 per structure. In the assessment of risk no account has been taken as to the depth of the unsaturated zone.

3. FIELD SITES

The following section is a summary the of site descriptions for the 3 Chalk and 5 sandstone sites contained in the year 1 (Gooddy et al, 1998b) and year 2 (Gooddy et al, 1999) annual reports. The sites selected are the result of extensive surveying work in which some 67 potential sites were investigated for possible field study.

3.1 Chalk

3.1.1 Chalk Site 1

Chalk Site 1 is situated about 5 km from Salisbury in Wiltshire. The farm is situated on the Upper Chalk above a high river valley and so is missing any possible alluvium or gravel sequences. A water table around 40 m below ground level (bgl) has been measured at the farm borehole. The solid and liquid slurry from a herd of roughly 160 cows is temporarily stored in a small pit approximately 15 m long, 6 m wide and 2 m deep (180 m^3). The lagoon was excavated in 1978 and has been constructed so as to be level with the surrounding ground. This enables easy handling of waste from the adjacent cow housing. Two boreholes were drilled here, one beneath the pit at an incline of 45° to a depth of 17 m bgl, the other adjacent to the pit to a depth of 15 m bgl.

3.1.2 Chalk Site 2

Chalk Site 2 is situated about 8 km from Salisbury, Wiltshire. The farm is situated on the boundary of the Middle and Upper Chalk in a river valley and so is overlain by alluvium and gravels. The lagoon however is on top of a hill and so free of any gravel layer. By extrapolation the water table has been estimated at 30-40 m bgl. The solid and liquid slurry from a large herd of roughly 200 cows is transferred into a moderately sized lagoon approximately 20 m long, 8 m wide and 2.5 m deep (400 m^3). This earth-walled lagoon was constructed in 1983 and is built on a hill which reaches the cattle sheds at its upper most point. The lagoon has been constructed so as to counter this incline, the banks reaching a height of 4 m at the point furthest from the cattle sheds. Two boreholes were drilled here, one beneath the pit at an incline of 45° to a depth of 18 m below ground level (bgl), the other adjacent to the pit to a depth of 15 m bgl. Specially designed gas samples were installed in the inclined hole at this site.

3.1.3 Chalk Site 3

Chalk Site 3 is situated about 7 km north-west of Stevenage, Hertfordshire. The site is on the side of a steeply sloping valley on the Upper Chalk close to the boundary with the Middle Chalk. The water table here is estimated at a little over 20 m bgl. Litter from a turkey farm, which by its nature is mainly solid and very dry, has been stored directly on the ground surface in an area roughly 15 m x 15 m for the past 20-30 years. Two fully cored boreholes were drilled vertically, directly on top of the area used for storage. One was drilled towards the edge of the source area and one towards the middle. They were drilled to depths of 15 m bgl and 20 m bgl.

3.2 Sandstone

3.2.1 Sandstone Site 1

Sandstone Site 1 is situated about 10 km from Exeter, Devon. The site is on the Littleham Mudstone which is a formation near the base of the Permo-Triassic sequence. The water table is estimated to be at 20-25 m. Slurry is crudely separated into solid and liquid components and transferred accordingly into two earth lined lagoons both roughly 20 m long, 15 m wide and 2.5 m deep (750 m^3). These were both constructed in 1983. One inclined borehole (45°) and one vertical borehole were drilled at each of the lagoons. Borehole depths were 20 m and 15 m for the vertical and inclined holes respectively beneath the solid waste store, and 18 m and 15 m for the vertical and inclined holes respectively beneath the liquid waste store. In addition, gas samples were inserted into the inclined borehole beneath the liquid waste pit.

3.2.2 Sandstone Site 2

Sandstone site 2 is situated about 7 km north-west of Derby, Derbyshire. The site is located on the Keuper Waterstones (old nomenclature), a lower component part of the Mercia Mudstone (new nomenclature) which is now generally regarded as a transition bed between the Sherwood Sandstone underneath and the Mercia Mudstone above. This is a generally fine grained, dark red-brown, well-cemented sandstone. During the drilling of both boreholes, a shallow water table was intersected. This was reported at a depth of 12 m in the 'solids' borehole and at 5 m with a further strike at 19 m in the 'liquids' borehole. The slurry from the 160 head of cattle on this farm is disposed of into two separate pits approximately 200 - 300 m apart. Solid slurry is transferred to one store, up gradient of a second store in a separate field, into which liquid slurry and farmyard washdown/wastewater is allowed to drain. The solids store is approximately 25 m long, 10 m wide and 2 m deep (500 m^3), whilst the liquids lagoon is approximately 10 m square and 2 m deep (200 m^3). Both of these are earth walled and unlined. The pits were constructed in 1983. It was decided to drill one fully cored inclined borehole to a depth of 17 m bgl at each of the stores.

3.2.3 Sandstone Site 3

Sandstone site 3 is situated about 10 km south-west of Stoke-on-Trent, Staffordshire. The site is located on the Sherwood Sandstone at outcrop and has no covering of Superficial Deposits. It is placed in the sub-division known as the Wildmoor Formation, formerly known as the Upper Mottled Sandstone. During the drilling of the borehole the water table was intersected at around 12 m bgl. The end of drilling was completed below the water table despite 18 m of casing attempting to delay the entry of groundwater.

The solids and liquid slurry from this cattle farm is disposed of into one very small pit, used as a temporary (few days) store before spreading. The pit is only approximately 5 m square and approximately 1 m deep (25 m^3). It had been crudely scraped out of the pre-existing ground surface 5-6 years ago and has bare bedrock walls and base. Problems with access resulted in a borehole drilled at an angle of just 8° to the vertical. The borehole was drilled to a total drilled length of 20.5 m.

3.2.4 Sandstone Site 4

Sandstone site 4 is situated about 15 km north-west of Derby, Derbyshire. The site is on the Sherwood Sandstone at outcrop with no covering of Superficial Deposits. It is placed in the sub-division known as the Kidderminster Formation, formerly known as the Bunter Pebble Beds. The solids and liquid slurry from the 160 head of cattle on this farm is stored in one pit, which is approximately 10 m square and approximately 2.5 m deep (250 m^3). It was constructed in 1987. One fully cored borehole was drilled at an angle of 45° directly under the pit to a depth of 17 m bgl. During the drilling of the borehole, the water table was intersected at 12 m bgl.

3.2.5 Sandstone Site 5

Sandstone Site 5 is situated about 15 km north-west of Derby. The site is on the Sherwood Sandstone at outcrop with no covering of Superficial Deposits. The site is close to, but topographically lower than, Site 4. The sandstone was expected to be much thinner before passing down into the underlying Carboniferous strata. Like site 4, it is placed in the sub-division known as the Kidderminster

Formation, formerly known as the Bunter Pebble Beds. The solids and liquid slurry from the 180 head of cattle on this farm is transferred into a pit approximately 25 m long, 10 m wide, and 2.5 m deep (625 m^3). It was scraped out of a sloping ground surface in 1979 and extended in 1987 and has an artificially constructed earth bank to two sides, the others being the natural slope of the land. One fully cored borehole at an angle of 45° was drilled 17.5 m bgl directly under the pit. During the drilling of the borehole, the water table was intersected at around 13 m bgl.

4. FIELD SITE RESULTS

Field results are summarised for all 8 sites sampled. Due to the greater detail in profiling, more emphasis has been placed on Chalk Site 1, Chalk Site 2 and Sandstone Site 3. The tables in this section have generally been designed to give an average 'plume' (if present) composition by considering the mean concentration for a given constituent in both inclined and vertical holes combined, at a depth greater than 10 m. This should give an approximation as to the contaminant plume concentration and the rate of movement over the lagoon's lifetime.

4.1 Chalk Sites

Chemical parameters of groundwater within Chalk aquifers in the UK have been determined by Edmunds et al (1989) and are shown in Table 4.1. The study in Berkshire is of an unconfined aquifer, whereas the London Basin is confined. The two have been compared to provide a likely spectrum of values for UK Chalk groundwaters. Although there is a good deal of variation between the two, clear water quality trends can be seen. We therefore might expect a 'typical' chalk groundwater to have a conductivity around 700 μS/cm, a pH of about 7.5, roughly 300 mg/L bicarbonate, 80 mg/L calcium, 50 mg/L of chloride and sodium and 6 mg/L potassium.

Table 4.1 Mean concentrations of groundwater sampled from Chalk of England (Data from Edmunds et al, 1989)

	SEC	pH	Cl	HCO_3	SO_4	NO_3-N	Na	K	Ca	Mg
Site	μS/cm					mg/L				
Berkshire (*n=26*)	320	7.9	40	304	33	3.1	23	5.3	86	13
London Basin (*n=21*)	931	7.2	65	340	118	1.5	100	8.1	74	21
Combined (*n=47*)	676	7.6	51	326	71	1.9	57	6.1	82	17

4.1.1 Chalk Site 1

Selected porewater data from Chalk Site 1 are shown in Figure 4.1. Observation of the core showed visible slurry along fractures within the chalk matrix (Gooddy et al 1998). This is reflected in the chemical results reported below. Table 4.2 demonstrates that the porewaters are grossly contaminated throughout the depth of the two profiles with highest concentrations occurring below 10 m. Bicarbonate is roughly 10 times baseline concentrations (Table 4.1) and potassium nearly 2 orders of magnitude greater than baseline. Calcium concentrations are clearly reduced relative to baseline, nearly a factor of 10 lower for the deeper porewaters from both boreholes. DOC and ammonia concentrations are both very high, 2 and 3 orders of magnitude above a typical baseline value (Gooddy et al, 1998a).

Table 4.2 Mean concentrations of groundwater sampled from Chalk Site 1

	PH	Cl	HCO_3	SO_4	DOC	NO_3-N	NH_4-N	Na	K	Ca	Mg
Borehole						mg/L					
Vertical (*n=17*)	8.2	307	2350	47	154	3.1	284	97	785	26	27
>10 m (*n=6*)	8.3	353	2710	45	203	1.7	361	114	867	7.2	24
Inclined (*n=32*)	8.2	297	2120	53	160	5.2	263	89	722	33	23
>10 m (*n=14*)	8.3	322	2400	49	207	0.8	316	99	809	6.7	19
Combined (*n=49*)	8.2	300	2200	51	158	4.4	270	92	745	30	25
>10 m (*n=20*)	8.3	332	2490	48	206	1.1	330	104	827	6.9	21

Chloride, conductivity and dissolved organic carbon (DOC) all show fluctuation through the drilled length but with a trend for increasing concentration with depth. Chloride displays slightly lower values within the top of the profile (200 mg/L) with a steady value (400 mg/L) below 4 m. Conductivity shows a similar stepped increase with lower values in the top 3 m (2 mS/cm) than below (5 mS/cm). TOC shows an initial sharp increase in the top 3 m (2 to 200 mg/L at 3 m) and subsequent stepped increase to a maximum at 12 m bgl (300 mg/L). Between 12 and 14 m bgl a slight decrease then occurs. Nitrogen species comprising nitrate and ammonia (both expressed in terms of N) behave inversely within the profile. Ammonia is largely absent from the upper 2 m, increasing rapidly between 2-4 m (up to 400 mg/L) after which point it remains relatively constant to the bottom of the borehole. In contrast nitrate is at its maximum at the top of the profile and is depleted rapidly in the top 2 m (from 75 mg/L to <0.1 mg/L). Sulphate decreases sharply from a maximum in the top 3 m bgl (from 170 mg/L to 30 mg/L) after which point it remains low. Phosphorus (shown as total P) initially increases in the top 4 m bgl (from 2 mg/L at 2 m to peak values of 20 mg/L at 4 m) before declining steeply to minimal values below 10m (<5 mg/L below 10 m). Bicarbonate remains low in the top 2 m (400 mg/L) prior to a sharp increase below 2 m bgl (2500 mg/L at 4 m bgl). Below 4 m bgl it remains relatively stable at 3000 mg/L. Calcium shows an inverse relationship with bicarbonate and decreases rapidly from a maximum (150 mg/L) in the top 1 m bgl to negligible values (20 mg/L) below 3 m bgl (remaining suppressed throughout the rest of the borehole). Potassium shows an initial rapid increase within the upper 4 m bgl (from 400 mg/L 0-2 m to 1000 mg/L at 4 m) below which it falls slightly to a stable concentration (800 mg/L) and remains constant.

Microbiological data have been summarised in Table 4.3. The high total clostridia counts demonstrate faecal contamination at 15 m bgl but the absence of *E.coli* and faecal enterococci suggest this occurred some considerable time before sampling. The concentrations of clostridia are fairly similar between the two boreholes with the vertical borehole appearing to be more contaminated. It is however important to note the absence of other pathogens such as *E.coli* O157, salmonella and *Cryptosporidium parvum* in all samples.

Analysis of the slurry from this site showed a dry matter content of 1.3% and total N as 0.7 kg/m^3.

Table 4.3 Microbiological data for Chalk Site 1.

Depth (m bgl)	Coliforms	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E. coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	CFU/50 g	CFU/g	Pres./Abs. /25g
Slurry			Absent	330000	2		
Vertical							
3.75-4.50	10	<10	Absent	370000	Absent	<10	Absent
5.25-6.00	<10	<10	Absent	630000	Absent	<10	Absent
9.60-10.20	10	20	Absent	49000	Absent	<10	Absent
13.50-15.00	70	<10	Absent	29000	Absent	<10	Absent
Inclined							
2.83-3.54	2600	<10	Absent	80000	Absent	<10	Absent
6.36-7.07	<10	<10	Absent	21000	Absent	<10	Absent
9.90-10.61	<10	<10	Absent	8000	Absent	<10	Absent
13.26-13.79	30	<10	Absent	600000	Absent	<10	Absent
16.44-16.97	<10	<10	Absent	35000	Absent	<10	Absent

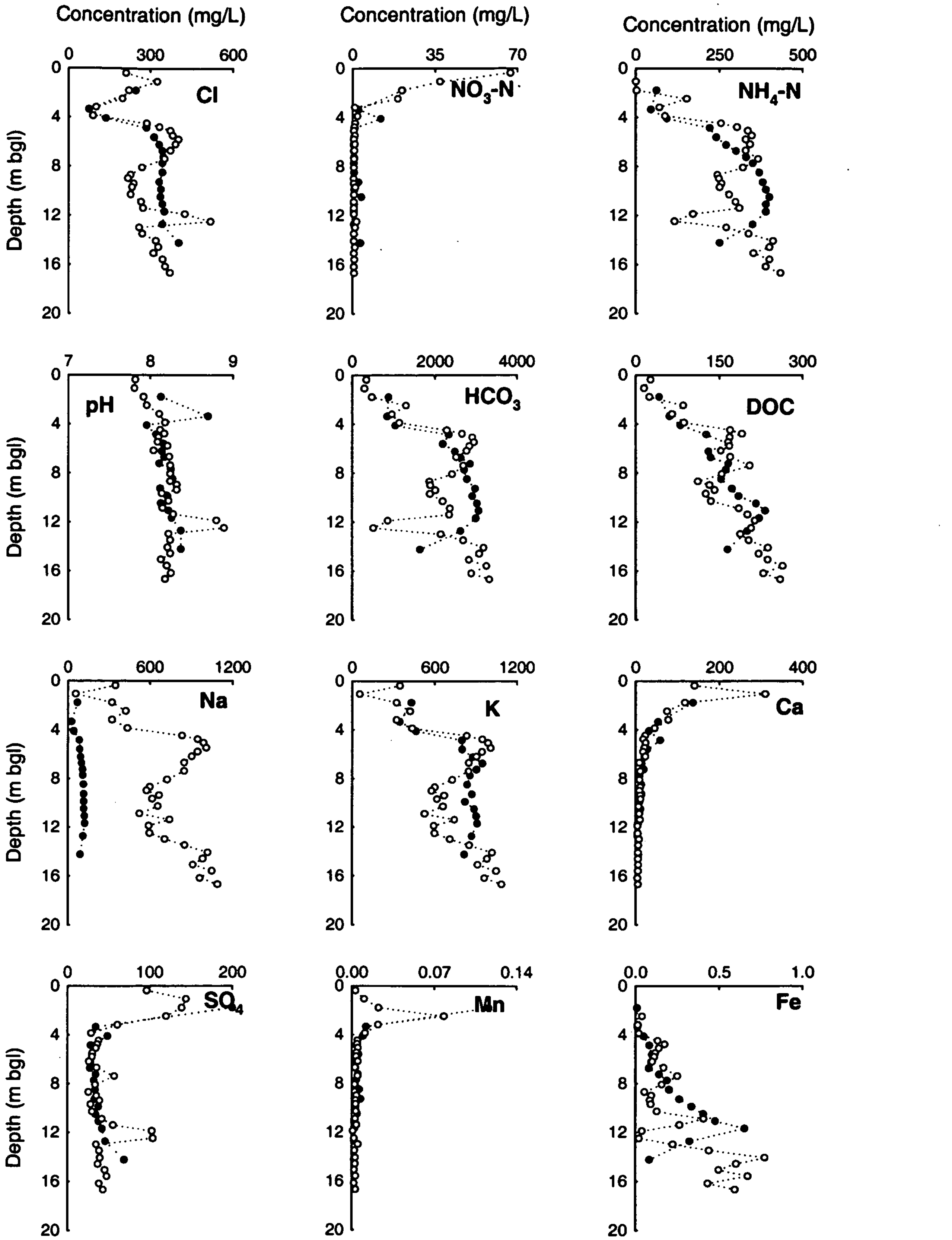


Figure 4.1 Porewater profiles for cores taken beneath Chalk Site 1. Vertical borehole indicated by closed circles, inclined borehole indicated by open circles. All concentrations are in mg/L and depths are metres below ground level.

4.1.2 *Chalk Site 2*

Cores from Chalk Site 2 also show raw slurry along fracture planes of the chalk matrix although to a lesser extent then Chalk Site 1. Again the borehole was located in the unsaturated zone with a decreasing moisture content throughout the profile (Gooddy et al, 1998b). Different trends can be seen between the inclined and vertical boreholes which may suggest they are intersecting different parts of the plume (Figure 4.2). In the reporting below, more weight is attributed to results from the inclined well whose chemical behaviour was characteristic of the plume.

Table 4.4 Mean concentrations of groundwater sampled from Chalk Site 2

	pH	Cl	HCO_3	SO_4	DOC	NO_3-N	NH_4-N	Na	K	Ca	Mg
Borehole						mg/L					
Vertical (*n=16*)	7.9	346	164	142	15	285	0.2	144	914	170	66
>10 m (*n=6*)	7.9	350	130	176	12	266	0.1	121	666	176	52
Inclined (*n=41*)	8.2	483	574	212	37	199	2.2	182	621	71	55
>10 m (*n=23*)	8.3	564	815	242	50	83	3.9	205	1005	28	47
Combined (*n=57*)	8.1	445	459	193	31	166	1.6	171	831	99	58
>10 m (*n=29*)	8.2	520	673	228	42	121	3.1	188	935	59	48

Chloride shows a sharp increase between 1 m bgl and 8 m bgl (0 to 600 mg/L) after which point it remains stable (roughly 500 mg/L). Conductivity closely follows the trend seen in chloride, with lower values at the surface, and maximum values at 6 m (0 –5 mS/cm) after which it is relatively stable (4 mS/cm). DOC shows lower values between 0 – 6 m (25 mg/L) prior to a sharp increase below this depth to a maximum at 11 m (75 mg/L) and subsequent sharp decline in the last part of the borehole (to <25 mg/L at 13 m). Nitrogen species (nitrate and ammonia) again behave inversely with regards each other but unlike Chalk Site 1 nitrate constitutes the more prolific species present. Nitrate increases in the upper 6 m bgl (40 mg/L at 1 m bgl to 380 mg/L at 6 m bgl) prior to declining sharply between 6 and 10m (<20 mg/L). Conversely, at 6 m bgl ammonia is largely undetectable, increasing sharply from 9m onwards (to a maximum 20 mg/L). Sulphate shows a steady increase from lower values to a maximum between 0 and 6 m bgl (from 50 to 200 mg/L). Below 6 m bgl concentrations show some decrease with depth (150 mg/L at 11 m bgl) but not the same dramatic disappearance as seen at Site 1. Phosphorus (as total P) shows low values between 0 and 6 m (<1 mg/L). They increase marginally between 6 to12 m (averaging 1 mg/L) with isolated peaks between 8 and 10 m (4 mg/L). The bicarbonate profile shows a low concentration in the top 6 m bgl of the borehole (200 mg/L) increasing between 6 and 10 m bgl to a maximum (1000 mg/L) after which there is a decrease to 500 mg/L at 12 m. Calcium again shows an inverse relationship with bicarbonate, with maximum values in the upper 4 m of the profile (200 to 400 mg/L) before falling to a minimum at 8m (<25 mg/L) for the remainder of the borehole. Potassium is low within the upper 2 m of the profile (60-70 mg/L at 1 m) but increases sharply between 2 to 6 m to a maximum at 6 m (1300 mg/L) prior to a slight decline with depth in the remaining length (1000 mg/L at 12m). Iron was undetectable between 0 and 8 m bgl, except for isolated values (0.3 mg/L). Below 9 m iron is present with a scatter of points (0.1 – 1 mg/L).

Microbiological data are presented in table 4.5. Clostridia were present throughout both boreholes but at lower levels than Chalk Site 1. Also contrary to Chalk Site 1, levels of clostridia in the inclined hole were significantly higher than those in the vertical hole. This does suggest greater contamination was coming from the bottom of this lagoon rather than from the sides. No other test microorganisms were detected at this site suggesting the faecal contamination occurred some time before sampling.

Analysis of the slurry from this site showed a dry matter content of 1.4% and total N as 1.2 kg/m^3.

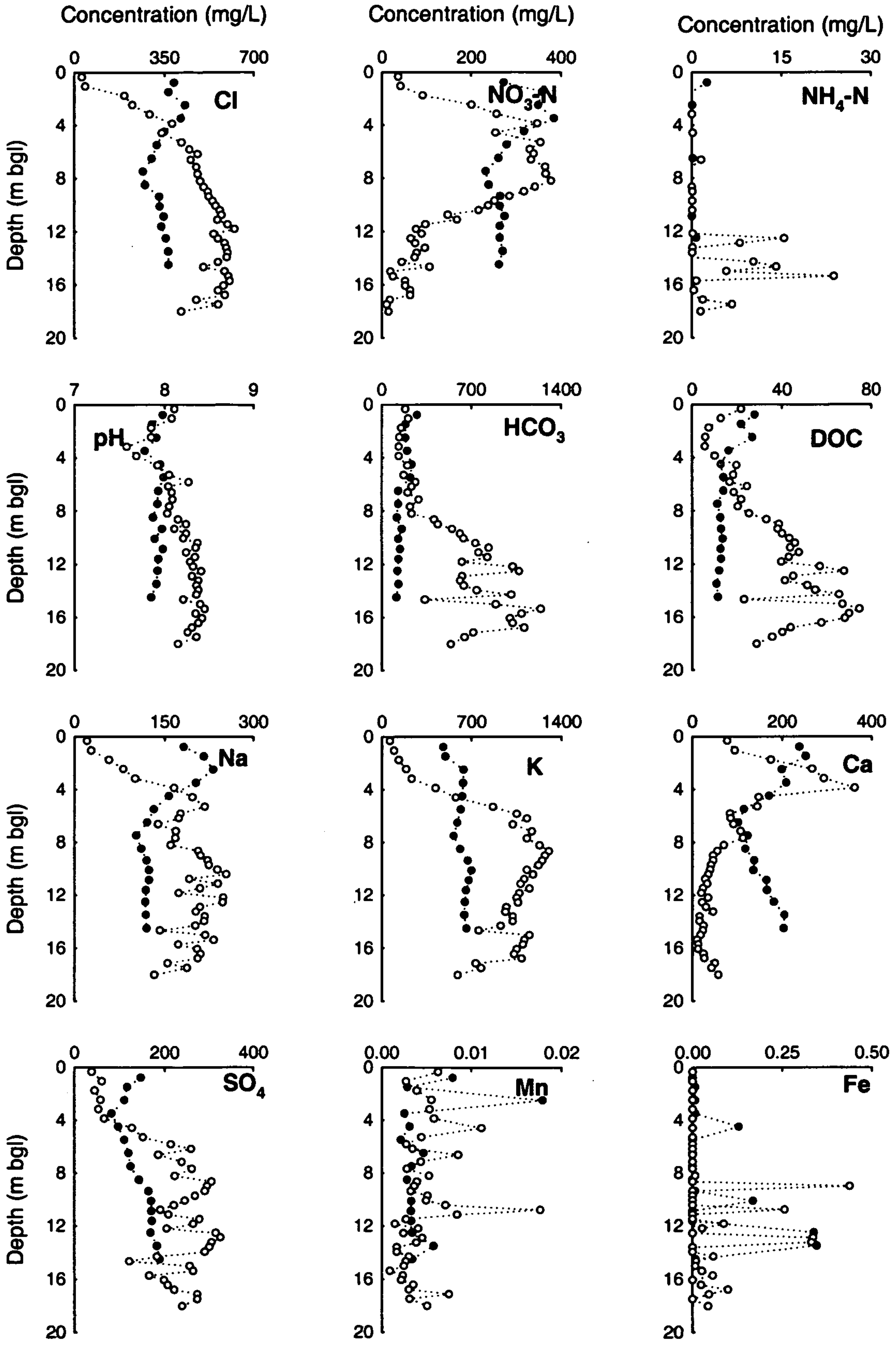


Figure 4.2 Porewater profiles for cores taken beneath Chalk Site 2. Vertical borehole indicated by closed circles, inclined borehole indicated by open circles. All concentrations are in mg/L and depths are metres below ground level.

Table 4.5 Microbiological data for Chalk Site 2.

Depth (m bgl)	Coliforms	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E. coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	CFU/50 g	CFU/g	Pres./Abs. /25g
Slurry			Absent	29000	2		
Vertical							
2.00-3.00	<10	<10	Absent	91000	Absent	<10	Absent
4.00-5.00	<10	<10	Absent	9300	Absent	<10	Absent
8.00-9.00	<10	<10	Absent	6200	Absent	<10	Absent
9.75-10.50	<10	<10	Absent	9700	Absent	<10	Absent
14.00-15.00	<10	<10	Absent	3200	Absent	<10	Absent
Inclined							
3.54-4.24	<10	<10	Absent	6500	Absent	<10	Absent
6.89-7.42	<10	<10	Absent	10000	Absent	<10	Absent
10.25-10.61	<10	<10	Absent	12000	Absent	<10	Absent
13.79-14.14	<10	<10	Absent	38000	Absent	<10	Absent
17.32-17.68	<10	<10	Absent	56000	Absent	<10	Absent

4.1.3 Chalk Site 3

Summary porewater concentrations for the borehole constructed through the centre of the litter store is presented in Figure 4.3a. It can clearly be seen that in the top part of the profile solute concentrations are very high, up to 50 times a baseline groundwater concentration for chloride (3000 mg/L) and even higher for ammonia (500 mg/L), potassium (10,000 mg/L) and dissolved organic carbon (3000 mg/L). However, concentrations decline rapidly and are at baseline level around about 15 m. The top 8 samples from this site were highly coloured, ranging from a crude oil black in the top 50 cm, through whiskey brown and ending in a pale straw yellow by about 5 m. Solutes appear to decline in concentration and then peak at 3.5 m before declining again. This may reflect the very slow movement of a contaminant front, a front which has moved less than 5 metres in 20 years, due to the relatively impermeable nature of the turkey litter to recharging rainwater. Beneath the top 1 m little ammonia is present in the porewater suggesting that conditions are highly oxidising. Nitrate concentrations also peak at around 3000 mg/L at 3.5m and decline rapidly after this suggesting both limited movement of a contaminant plume and maybe rapid rates of denitrification.

Table 4.6 Mean concentrations of groundwater sampled from Chalk Site 3

	pH	Cl	HCO_3	SO_4	DOC	NO_3-N	NH_4-N	Na	K	Ca	Mg
Borehole						mg/L					
Middle (1) ($n=38$)	7.6	771	786	575	190	336	168	223	1210	929	28
>10 m ($n=18$)	7.7	107	252	93	4.6	66	0.01	29	2.2	239	4.1
Edge (2) ($n=29$)	7.6	682	188	395	60	23	2	169	742	948	31
>10 m ($n=9$)	7.6	57	302	171	2.8	24	0.1	16	1.3	216	3.9
Combined ($n=67$)	7.6	732	459	497	130	201	96	200	1007	937	29
>10 m ($n=27$)	7.7	90	269	119	4.0	52	0.04	24.7	1.9	231	4.0

Summary porewater concentrations for the borehole constructed through the edge of the litter store are presented in Figure 4.3b. Over the length of the profile, solute concentrations decrease by an order of magnitude to end in levels close to baseline. The chloride profile again shows a peak in concentration at around 3.5 m (4000 mg/L), although profiles for other solutes are more noisy suggesting the loading of litter at this point has been considerably more variable over the years. Consequently nitrate and ammonia concentrations are much lower than the other borehole (maxima of 70 mg/L and 25 mg/L respectively). The possibility that litter coverage was less dense is supported by higher moisture contents (generally 5-10% higher than borehole 1) and may explain the large peak in nitrate concentration around 10 m. It is considered that this pulse of contamination could move through the unsaturated zone more rapidly in the areas not always covered by a thick matting of litter.

Microbiological data have been tabulated in Table 4.7. *Cryptosporidium* and *E.coli* O157 were not determined at this site as turkey litter is not considered a probable source for either of these microorganisms. However, *campylobacter* is more commonly found in poultry than it is cattle, pigs or sheep and so samples were examined accordingly. With the exception of the top 50 cm, where low levels of clostridia were isolated, none of the test microorganisms were detected. These data support the chemical analysis by indicating very slow movement of the contaminant front.

Analysis of the slurry from this site showed a dry matter content of 62.3% and total N as 27.1 kg/m^3 reflecting the considerable difference between cattle slurry and turkey litter.

Table 4.7 Microbiological data for Chalk Site 3

Depth (m bgl)	Coliforms 30°C	Faecal enterococci	Total clostridial count	*Campylobacter*	*E.coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	Pres./Abs. /25g
0.00-0.45	<10	<10	640	Absent	<10	Absent
2.00-2.45	<10	<10	<10	Absent	<10	Absent
4.00-4.45	<10	<10	<10	Absent	<10	Absent
6.00-6.45	<10	<10	<10	Absent	<10	Absent
8.00-8.45	<10	<10	<10	Absent	<10	Absent
12.06-12.51	<10	<10	<10	Absent	<10	Absent
13.90-14.35	<10	<10	<10	Absent	<10	Absent
16.22-16.67	<10	<10	<10	Absent	<10	Absent
17.90-18.35	<10	<10	<10	Absent	<10	Absent
19.58-20.03	<10	<10	<10	Absent	<10	Absent

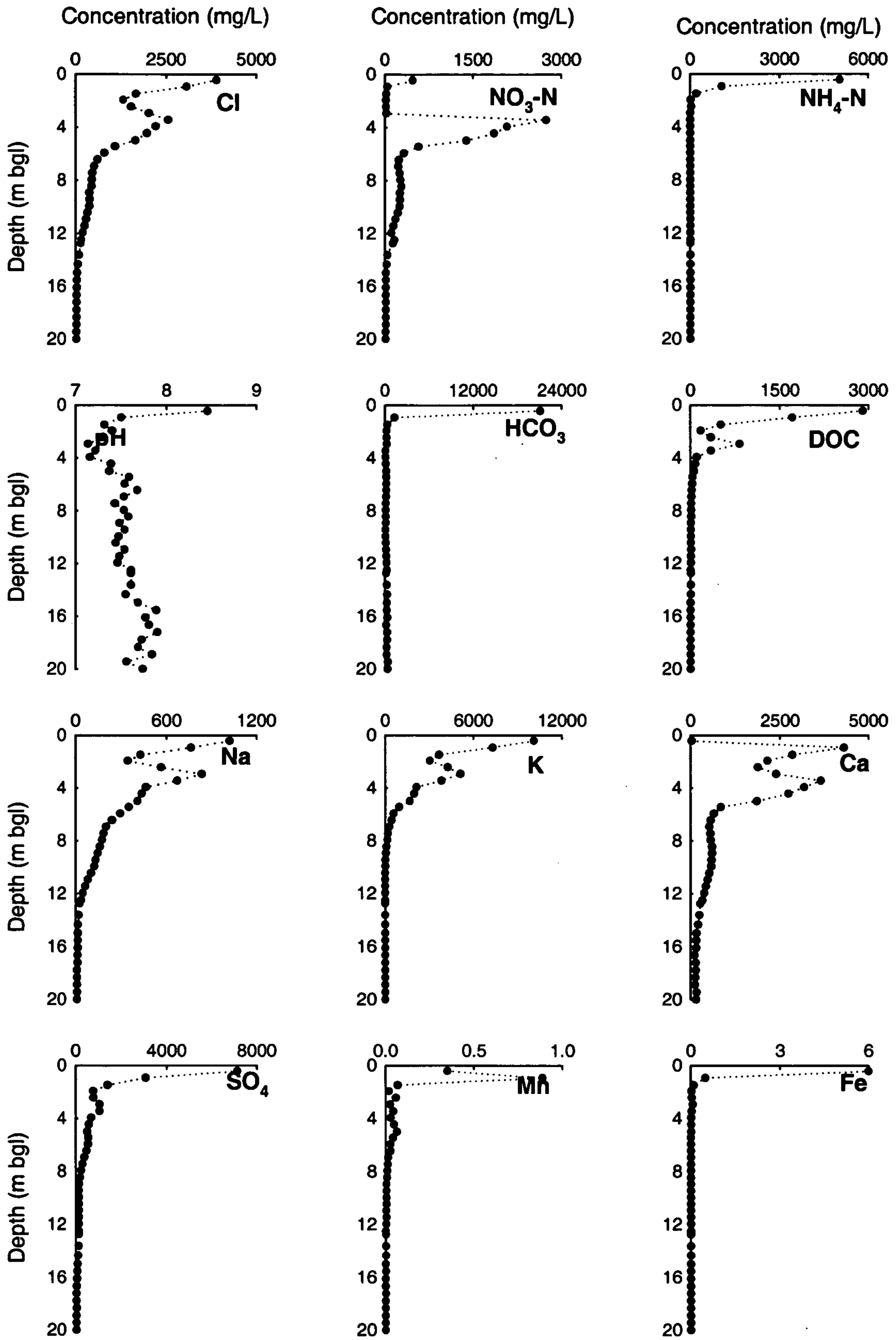


Figure 4.3a Porewater profiles for cores taken beneath Chalk Site 3 (centre of site borehole). All concentrations are in mg/L and depths are metres below ground level.

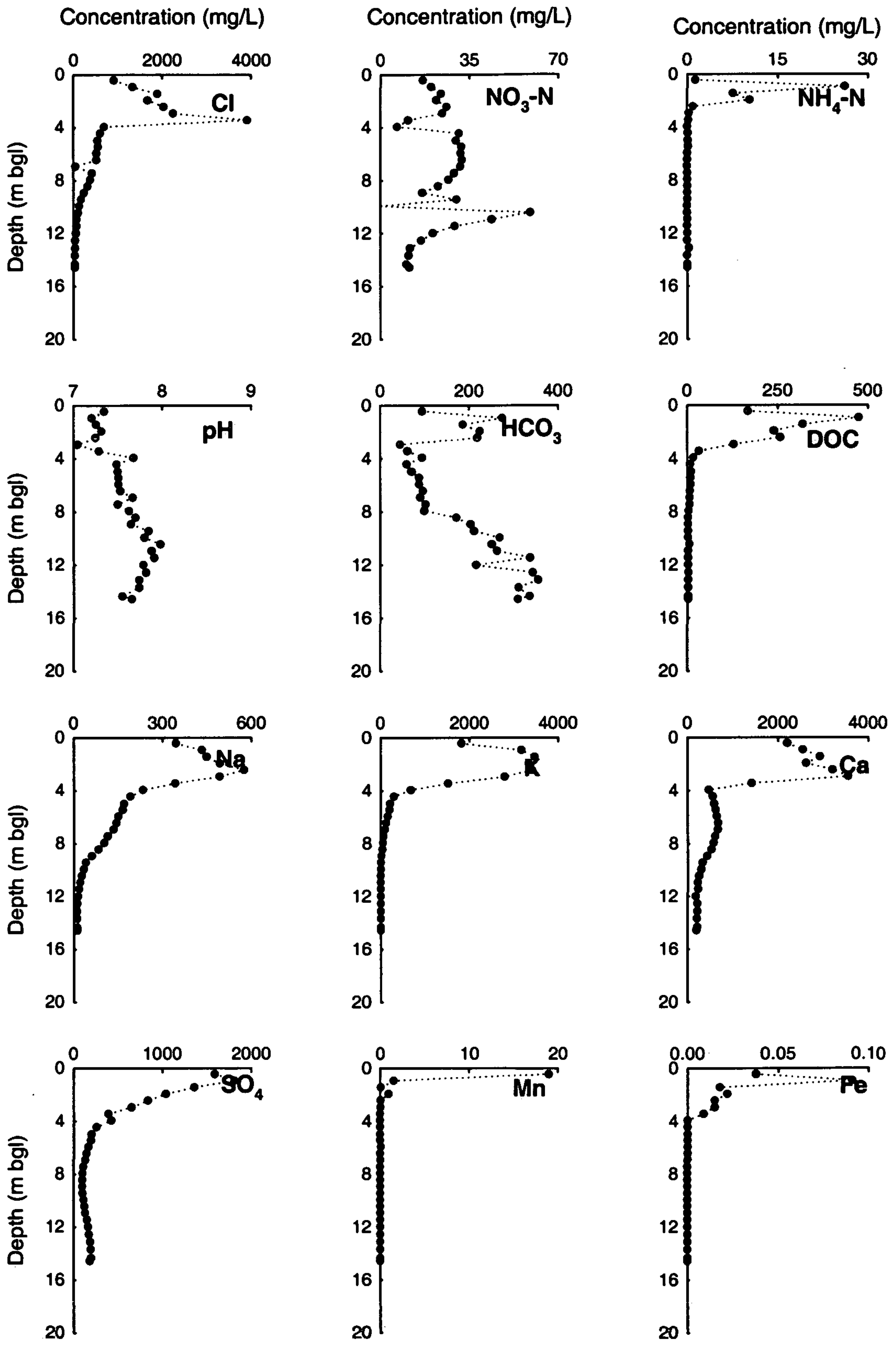


Figure 4.3b Porewater profiles for cores taken beneath Chalk Site 3 (edge of site borehole). All concentrations are in mg/L and depths are metres below ground level.

4.2 Sandstone Sites

Baseline concentrations for groundwater samples taken from 70 Sandstone sites in the UK are presented in Table 4.8. This is intended for comparative purposes for the following 5 sandstone sites. For a potable water it shows that conductivity in this aquifer type would be around 500 μS/cm, pH 7.0, bicarbonate of roughly 200 mg/L, calcium 70 mg/L, chloride could be expected to be in the range of 40-50 mg/L, sodium around 25 mg/L and potassium about 3 mg/L. It is interesting to note that average nitrate concentrations are roughly double in the Sherwood and Permo-Triassic sandstones when compared with the Chalk of Berkshire and London.

Table 4.8 Mean concentrations of groundwater sampled from Sherwood and Permo-Triassic Sandstones (Edmunds et al, 1989)

	SEC	pH	Cl	HCO_3	SO_4	NO_3-N	Na	K	Ca	Mg
Sandstone	μS/cm					mg/L				
Sherwood (*n=40*)	565	7.0	51	210	37	6.2	25	2.9	78	13
Permo-Trias (*n=30*)	478	6.7	38	173	52	6.7	25	3.3	66	12
Combined (*n=70*)	502	6.9	46	194	43	6.4	25	3.1	73	13

During the drilling in the Permo-Triassic Sandstone a number of difficulties were encountered in the recovery of core material and also the subsequent extraction of interstitial waters. Sandstones are highly variable by their very nature and the problems encountered included; the material being to heavy and clay like; the material being too soft; the material being too dry; and the material being interspersed with layers of gravel. For this reason profiles have only been presented for Sandstone Site 1, where some continuous coring was possible although it was difficult to extract much water from the material, and Sandstone Site 3, where continuous coring was problematic due to the highly friable nature of the Wildmoor Formation.

4.2.1 Sandstone Site 1

The core material that came from Sandstone Site 1 was predominantly mudstone and yields of water were correspondingly low. Yields were typically around 2-3% but did range from 0.3-7%. A great deal of effort was required to extract sufficient porewater for just chloride and nitrate analysis. Consequently only a few samples had a complete elemental analysis. Chloride, nitrate and ammonia profiles are shown in Figure 4.4. In general , both inclined and vertical profiles follow a similar trend (Table 4.9) with concentrations of chloride highest beneath the solid wastes pit (a mean of 176 mg/L compared with 96 mg/L for the liquid wastes). Nitrate concentrations were similar beneath both pits (mean concentrations of 4.0 mg/L and 4.6 mg/L for the solid and liquid waste pits respectively). Analysis of the farm borehole showed conductivity as 555 μS/cm, chloride at 38 mg/L and nitrate-N as 8.2 mg/L. Nitrate concentrations in the cored boreholes are therefore roughly half the concentration from the farm borehole. Limited ammonia data are available, with concentrations averaging 0.03 mg/L and 0.01 mg/L beneath the solid and liquid pits.

Table 4.9 **Mean conductivities and anion concentrations in vertical and inclined holes beneath the solid and liquid stores at Sandstone Site 1**

	SEC	Cl	NO_3-N
Solid Store	(μS/cm)	mg/L	
Vertical (*n=16*)	803	200	2.9
>10 m (*n=9*)	760	210	3.5
Inclined (*n=18*)	773	154	4.9
>10 m (*n=9*)	538	92	1.7
Combined (*n=34*)	787	176	4.0
>10 m (*n=18*)	649	151	2.6
Liquids Store			
Vertical (*n=13*)	545	93	5.3
>10 m (*n=8*)	587	95	6.1
Inclined (*n=14*)	553	98	4.0
>10 m (*n=6*)	594	107	6.1
Combined (*n=27*)	549	96	4.6
>10 m (*n=14*)	590	100	6.1

No microbial contamination was found in any of the extracted cores (Table 4.10). As this was the first of the sites to be sampled, we were able to demonstrate that the handling and processing protocols developed for this project were introducing no exogenous contamination to the samples.

The inference of similar concentrations in each pair of boreholes is that leakage is occurring from the bottom and sides of both stores. There is some evidence to suggest that leakage is occurring at a slightly greater rate from the sides of the solid waste pit from the higher conductivity values in the vertical hole compared with the inclined hole. This may be due to some sealing of the pit bottom which does not occur at the sides. The rate and degree of leakage is still small, with slightly more leakage coming from the solids pit. The data suggests that conditions directly beneath the pit are largely aerobic. The threat to groundwater from this site is considered to be negligible.

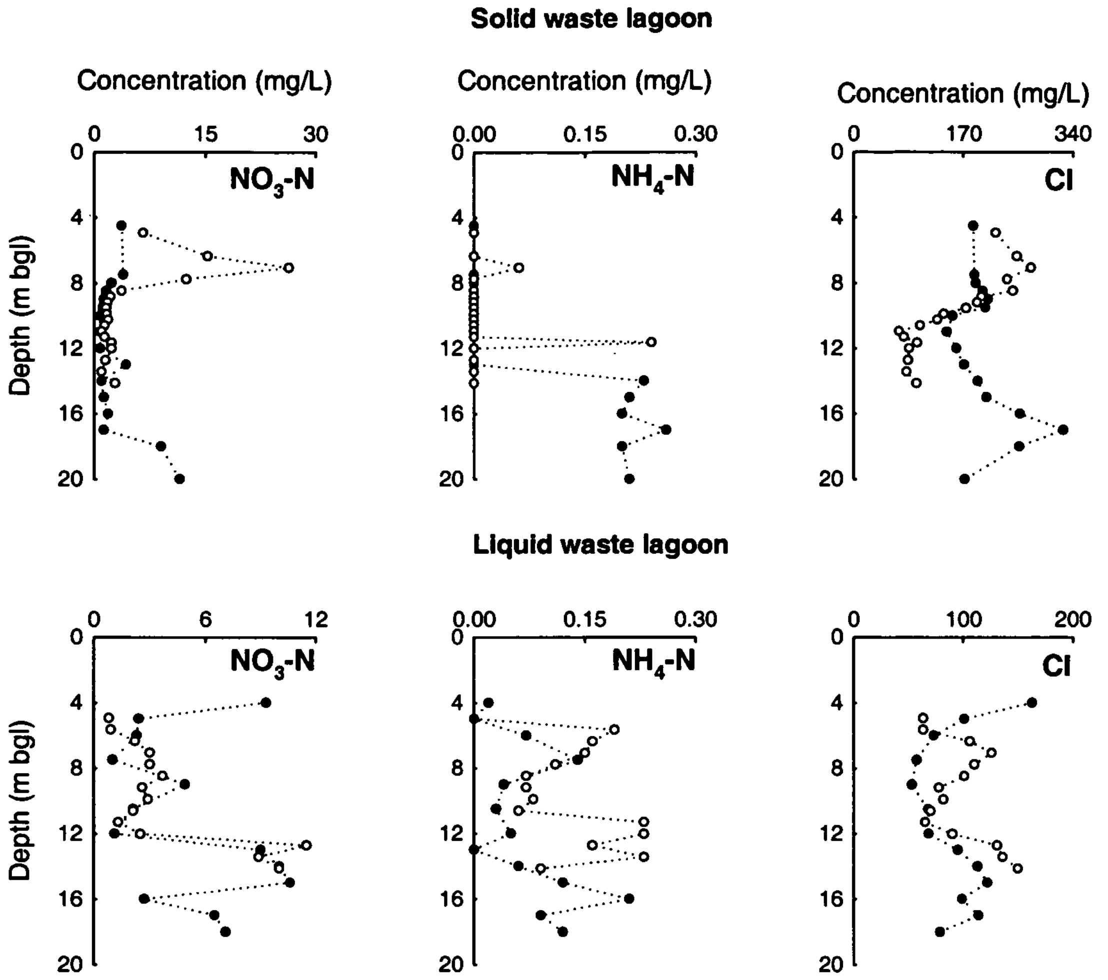


Figure 4.4 **Porewater profiles for cores taken beneath Sandstone Site 1. Vertical borehole indicated by closed circles, inclined borehole indicated by open circles. All concentrations are in mg/L and depths are metres below ground level.**

Table 4.10 Microbiological data for Sandstone Site 1.

Sample	Coliforms	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E. coli*	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g		CFU/g	Pres./Abs. /25g
Vertical (solids lagoon)							
8.50-9.00	<10	<10	Absent	10	N/A	<10	Absent
9.00-9.50	<10	<10	Absent	<10	N/A	<10	Absent
9.50-10.00	<10	<10	Absent	<10	N/A	<10	Absent
10.00-11.00	<10	<10	Absent	<10	N/A	<10	Absent
11.00-12.00	<10	<10	Absent	<10	N/A	<10	Absent
12.00-13.00	<10	<10	Absent	<10	N/A	<10	Absent
13.00-14.00	<10	<10	Absent	10	N/A	<10	Absent
14.00-15.00	<10	<10	Absent	<10	N/A	<10	Absent
15.00-16.00	<10	<10	Absent	<10	N/A	<10	Absent
16.00-17.00	<10	<10	Absent	30	N/A	<10	Absent
17.00-18.00	<10	<10	Absent	10	N/A	<10	Absent
18.00-19.00	<10	<10	Absent	10	N/A	<10	Absent
19.00-20.00	<10	<10	Absent	20	N/A	<10	Absent
Inclined (solids lagoon)							
4.24-4.95	<10	<10	Absent	10	N/A	<10	Absent
6.36-7.07	<10	<10	Absent	120	N/A	<10	Absent
7.07-7.78	<10	<10	Absent	20	N/A	<10	Absent
7.78-8.49	<10	<10	Absent	10	N/A	<10	Absent
8.49-8.84	<10	<10	Absent	<10	N/A	<10	Absent
8.84-9.19	<10	<10	Absent	10	N/A	<10	Absent

4.2.2 Sandstone Site 2

Table 4.11 summarises porewater data for the borehole drilled directly under the liquid slurry store at Sandstone Site 2. For the whole profile, concentrations of chloride and nitrate-nitrogen are roughly 3 times higher than the baseline chemical composition. For the portion of the profile which is deeper than 10 metres below ground however, concentrations are slightly lower. This implies that the lagoon does have an influence over the immediate unsaturated zone chemistry although this influence is very small and almost certainly negligible on the catchment scale. It is likely that the comparatively small solid content of this liquid waste has not been able to form a very effective seal at the base of the lagoon. The lack of any ammonia suggests the environment is well oxidising.

Table 4.12 presents data for the porewaters obtained from beneath the solid slurry store. Concentrations are significantly lower than beneath the liquid store and fairly close to baseline. This implies little or no movement of slurry components from the store through the aquifer. Dissolved organic carbon concentrations are surprisingly high but may reflect the organic content of the underlying carboniferous rocks.

Table 4.11 Mean concentrations of porewaters from beneath the liquid slurry store of Sandstone Site 2.

	SEC	Cl	NO_3-N	NH_4-N	DOC
	(μS/cm)		mg/L		
Whole Profile (*n=20*)	984	110	24	0.0	8.8
>10 m (*n=12*)	815	73	21	0.0	5.7

Table 4.12 Mean concentrations of porewaters from beneath the solids store of Sandstone Site 2

	SEC	Cl	NO_3-N	NH_4-N	DOC
	(μS/cm)		mg/L		
Whole Profile (*n=9*)	589	59	15	0.0	8.8
>10 m (*n=7*)	612	64	12	0.0	11

Microbiological samples for core taken beneath both of these site are shown in table 4.13. No evidence of any microbial contamination has been found at this site. The level of *Cryptosporidium* found in the cattle slurry was however the second highest of all the sites visited.

Analysis of the liquid slurry from this site showed a dry matter content of 0.2% and total N as 0.25 kg/m^3. Analysis from solids store showed a dry matter content of 2.5% and total N as 1.4 kg/m^3.

Table 4.13 Microbiological data for Sandstone Site 2.

Depth (m bgl)	Coliforms 30°C	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E.coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	/ 50g	CFU/g	Pres./Abs. /25g
Slurry			Absent	2000	18		
Solid Store							
5.66-6.36	<10	<10	Absent	<10	Absent	<10	Absent
9.55-9.90	<10	<10	Absent	<10	Absent	<10	Absent
13.44-14.14	<10	<10	Absent	<10	Absent	<10	Absent
17.32-17.68	<10	<10	Absent	<10	Absent	<10	Absent
Liquid Store							
5.66-6.01	<10	<10	Absent	<10	Absent	<10	Absent
8.49-8.84	<10	<10	Absent	<10	Absent	<10	Absent
9.90-10.96	<10	<10	Absent	<10	Absent	<10	Absent
13.08-13.79	<10	<10	Absent	<10	Absent	<10	Absent
14.85-16.26	<10	<10	Absent	<10	Absent	<10	Absent

4.2.3 Sandstone Site 3

Porewater concentrations for selected determinants are presented in Table 4.14. Profiles are shown in Figure 4.5. It is clear that there has been gross contamination of this site by slurry components. Porewaters obtained from this site were not only a definite straw yellow colour but also carried a considerable odour. The degree of contamination appears to increase with depth. This is as a result of having to drill at a much shallower angle than normal so that the middle of the pit was not crossed until the borehole was 12 m deep. Unfortunately the borehole was not constructed beyond 18 m so the extent to which contamination has penetrated is hard to estimate. Below 10 m, chloride and ammonia concentrations are typical of the sort of levels found beneath the heavily contaminated Chalk sites in year 1 of the project (Gooddy et al, 1998a). Conductivity and chloride concentration are an order of magnitude higher than baseline. The near absence of nitrate suggests highly reducing conditions beneath and around the store. The dissolved organic carbon concentrations are considerably higher than at any other site visited. pH values indicate acidic conditions (pH <6) which is in contrast to the contaminated Chalk sites which are all basic (pH >8). Also in contrast to the Chalk sites concentrations of both iron and especially manganese are very high. In addition, concentrations of arsenic have been found up to 1 mg/L.

Table 4.14 Mean concentrations of porewaters beneath Sandstone Site 3

	pH	Cl	HCO_3	SO_4	DOC	NO_3-N	NH_4-N	Na	K	Ca	Mg
						mg/L					
Profile (*n=18*)	7.2	454	79	126	2900	0.5	256	122	673	545	119
>10 m (*n=7*)	5.9	831	<1	175	7200	0.3	622	193	1610	1200	280

With the very high organic carbon concentrations and strong odour it is perhaps somewhat surprising that microbial examination of the core material revealed little by way of microorganisms (Table 4.15). Faecal enterococci were found in the first sample (down to a depth of 2.5 m) and clostridia were found in limited numbers down to about 7 m. This suggests that the Sandstone is acting as a very efficient filter. Due to the often unconsolidated nature of the rock at this site it was not possible to obtain a sample for mercury porosimetry which would have provided a pore size distribution.

Analysis of the slurry from this site showed a dry matter content of 13.9% and total N as 5.7 kg/m^3 which is significantly different from the other cattle slurry determinations.

Table 4.15 Microbiological data for Sandstone Site 3.

Depth (m bgl)	Coliforms 30°C	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E.coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	CFU/50 g	CFU/g	Pres./Abs. /25g
Slurry			Absent	270000	3		
1.98-2.48	<10	70	Absent	1200	Absent	<10	Absent
4.36-4.75	<10	<10	Absent	50	Absent	<10	Absent
5.15-5.55	<10	<10	Absent	140	Absent	<10	Absent
5.55-5.94	<10	<10	Absent	20	Absent	<10	Absent
6.93-7.33	<10	<10	Absent	10	Absent	<10	Absent
8.12-8.52	<10	<10	Absent	<10	Absent	<10	Absent
13.86-14.36	<10	<10	Absent	<10	Absent	<10	Absent
16.24-16.64	<10	<10	Absent	<10	Absent	<10	Absent
17.43-17.82	<10	<10	Absent	<10	Absent	<10	Absent

4.2.4 Sandstone Site 4

Data for Sandstone site 4 have been summarised in Table 4.16. Due to the very poor core recovery from this site only a few samples could be taken and there was insufficient sample for any microbiological examination. The water table was reached at about 18 m and it is significant that porewaters after this depth generally had lower solute concentrations. The high concentrations of ammonia however do raise some concerns although the concomitant lack of DOC implies this may not be due to slurry infiltration. Despite the relative lack of quality data it is considered that any impact from this farm waste store is minimal. A microbiological sample of the farm slurry was taken and found to contain no *Cryptosporidium parvum* (in 50 g) or *E.coli* O157.

Analysis of the slurry from this site showed a dry matter content of 4.6% and total N as 2.3 kg/m^3.

Table 4.16 **Mean concentrations of porewaters beneath Sandstone Site 4**

	SEC	Cl	NO_3-N	NH_4-N	DOC
	(μS/cm)		mg/L		
Whole Profile (*n*=9)	1390	184	15	3.9	7.1
>10 m (*n*=4)	1029	130	12	8.6	1.0

4.2.5 Sandstone Site 5

Porewater profiles have been summarised for Sandstone Site 5 in Table 4.17. This site is very close to Sandstone site 4 although considerably down gradient. Solute concentrations are again slightly elevated compared to baseline but not to any significant degree, especially for agricultural farmland.

Table 4.17 **Mean concentrations of porewaters beneath Sandstone Site 5**

	SEC	Cl	NO_3-N	NH_4-N	DOC
	(μS/cm)		mg/L		
Whole Profile (*n*=9)	1316	190	19	4.7	14
>10 m (*n*=6)	1150	170	17	0.1	11

The level of *Cryptosporidium* in the cattle slurry is by far the highest found at any of the stores (Table 4.18). In addition, this is the only site where *E.Coli* O157 was detected. Microbial examination of the core material however, only revealed a very small number of clostridia present in the top 12 m with the pathogens absent.

Analysis of the slurry from this site showed a dry matter content of 2.9% and total N as 2.3 kg/m^3.

Table 4.18 **Microbiological data for Sandstone Site 5**

Depth (m bgl)	Coliforms 30°C	Faecal enterococci	*E.coli* O157:H7	Total clostridial count	*Cryptosporidium parvum*	*E.coli* 44°C	*Salmonella* spp.
	CFU/g	CFU/g	Pres./Abs. /25g	CFU/g	CFU/50 g	CFU/g	Pres./Abs. /25g
Slurry			Present	7100	234		
3.47-5.94	<10	<10	Absent	250	Absent	<10	Absent
8.91-11.88	<10	<10	Absent	50	Absent	<10	Absent
11.88-14.85	<10	<10	Absent	<10	Absent	<10	Absent

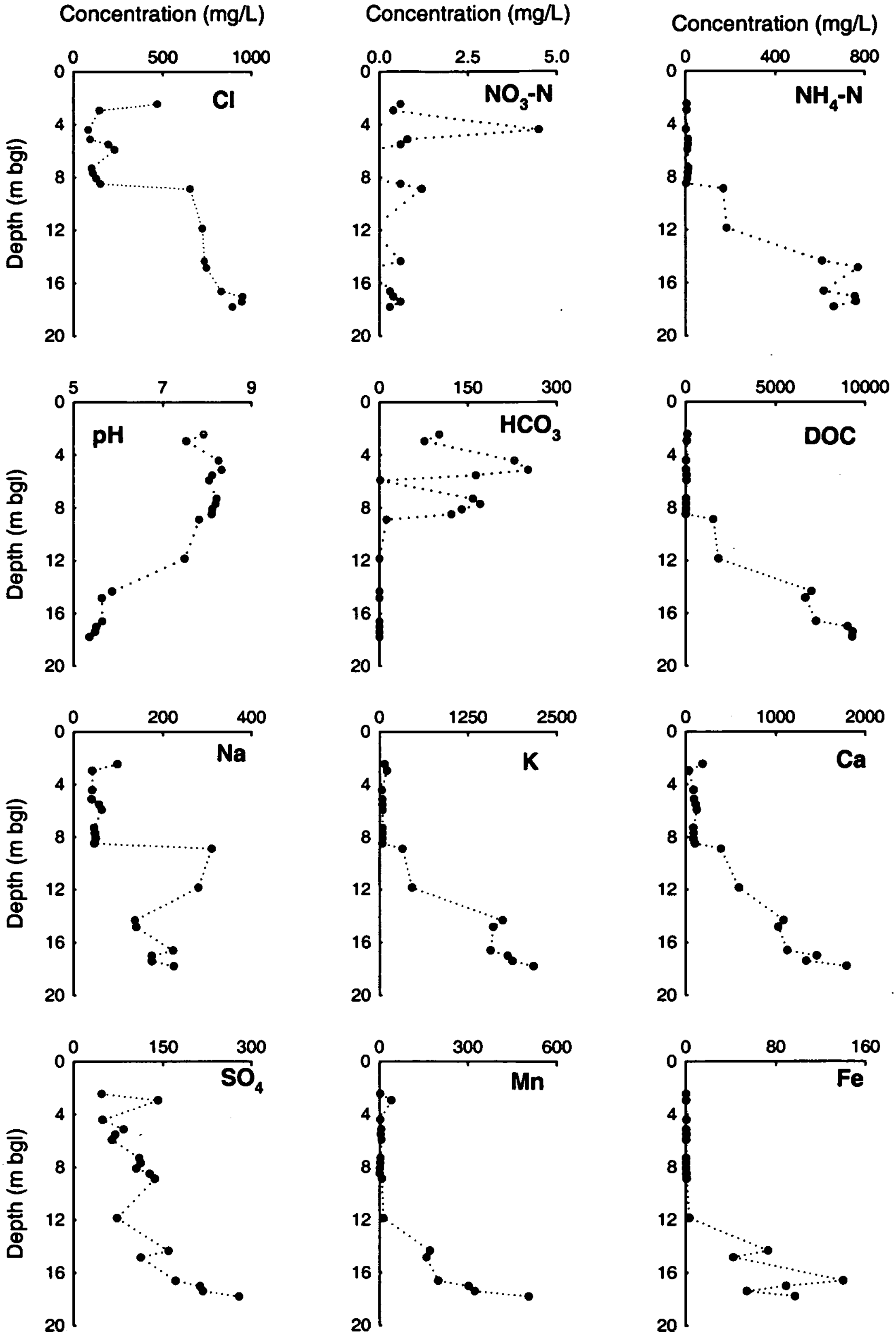


Figure 4.5 **Porewater profiles for cores taken beneath Sandstone Site 3. Inclined hole drilled at an angle of 8° to the vertical. All concentrations are in mg/L and depths are metres below ground level.**

4.3 Gas Samplers

Baseline gas sampling data has been prepared by Darling et al (1997) and this is summarised in Table 4.19 below.

Table 4.19 Mean concentrations of gases found in the unsaturated zone atmosphere of the Chalk and Sherwood Sandstone.

	N_2	O_2 %	CO_2	CH_4 vpm	N_2O vpm	N_2/Ar
Chalk	77.69	19.49	1.52	<0.1	4.24	83.9
Sandstone	77.72	19.62	1.53	0.26	2.35	83.9
Atmospheric	78.08	20.95	0.035	1.8	0.3	83.6

4.3.1 Sandstone Site 1

Data for the two sampling periods for Sandstone Site 1 has been plotted in Figure 4.6. The data from the two sampling periods agree well, suggesting that there is little seasonal variation. Oxygen concentrations are slightly lower and carbon dioxide concentrations are slightly higher for the second sampling implying that the samplers were perhaps not fully acclimated for the first sampling. A previous study (Kinniburgh et al, 1999) suggested that gas samplers take roughly 6 months to acclimatise, however in a polluted environment it would appear that this acclimation period is slightly longer. Oxygen concentrations from the second sampling are a fairly consistent 9% lower than for the baseline data set although carbon dioxide concentrations are roughly the same. Nitrous oxide (N_2O) concentrations are about an order of magnitude higher than baseline, and coupled with the elevated nitrogen to argon ratio (average of 84.46 ± 0.52) data suggests some biological activity and a small degree of denitrification is likely to be taking place.

4.3.2 Chalk Site 2

Chalk Site 2 exhibits a radically different gas chemistry relative to baseline and also took considerably longer to equilibrate, with the samples taken after 428 days and 569 days showing much closer agreement. Profiles for gas samples taken on these occasions are shown in Figure 4.7. The act of borehole construction and inevitable introduction of atmospheric air had a significant impact on both oxygen and methane concentrations. Carbon dioxide (CO_2) concentrations have remained remarkably similar from one sampling to the next. Concentrations of methane at depth increased by five orders of magnitude from the first sampling to the second (>10% methane), with the concentration of methane found at 17 m being of the same order of magnitude as that found in landfill sites. By the third round of sampling, this methane concentration has reduced considerably to below 1%.

The implications of this very high concentration of methane at depth are significant especially when combined with the porewater data. Porewaters showed increasing concentrations with depth of chloride, sulphate, dissolved organic carbon and ammonia. Concentrations peaked at around 16 m most likely as a result of the operation of the store during its early life, when the base had not sealed. The very high concentrations of methane indicate considerable microbial activity at depth. Interestingly, the $\delta^{13}C$-CO_2 ratio does not change during the large change in methane concentrations.

The high degree of microbial activity is reflected in a high nitrogen to argon ratio which, for samplers deeper than 7 m bgl sampled after 428 and 569 days, averages 90.54 ± 4.86. The maximum in N_2O concentration occurs at around 10 m, although the peak in the nitrogen to argon ratio occurs around 15 m bgl, concurrent with a minimum of N_2O. At this point a large enrichment of the ^{15}N isotope can also be found.

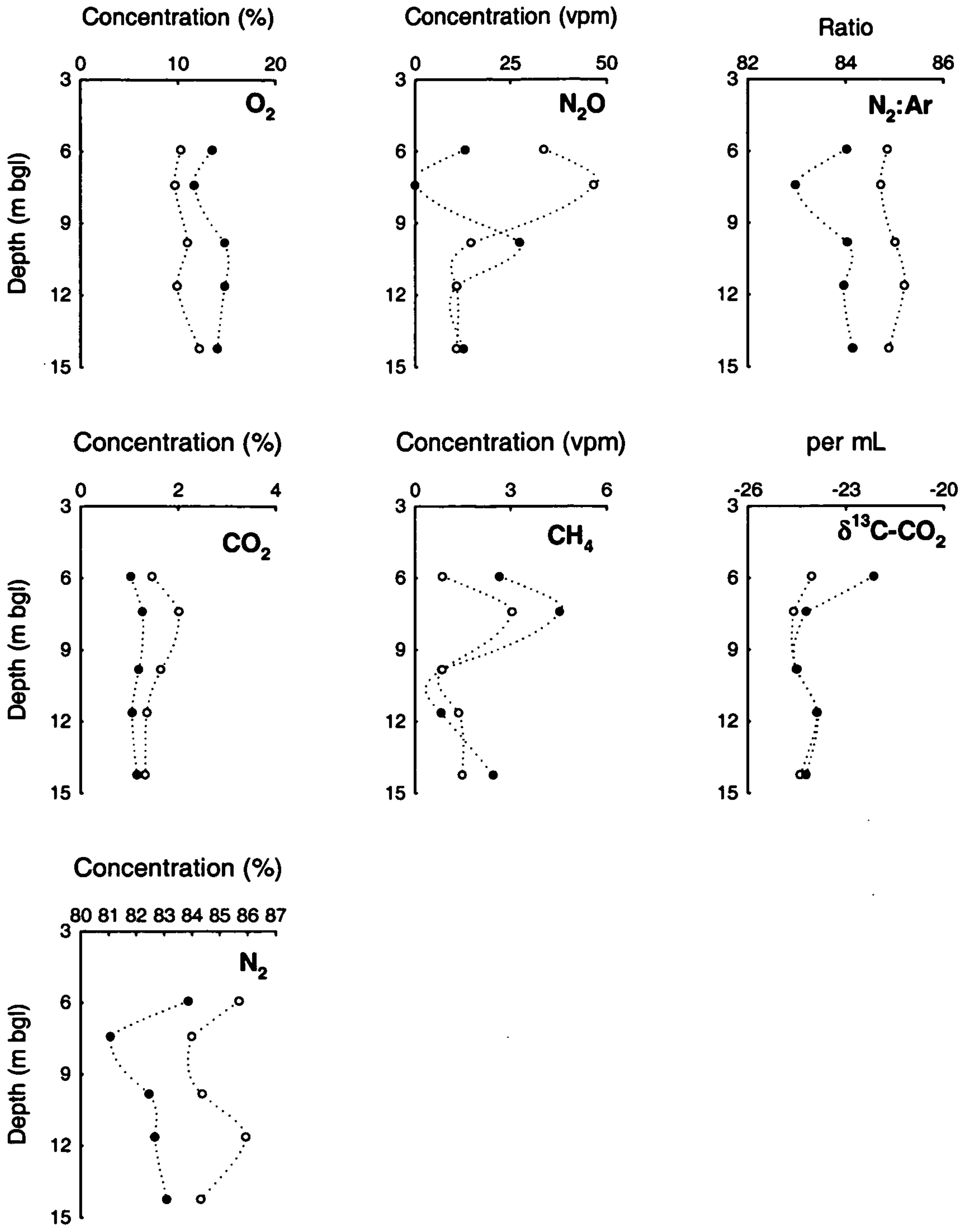


Figure 4.6 Unsaturated zone gas samples taken from samplers beneath the liquid slurry store at Sandstone Site 1. Filled circles represent samples taken 243 days after installation, open circles represent samples taken 465 days after installation.

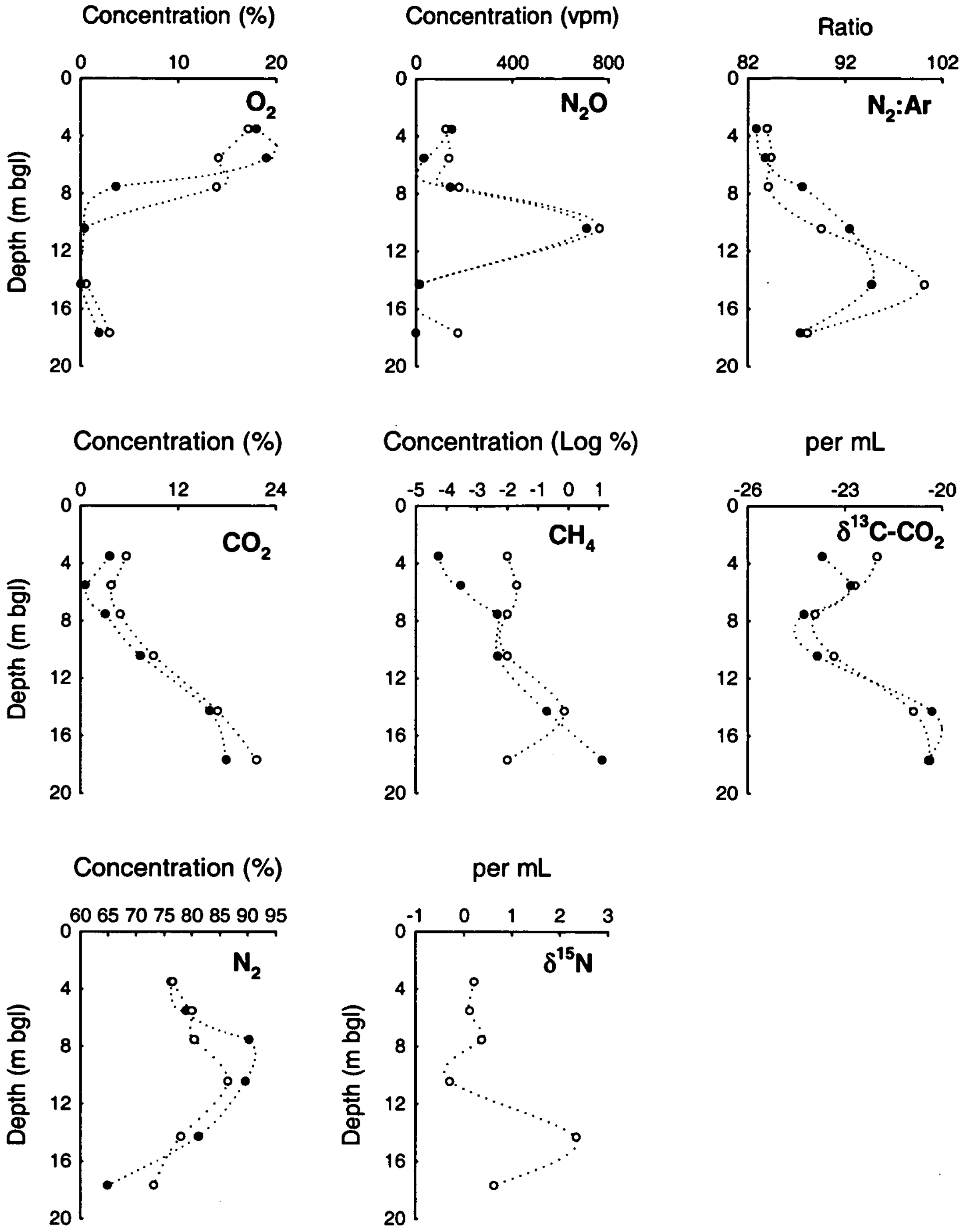


Figure 4.7 **Unsaturated zone gas samples taken from samplers beneath the slurry store at Chalk Site 2. Filled circles represent samples taken 428 days after installation, open circles represent samples taken 569 days after installation.**

4.4 Summary

Eight sites have been fully investigated with the construction of 1 or 2 cored boreholes at each farm waste store. Chalk Sites 1 and 2 have shown to have porewater chemical concentrations well in excess of baseline values, most notably for nitrate, ammonia and dissolved organic carbon. The chemical contamination appears to have moved down at least 20 m in roughly 20 years. Chalk Site 3, drilled beneath a turkey litter store only showed elevated concentrations of nitrate and ammonia in the top few metres of the porewater profile. The appears to be limited movement of the contaminant most likely due to the substantially reduced recharge that occurs beneath a dry matting of turkey litter. Microbial observations beneath the cattle slurry lagoons on Chalk showed evidence of contamination of the unsaturated zone by clostridia. No faecal microorganisms were observed beneath the turkey litter.

With the exception of Sandstone Site 3, little evidence was obtained from microbial or chemical porewater profiling to suggest significant contamination. Porewater profiles from beneath Sandstone Site 3 were grossly contaminated down to a depth of at least 20 m. Ammonia and dissolved organic carbon were the principal contaminants, however microbial observations revealed no microorganisms were penetrating the subsurface.

Data from gas samplers installed at Sandstone Site 1 implies limited biological activity with some denitrification possibly taking place. Data from gas samplers installed at Chalk Site 2 show a large degree of microbial activity with greatly elevated concentrations of nitrous oxide and methane and a very high nitrogen/argon ratio suggesting significant denitrification.

5. DISCUSSION OF FIELD SITE RESULTS

Waters at Chalk Sites 1 and 2 and Sandstone Site 3 display high concentrations of chloride, sulphate, nitrogen species (nitrate or ammonia), potassium, phosphate and much greater concentrations of bicarbonate. These determinants correspond with those associated with cattle slurry by previous studies (Gooddy et al, 1998a).

The bulk of slurry will be enzymatically oxidised by aerobic respiration. In doing so this will break down proteins into their constituent amino acids containing both nitrogen and sulphur compounds. These are ultimately broken down into inorganic species such as ammonia, nitrate, and sulphate and cations such as sodium and potassium in the mineralisation process.

5.1 Redox reactions

A major component of the slurry is organic matter as indicated by high dissolved organic carbon values. Within the Chalk and Sandstone matrix the primary terminal electron acceptors (TEA's) available for microbial degradation comprise dissolved oxygen, nitrate and sulphate. In the Sandstone matrix there is also likely to be iron and manganese. By examining the profiles at Chalk Sites 1 and 2 and Sandstone Site 3, clear geochemical redox zones can be seen associated with degradation of the slurry and sequential consumption of the available TEA's. Table 5.1 provides a summary of the geochemical indicators based on the predominate redox process occurring.

Table 5.1 Geochemical Indicators of Redox Zones

Redox Zone	Indicators
Oxic (aerobic)	*Low* HCO_3, TOC, NH_4
	High NO_3, Ca
Nitrate reducing (anaerobic)	*Increasing* HCO_3, TOC, NH_4
	Decreasing NO_3, Ca
Sulphate reducing (anaerobic)	*Low* SO_4, Ca
	High HCO_3, TOC, NH_4, Fe, Mn

All these processes result in the degradation and mineralisation of organic matter, principally by the donation of electrons from organic matter to the TEA species. However, a clear distinction must be drawn between the process of aerobic respiration which uses oxygen as the TEA, and those which utilise other species and constitute anaerobic respiration.

5.1.1 Oxygen

The zone of aerobic respiration is apparent by the presence of nitrate and sulphate, which are removed by anaerobic respiration in the sub oxic section of the profiles. In the case of Chalk Site 1, only the upper 1 to 2 m bgl is aerobic, while at Chalk Site 2 the aerobic zone is 5m thick. The aerobic zone at Sandstone Site 3 extends down to roughly 8 m bgl. The extent of the aerobic zone is significant in terms of organic degradation, which occurs most efficiently by aerobic respiration (1).

$$CH_2O + O_2 \Rightarrow CO_2 + H_2O \qquad (1)$$

5.1.2 Nitrate and Sulphate

Both nitrate and sulphate reduction constitute processes of anaerobic respiration. At Chalk Site 1, nitrate reduction begins at 2 m bgl and sulphate reduction at 3 m bgl. This is evident by a rapid depletion of nitrate and sulphate. Sulphate reduction must continue to at least 9 m, as some residual sulphate is present (20 mg/L) in combination with organic matter. At Sandstone Site 3 it would appear nitrate reduction occurs around 8 m bgl although the high concentrations of sulphate at depth would suggest little sulphate reduction. Nitrate and sulphate reduction are largely exclusive processes and this can be seen as a transition between nitrate and sulphate reduction occurring at nitrate concentrations of <1 mg/L (Strebel et al, 1990).

At Chalk Site 2, the beginnings of nitrate reduction occur at 5m with nitrate suppressed below 9 m bgl to the end of the drill length. Sulphate reduction (2) is more uncertain, with Figure 4.2 suggesting that sulphate is relatively stable, albeit with a slight reduction below 9 m bgl.

$$2CH_2O + SO_4^{--} \Rightarrow H_2S + 2HCO_3^- \qquad (2)$$

Variations in the concentration of sulphate correspond with those in chloride, suggesting that heterogeneity of the plume could be the primary cause of variation rather than sulphate reduction. From 9 m bgl sulphate remains at a significant concentration at the base of the borehole (150 mg/L), suggesting that if sulphate reduction is occurring it is not complete.

Both ammonia and sulphate occur in anaerobic conditions, suggesting these exist below 2 m bgl at Chalk Site 1 and from approximately 5 m bgl at Chalk Site 2.

5.1.3 Trade off between aerobic – anaerobic conditions (nitrate and ammonia)

As would be expected, an inverse relationship exists between oxidised and reduced nitrogen species (nitrate and ammonia) corresponding with the crossover between aerobic and anaerobic conditions; the inverse trade off can be seen at approximately 2 m bgl at Chalk Site 1, 8 m bgl at Chalk Site 2 and 8-12 m bgl at Sandstone Site 3. Ammonia is usually oxidised to nitrate in an aerobic environment by chemoautotrophic bacteria for an energy yield and carbon dioxide derived carbon source, as shown in reaction 3. This reaction also generates protons which require buffering.

$$NH_4^+ + 2O_2 \Rightarrow NO_3^- + 2H^+ + H_2O \qquad (3)$$

5.1.4 Reduction using Iron and Manganese

The third possible route of reduction is via the use of iron or manganese. Manganese will be used in preference to iron as a TEA and is stable in solution over a greater range of conditions. Iron is present to some extent from the slurry and its distribution within the profiles of the Chalk Sites may indicate ferric iron reduction. Particularly at Chalk Site 2 a scatter of raised iron concentrations occurs between 8-10 m bgl following the depletion of nitrate and this could feasibly reflect a crossover between nitrate and iron reduction zones. At Chalk Site 1, iron increases linearly within the anaerobic zone following consumption of nitrate and in association with declining sulphate. In this case it does not show a peak between nitrate and sulphate and therefore, if the raised values of ferrous iron are indicative of iron reduction, both iron and sulphate reduction would have to be occurring in tandem at Chalk Site 1.

An alternative hypothesis is that while some reduction may be occurring, a second variable is affecting the distribution of manganese and iron. This comprises Eh potential of the profile which determines the phase of manganese and iron and consequently whether or not it is in solution. Where conditions are most reducing, iron will become soluble. Therefore peaks in iron concentration may also reflect the areas of manganese or iron liberation associated with low redox potentials within the reducing section of the profile (Feast et al, 1997) and not necessarily its use as a TEA. The occurrence of very high concentrations of manganese and iron from 12 m to the bottom of the Sandstone Site 3 borehole are therefore likely to reflect the fact that both are present in the sandstone matrix and become soluble at low redox potentials.

5.1.5 Dominant process for microbial degradation of organic matter

The reactions associated with the redox zones occurring are recapped in Figure 5.1. From these reactions it is clear that the combination of aerobic and anaerobic respiration must be producing carbon dioxide and bicarbonate respectively as products. It would be anticipated that these products would in turn coincide with the redox zones identified and discussed above. In practice this can be seen, with a large increase in bicarbonate immediately below the aerobic zone associated with anaerobic respiration. By reference to the geochemical zones at the sites, large excess quantities of bicarbonate are present in the anaerobic section of the boreholes (below 2 m bgl Chalk Site 1, 5 m bgl Chalk Site 2 and 8 m bgl Sandstone Site 3). The predominance of bicarbonate therefore indicates that anaerobic respiration is prevailing over the majority of the profile in terms of depth.

Oxidation (aerobic respiration)

$$CH_2O + O_2 \Rightarrow CO_2 + H_2O$$

Bacterial Nitrate Reduction (denitrification)

$$5CH_2O + 4NO_3^- \Rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$$

Bacterial Sulphate Reduction

$$2CH_2O + SO_4^{--} \Rightarrow H_2S + 2HCO_3^-$$

Figure 5.1 Dominant redox reactions at sites

This is a significant finding, as anaerobic respiration as a mechanism is a much less efficient process than its aerobic counterpart and will not result in degradation of the plume to the same extent as if a larger aerobic zone were present. The decreasing efficiency of anaerobic processes is evident in the stepped increase in DOC with depth. It would be anticipated that the maximum degradation of DOC would occur by aerobic respiration which is capable of completely oxidising a wide range of organic compounds to carbon dioxide. In the profiles, low DOC values in the aerobic zone support this, suggesting that most of the organic matter within these zones is degraded.

Subsequent anaerobic processes are sequentially less efficient and are also incapable of directly degrading some complex forms of organic matter. This is resulting in less organic breakdown with depth. DOC increase inversely with depth in the anaerobic profile as more organic matter survives microbial attack.

Other nutrients such as potassium and phosphate (not shown) also show maximum values in the anaerobic zone and suppressed values where aerobic respiration is occurring. Comparison between these species and Cl (as a conservative tracer) suggests both potassium and phosphorus concentrations are being suppressed by aerobic respiration in the upper profile similarly to DOC. Therefore, while anaerobic respiration may be the most widespread process occurring (in terms of depth over the profile), it is aerobic respiration which accounts for most mineralisation of organic matter. The fact that high DOC values occur in the anaerobic zone suggests the failure of these mechanisms to degrade the slurry. This last point is of significance in terms of the potential for pollution migration from the slurry lagoons. In the absence of large aerobic zones it seems unlikely that the cattle slurry will be degraded fully with the available 'redox drivers' in the chalk (e.g. slurry has <1% S). Therefore there is a significant risk of effluent migration in an undegraded form. Further evidence for this came from the high concentrations of methane found in the deep gas sampler at Chalk Site 2.

5.1.6 Carbonate equilibria reactions

Based on the dichotomy of aerobic and anaerobic process in the profiles an associated reverse in the direction of carbonate equilibria is anticipated with depth in the profile. According to carbonate equilibrium and Le Chattelier's principle, excess carbon dioxide generation and in turn proton liberation (by disassociation of H_2CO_3) in the aerobic profile is likely to result in the dissolution of calcite. Conversely, anaerobic reduction of organic matter will result in the formation of bicarbonate (over the remainder of the profiles) promoting saturation and precipitation of calcite. This situation is illustrated in Figure 5.2, indicating the alternative directions of carbonate equilibria in the aerobic and anaerobic zones.

Aerobic:	CO_2 from respiration $\Rightarrow$ **Dissolution of calcite**
	$CaCO_3 + 2H^+ \Leftrightarrow 2\ HCO_3^- + Ca^{2+}$
Anaerobic:	**Precipitation of calcite** $\Leftarrow$ HCO_3^- from reduction

Figure 5.2 Carbonate equilibria in aerobic and anaerobic zones

As anticipated there is evidence to suggest calcite dissolution in the upper profiles (0–2 m bgl at Chalk Site 1, 0–5 m bgl at Chalk Site 2, and 0-8 m bgl Sandstone Site 3). This is evident by the presence of calcium, formed by dissociation of chalk. However, over the majority of the profiles, anaerobic conditions prevail resulting in excess generation of bicarbonate, leading to calcite precipitation. As would be expected based upon carbonate equilibria, bicarbonate and calcium are inversely related with calcite precipitation (or increasing saturation) resulting in the consumption of all available calcium in the anaerobic section of the profile. The cross over between aerobic and anaerobic boundaries is therefore in evidence by the rapid depletion of calcium.

At Sandstone Site 3 the zone beneath 8 m is clearly anaerobic yet calcium concentrations increase whilst bicarbonate falls to less than 1 mg/L. At this same point, pH declines to near 5. It appears that any calcite present in the matrix of the sandstone has been dissolved, possibly as a result of the oxidation of organic matter combined with the generation of protons during ammonia oxidation. Calcite formation and precipitation may have been inhibited by the extremely high concentrations of dissolved organic matter present (Inskeep and Bloom, 1986) or the absence of bicarbonate at this pH. At low pH values insoluble heavy metals often become mobilised and can therefore migrate through the porewater profile. Arsenic is often associated with iron and so can also be present in the sandstone matrix. It is likely that the combination of a low pH and low redox potential have given rise to very high concentrations (up to twenty times the EU maximum admissible concentration and 100 times the WHO guideline) of arsenic in the porewaters.

Figure 5.3 shows the relationship between HCO_3 and U which are strongly positively correlated. Uranium forms strong complexes with bicarbonate which helps to keep it in solution. One possible source of the uranium is from the Chalk matrix itself. However, It is likely that the uranium originates from another source rather than dissolution reactions since the best correlations occur in the inclined boreholes where conditions are more reducing and calcite is being precipitated. It has previously been postulated by Gooddy et al (1998a) that NPK fertilisers could be the origin of the uranium since phosphate rocks used in the manufacture of these products are rich in uranium, typically containing 10 - 100 mg/kg (Zielinski et al, 2000). The evidence presented here tends to support that theory.

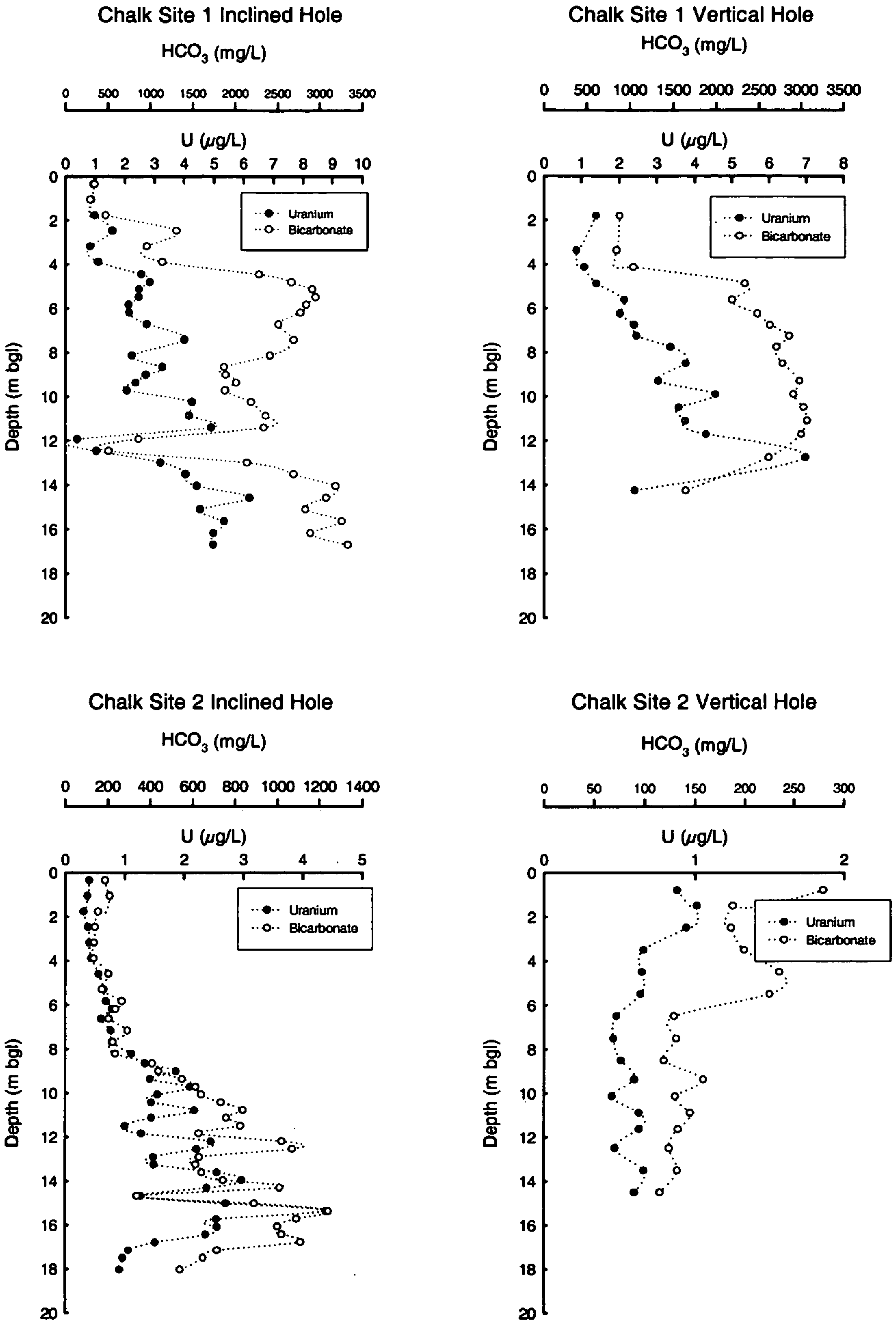


Figure 5.3 Porewater profiles for bicarbonate and uranium concentration taken from cores extracted beneath Chalk Sites 1 and 2. Concentrations of bicarbonate (open circles) are in mg/L whereas uranium concentrations (closed circles) are in μg/L.

5.2 Unsaturated Zone Gas Behaviour

5.2.1 Carbon Isotope data

Additional information on the geochemical processes in Chalk Site 2 is also available from unsaturated zone gas samplers. Carbon isotope analyses show that the $\delta^{13}C$ signal is between -22.5 and -26.5 ‰ suggesting that the carbon is of biological origin. Beneath the slurry lagoon carbon dioxide is produced as a result of the oxidation of large amounts of organic matter as the cattle slurry penetrates the aquifer. The methane production at 18 m may have been stimulated by the penetration of atmospheric air into the relatively anaerobic unsaturated zone during the construction of the borehole and installation of the gas samplers. Isotopic fractionation during the reduction of carbon dioxide normally results in isotopically 'light' (more negative) methane and rather 'heavier' (more positive) carbon dioxide. However, the $\delta^{13}C\text{-}CO_2$ concentration remains unchanged in the presence or absence of methane. Either the methane migrated from elsewhere, or some compensation process took place during the methanogenesis. Ammonia oxidation generates protons and could lead to the production of carbon dioxide via calcium carbonate dissolution, but this would result in isotopically heavy carbon dioxide. The identical $\delta^{13}C\text{-}CO_2$ at 18 m therefore remains difficult to explain but on the basis of carbon mass-balance considerations, for a 10% decline in methane concentration compared with a 4% rise in carbon dioxide, it appears that much of the methane produced has subsequently been dispersed by advection.

5.2.2 Denitrification and Calculation of the rate of nitrate removal

Denitrification occurs when nitrate is used as a terminal electron acceptor instead of oxygen, although most denitrifying bacteria are not strict anaerobes but are facultative organisms which use nitrate when oxygen is not available. The process of denitrification occurs in a series of steps:

$$NO_3^- \Rightarrow NO_2^- \Rightarrow (NO) \Rightarrow N_2O \Rightarrow N_2 \qquad (4)$$

Most denitrifying bacteria are *heterotrophic* microorganisms which require a reduced organic substrate for energy and cell synthesis. The species of bacteria which are the most active denitrifiers in the natural environment are from the genus *Pseudomonas.* Unlike anaerobic bacteria, few denitrifiers are able to ferment and so they would not be expected to survive under strongly anaerobic conditions in the absence of nitrogen oxides. Some denitrifiers can reduce NO_2^- but not NO_3^- whilst many can reduce NO_3^- to N_2O but not to N_2 (Tiedje, 1982).

Autotrophic bacteria can also achieve denitrification using hydrogen gas or various reduced-sulphur compounds as energy sources. These bacteria do not require a source of organic carbon and utilise carbon dioxide or bicarbonate for cell synthesis. Some of these microorganisms can also grow heterotrophically if an organic carbon source is present. For example, *Thiobacillus denitrificans* can denitrify using reduced-sulphur compounds but can also metabolise heterotrophically.

Denitrification rates have been calculated by using an approach adopted by Kinniburgh et al (1999). This calculation is crude and contains no element of transport, however it does provide an estimate as to the potential maximum rates of denitrification taking place beneath the slurry store at Chalk Site 2.

Calculation

From measured moisture contents, the average moisture content between 14 and 16 m is 22%. The crystal density of Chalk is assumed to be 2.71 kg/L.

On this basis, 1 litre of aquifer would be composed of:

water = 38%
air = 2%
rock mass= 60%

For complete conversion of 1 mg/L NO_3-N to N_2:

Weight of N_2 produced

$$= 0.38 \times 1.0$$

$$= 0.38 \text{ mg}$$

Converting weight of N_2 to a volume of gas (at 10°C)

$$= \frac{0.38}{28 \times 10^3} \times 22.4 \times \frac{283}{273}$$

$$= 0.315 \text{ cm}^3$$

Partitioning N_2 between gas and liquid phases and using a gas filled porosity of 2% and an Ostwald coefficient at 10°C of 0.01959 we obtain the total volume of gas, V_T

V_T= volume in gas phase + volume in dissolved phase.

$$= \frac{1}{K_{Ostwald}} \times \frac{Porespace_{vol}}{Solution_{vol}}$$

$$= \frac{1}{0.01959} \times \frac{0.02}{0.38}$$

$$= 2.69$$

$$V_T = V_g\left(1 + \frac{1}{2.69}\right)$$

$$V_g = \frac{V_T}{1.37}$$

$$= 0.230 \text{ cm}^3$$

Therefore the increase in N_2 in the pore space

$$= \left(\frac{0.230}{20}\right) \times 100$$

$$= 1.2\%$$

This all assumes a closed system.

Closer examination of the gas sampler profiles for Chalk Site 2 (Figure 4.7), reveals a maximum in the N_2/Ar ratio occurs around 15 m, coinciding with a minimum in the N_2O concentration. The increase in the N_2/Ar ratio to 100.2 from the background atmospheric value of 83.5 corresponds to a relative shift of 20% which, on the basis of the above calculation is equivalent to approximately 17.5 mg/L NO_3-N.

On the assumption that the concentration of NO_3-N at 14 m beneath the lagoon is 60 mg/L, a reduction in nitrate concentration by 17.5 mg/L is equivalent to a 22.5% fall, i.e. approximately one-fifth of the nitrate produced is lost by denitrification.

The average nitrate concentration from cores taken from the vertical borehole is roughly 250 mg/L (Figure 4.2). It is unlikely that denitrification can take place to the sides of the lagoon since the oxygen availability is so much greater and reducing conditions can not develop. The large discrepancy in nitrate concentrations between the inclined and vertical boreholes can not however be explained in terms of the calculated rate of denitrification alone. It is likely that the rate of transport to the sides of the lagoon where sealing is limited is considerably greater than beneath the lagoon and a greater mass of nitrate moves by this route.

Table 5.2 shows the relative changes in nitrate concentration observed throughout the inclined borehole profile. The figures used are averaged over the two values spanning the gas sampler at a given depth. The changes in nitrate concentration over these depth intervals are very large with the percentage changes in nitrate concentration increasing with depth; the rate of removal increases with depth. The porewaters from the deepest samples are the oldest waters and as such have had a greater time for denitrification to take place. The presently measured degree of denitrification, 17.5 mg/L may not reflect the rate at which denitrification has taken place during much of the profile development.

Table 5.2 Changes in nitrate concentration between gas samplers at Chalk Site 2

Sampler Depth (m)	Nitrate Concentration (mg/L)	Change in Concentration (mg/L)	% Change over interval	% of original concentration
7.60	366			
10.40	182	184	50	50
14.30	59.0	123	68	16
17.70	13.3	45.7	77	4

A maximum value for N_2O (760 vpm) is observed in the gas sampler placed at 10 m. (Figure 4.7). This value equates to roughly 1 mg/L of denitrification (Kinniburgh et al, 1999). Denitrification at this point therefore appears to have been inhibited (relative to the 14 m sampler) with the reaction unable to go to completion. Even with this terminal production of N_2O it appears that the calculated maximum rate of denitrification does not account for the observed nitrate removal demonstrated by Table 5.2. This suggests that there is significant advection of the gases and further work needs to be directed at modelling these processes.

5.2.3 Nitrogen isotope data

During denitrification, the nitrate which remains becomes progressively enriched in ^{15}N because the lighter ^{14}N is preferentially evolved in the gas phase. The composition of the nitrate (δ^{15}N) undergoing denitrification increases proportionally with the logarithm of the residual nitrate (Mariotti et al, 1988). Such behaviour provides positive evidence for denitrification but is rather insensitive until the majority of the nitrate has been denitrified.

Closed-system denitrification as indicated by δ^{15}N is described theoretically by the following form of the Rayleigh equation:

$$\delta^{15}N = \delta_0^{15}N + \varepsilon \ln(\tfrac{C}{C_0}) \qquad (5)$$

where $\delta^{15}N$ represents the isotopic composition of the substrate at time t and $\delta^{15}{}_0N$ that of the initial substrate. The factor ε is the isotopic enrichment factor of the reaction.

A ^{15}N value of 2.34 was determined at the point where most denitrification is assumed to be taking place (gas sampler at 14 m). From the shift in N_2 relative to atmospheric calculated in the previous section as 20%, the measured ^{15}N value needs to be multiplied by a factor of 5 to compensate for the dilution of the isotope by atmospheric nitrogen. This therefore gives an expected figure of 11.7 $\delta^{15}N$‰. Figure 5.4 shows the effect of the denitrification process on the $\delta^{15}N$ composition of the evolved nitrogen gas for two different values of $\delta^{15}{}_0N$ and ε with a starting nitrate concentration of 370 mg/L.

Herbel and Spalding (1993) suggest a $\delta^{15}{}_0N$ of >10‰ for groundwater contaminated with animal waste. In a study by Mariotti et al (1988) data is provided for the isotopic enrichment factor (ε) varying from -4.7 to -5.0‰. From the solid line in Figure 5.4 with a $\delta^{15}{}_0N$ of 10‰ and an isotopic enrichment factor of -5 it can be seen that a $\delta^{15}N$ of 11.7‰ corresponds to a nitrate concentration of roughly 95 mg/L. Allowing for variation in the porewater nitrate profile, this is in good agreement with measured concentrations. The values taken for $\delta^{15}{}_0N$ and ε therefore appear to be reasonable estimates. The figure also shows $\delta^{15}N$-N_2 is a relatively insensitive to the first 50% of the nitrate that is denitrified although it becomes increasingly sensitive as the remaining 50% is denitrified. A $\delta^{15}N$ of 11.7‰ for $\delta^{15}{}_0N$=10‰ and ε=-5 therefore indicates that denitrification is well advanced.

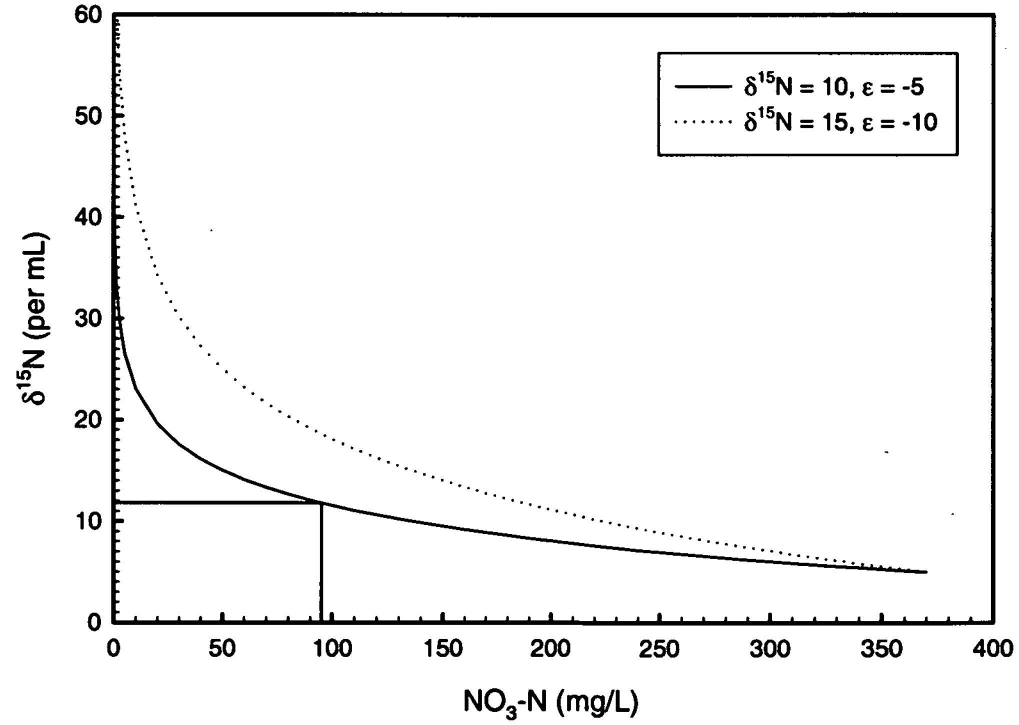


Figure 5.4 **The effect of denitrification processes on the $\delta^{15}N$ composition of the evolved nitrogen gas for the sampler at 14 m at Chalk Site 2. The measured $\delta^{15}N$ of 11.7 is shown to correspond to a porewater nitrate concentration of 95 mg/L for an initial $\delta^{15}N$ composition of 10‰ and a fractionation factor (ε) of -5.**

5.3 Microbiology

The presence of large numbers of clostridia in several of the sites is a good indicator that anaerobic conditions were present, particularly at Chalk Sites 1 and 2 and Sandstone Site 3, so corroborating evidence from the porewater chemistry. The dynamics of the microbial community are unclear since no systematic study of denitrifying or sulphate reducing bacteria was carried out. It seems likely that a succession of microbes utilised the available energy sources, although whether or not these microorganisms originated from the cattle slurry or are already present in the aquifer is an issue worthy of further investigation (Cho and Kim, 2000).

Coliforms, *E.coli,* faecal enterococci and clostridia will always be present in fresh animal manure in high numbers and have been found to be present in several of the slurry lagoons tested in this study. Enteric pathogens including *Salmonella*, *Campylobacter*, *E.coli* O157 and *Cryptosporidium parvum* may be present in some manures. However, no pathogens were isolated from the core samples taken. This suggests the environment is inimical to the survival of these bacteria. Indeed this supported by Jenkins et al (1998) who found that *Cryptosporidium* oocysts become deactivated by high concentrations of ammonia. Additionally it has been shown that *E. coli* O157 has a greatly reduced rate of survival in slurry and expected to live for less than 10 days (Kudva et al, 1998).

However, results from the Chalk sites need to be treated with caution. Both of these sites showed staining on fracture faces which could indicate a more rapid route to groundwater although no coliforms or *E.coli* were isolated from these areas indicating considerable time had elapsed between initial contamination and sampling. If this route is important then it would appear there is limited time for deactivation of these pathogens to occur although the results from the limited number of study sites suggest there is minimal risk of this occurring. Sampling was not carried out after recent refilling of a lagoon and this may be an important period in fracture activation.

5.4 Summary

A series of redox reactions have been observed beneath the slurry stores at Chalk Sites 1 and 2 and Sandstone Site 3. At Chalk Site 2 bacterial nitrate reduction (denitrification) is the dominant terminal electron acceptor process taking place. Evidence from nitrogen/argon ratios together with $\delta^{15}N$ isotope data has shown that denitrification removes at least 20% of the nitrate present and could account for the removal of up to 95% of the starting concentration although other process such as advection and dilution may also account for the large reduction in concentration. At Chalk Site 1 conditions are more reducing and sulphate reduction is the likely terminal electron acceptor process taking place. Reactions that are likely to generate protons (acidity) are all shown to be well buffered by the Chalk rock with little influence on pH. At Sandstone Site 3 this is not the case and the pH has fallen by 2 units which may mobilise potentially harmful heavy metals. Concentrations of iron and manganese are both very high at this site which reflects their presence in the sandstone rock matrix and the reducing conditions that prevail at depth. When electron acceptors other than oxygen are used, the degradation of organic matter becomes less efficient and higher concentrations of dissolved organic carbon are observed and the effluent is likely to migrate in the undegraded form.

The microbiological results confirm the presence of reducing conditions beneath the slurry stores. At all sites the movement of contamination appeared slow which suggests that the risks of any pathogens present in the store manures entering the groundwater would be small. The presence of fractures and the observation of slurry on fracture faces may suggest a rapid route for otherwise short lived pathogens to reach groundwater, especially in the early years of operation or after refilling following emptying.

6. MODELLING CONTAMINANT TRANSPORT

6.1 Unsaturated Zone Modelling

The model described in Section 2.7.2 was used to estimate possible fluxes through waste lagoons on sandstone and chalk. The mean fluxes modelled for each of 12 scenarios (detailed in Table 6.1) is given in Table 6.2. In each group of scenarios, the degree of sealing varied from complete sealing (scenario 1) with a thin layer (50 mm thick) with a conductivity one thousandth of that of the unmodified material, to a completely unsealed condition (scenario 4). Scenario 4 represents the initial condition of the pit before any material is added, and also represents the worst possible case, in which no sealing occurs. It is also the case that would be calculated if only geological information were used to estimate the fluxes.

Three groups of scenarios were generated; P relates to the Permo-Triassic Sandstone; C relates to the chalk; and M attempted to model chalk macropores. This last group of scenarios was an attempt to derive some estimate of the effect of macropores in the chalk, although those effects had not been directly measured in the field studies. Field observations indicated the importance of fractures for the preferential transport of water and pollutants, and so it was necessary to obtain some indication of the fluxes that might be carried through the macropore system. Macropores were thus modelled independently as a separate set of runs of the same unsaturated flow model as if they had a hydraulic conductivity one hundred times greater than the matrix pores, but occupied only 1% of the total pore volume. The macropore fluxes that are estimated by this means might be added to the normal "matrix" fluxes, to give an estimate of the total macro plus micro pore flows, although this will be an estimate because modelling the two as independent systems does not consider the possible interaction between them.

From the profiles generated by the model (not shown), it is clear that in each of these scenarios, an equilibrium flux has been established. In soil physical terms these reduce to an infiltration situation, in which a wetting front gradually moves down the soil profile, and behind the front the moisture content, θ, reaches an equilibrium value where the conductivity function $K(\theta)$ equals the flux maintained behind the wetting front. (however this simple situation is itself a reflection of the fact that the soil became more conductive with depth – the same is not true for other soil configurations).

Table 6.1 Scenarios for modelling fluxes through the pit bases

	Layer 1		Layer 2		Layer 3		Layer 4	
Scenario	K_{sat} (mm/hr)	Thickness (m)	K_{sat} (mm/hr)	Thickness (m)	K_{sat} (mm/hr)	Thickness (m)	K_{sat} (mm/hr)	Thickness (m)
P1	.0023	.05	.023	.15	2.33	.3	23.3	2.5
P2			.023	.2	2.33	.3	23.3	2.5
P3					2.33	.5	23.3	2.5
P4							23.3	3.0
C1	.00026	.05	.0026	.15	.026	.3	.26	2.5
C2			.0026	.2	.026	.3	.26	2.5
C3					.026	.5	.26	2.5
C4							.26	3.0
M1								
M2								
M3								
M4								

Table 6.2 **Modelled mean fluxes through pit bases for each scenario.**

Scenario	Mean flux, m/year
P1	0.1220
P2	0.3376
P3	1.9385
P4	4.2677
C1	0.0007
C2	0.0022
C3	0.0120
C4	0.0264
M1	0.06901
M2	0.2171
M3	0.8066
M4	2.3734

It is also clear that the major component of the flux is the daily addition of water to the store in the form of slurry, and any impact of rainfall and evaporation is secondary. This has the implication that we can use the same model for all locations within lowland Britain, where the variation in the effective rainfall amount is small compared with the 4 m flux of water added to the store.

The results also demonstrate the importance of the sealed layer. In the sandstone, the results without the sealed layer (scenario P4) show continued infiltration of all material added to the store. The slurry pit in this circumstance acts as a soak-away. With a thin sealing layer (P3), the pit still acts as a soak away, but gradually fills over a five year period. However, with a sealing layer reduced to a conductivity of 1% of the initial value, the fluxes become small, and no more than about 2-3 times the natural recharge (i.e. 450 mm as opposed to about 200 mm). Only with the thin layer with a conductivity 3 orders of magnitude lower than the unsealed material (P1) does the flux become lower than the natural recharge.

The patterns within the Chalk (scenarios C1 to C4) are very similar, although numerically smaller. Without a sealing layer (Scenario C4), the movement across the pit surface can even be in both directions, as summer evaporation engenders upwards movement of water. Apart from this, the results from the chalk are very similar to those already derived from the sandstone, although very much slower.

The modelled fluxes for the macropore scenarios are higher than for the chalk matrix, although still lower than the fluxes through the Permo-Triassic Sandstone. Again the sealing effect is important, and the result from scenario M4 shows that where unsealed macropores reach the surface the risk of pollution is high. However, the result from scenario M1 shows that where the macropores become as sealed as the surrounding matrix, the fluxes again become very low. Sealed macropores thus present no pollution threat.

These results demonstrate the importance of the sealing layer at the base of the pit. If this were not present, then pits in either sandstone or chalk would act as large soak-aways. Under those circumstances the pit remains empty of water each day and merely accumulates the solid material. However, under sealed circumstances, the rate of seepage is sufficiently small for the pits to present only a small danger to the underlying groundwater. This danger would be enhanced where the water table is particularly shallow.

6.2 Mass Balance Approach

The results from this analysis using concentration data from Table 2.1 are summarised in Table 6.3 As can be seen the leachate from the slurry pit only has a very significant effect on abstracted water quality in the case of the small abstraction. This is because in this case the area of the slurry pit is a significant proportion of the total catchment area of the well. Thus, this analysis suggests that the danger from contamination by soluble pollutants is only significant near the polluting farm.

It must be emphasised again that this analysis is for a dissolved contaminant which travels with the recharge water. Also it gives no indication of travel times and so it cannot be used as a relevant indication for bacterial contamination. If the contaminant is highly toxic even the small increases in concentration at the larger abstractions indicated in Table 6.3 might be significant. However, this investigation is only concerned with the effects of slurry pits and not pesticide soak-aways.

Table 6.3 Estimated nitrate concentrations (mg/L) at an abstraction borehole

Recharge rate (m/d)	Abstraction rate (m^3/d) 10	100	1000
0.0001	6.11	5.11	5.01
0.001	16.14	6.11	5.11

$C_{background} = 5$ mg/L, $C_{pit} = 500$ mg/L, $A_{pit} = 225\ m^2$

6.3 Site Scale Modelling

The model was developed so as to reproduce water level contours similar to those on the regional hydrogeological map by varying the recharge rate, hydraulic conductivity and river leakage. The values used in the calibrated model (Table 2.3) are considered to be reasonable for a Chalk aquifer.

Following refinement of the model, an abstraction borehole was introduced in the position shown in Figure 2.2. The abstraction rate was varied between 10 and 1000 Ml/d and the capture zone of the borehole was determined using MODPATH. The capture zone for an abstraction rate of 10 Ml/d (equivalent to a farm borehole) is shown in Figure 6.1. The capture zone is very narrow, having a width of less than 10 m. To check that this was not caused by numerical problems within the model the grid was further refined in the vicinity of the well to give grid squares of 10 m immediately around the well. This had no significant impact on the modelled shape of the capture zone.

An analytical approximation for the width of a capture zone, from Fetter (1994), was used to check the validity of the modelled capture zone. The equation:

$$Y_{max} = \pm \frac{Q}{2Kb\,i} \tag{1}$$

where Y_{max} is the half width of the capture zone as x approaches infinity.
Q is the pumping rate (m^3/d)
K is the hydraulic conductivity (m/d)
b is the initial saturated thickness of the aquifer (m) and
i is the hydraulic gradient of the flow field in the absence of the pumping borehole (no units)

gave an expected value of 7 m which is consistent with the model.

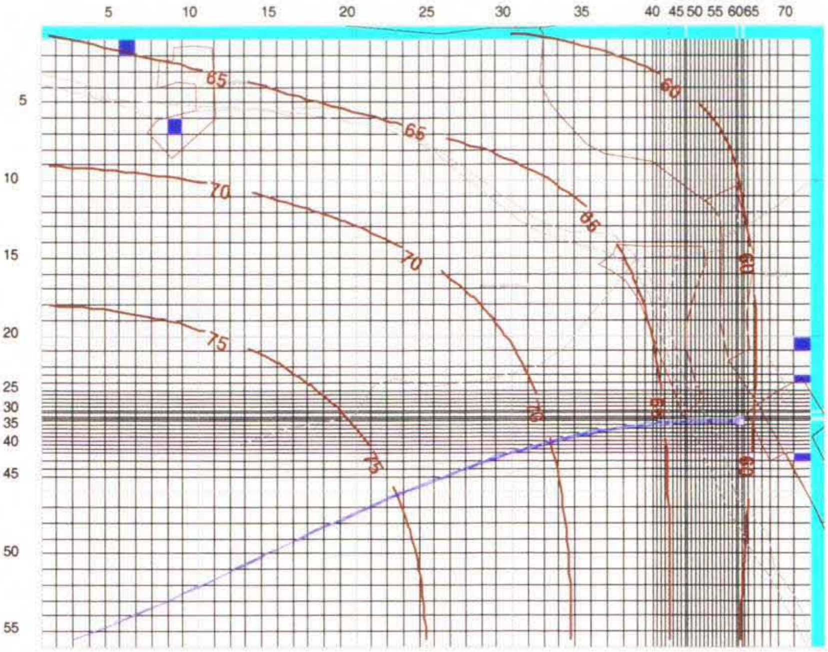


Figure 6.1 Borehole capture zone at an abstraction rate of 10 m^3/d.

6.4 Generic Model

The capture zones for the generic model are presented in Table 6.4. Comparing them with those for the site-based model show that there is a threefold increase in the width. This will have the result that at the lower gradients, the water flowing to the borehole is more likely to contain pollution from the farm waste store.

Table 6.4 Width of capture zone (m) for groundwater models used

Model	Abstraction rate (m^3/d)		
	10	100	1000
Generic	20	208	2080
Site-based	4	40	400

The time of travel of pollution from the farm waste store to a nearby borehole is summarised in Table 6.5. These results clearly demonstrates that for the likely distance from a farm waste store to a farm supply borehole (<1 km), the time for the contaminants to pass through the unsaturated zone matrix is greater than travel times in the saturated zone.

Table 6.5 **Time of travel of pollutants to a farm supply borehole**

Unsaturated zone		Saturated zone	
Depth of unsaturated zone (m)	Time of travel (year)	Distance form borehole (m)	Time of travel (year)
10	10	800	3.7
20	20	1900	11.1
40	40	4000	83.3

The assumptions used for these estimates are as follows;

- Solute travels through the unsaturated zone at the rate of 1 m/year
- Saturated flow in chalk can be represented as a porous medium with a porosity of 1%

To obtain a capture zone with a width likely to intercept a Farm Waste store leads to gradients being as low as 4 m in 1 km compared to 7 m in 1 km for the site-based model. These gradients, coupled with a very low recharge (equivalent to 35 mm/a) represent the worst case situation for the borehole to intercept leakage from the pits and are unlikely to be found very often in the field. Thus the most vulnerable boreholes according to the mass balance estimate are unlikely to intercept the pollution from a farm waste store.

Depending on the thickness of the unsaturated zone, the time of travel through the system is greater in the unsaturated zone than the saturated zone. This demonstrates the importance of characterising unsaturated zone processes in determining the impact of agricultural pollution on groundwater quality. The time taken to travel through the unsaturated zone means that even if Farm Waste stores are removed now, then there is a significant time (~10s years) before this affects water quality at nearby abstraction points.

6.5 MAP Modelling

Both sandstone and Chalk groundwater abstractions show large temporal variations in measured nitrate concentrations which cannot be modelled with MAP (or any other model). This is shown in Figure 6.2 for a Sandstone site along with the best model fit found during the previous modelling work (Chilton et al 1999). The MAP model can be seen to simulate the trend in the measured data reasonably well but the short term variations are attributed to the management of the source (turning the pump on and off, using nearby sources etc). Figure 6.2 also shows the predicted nitrate concentrations after the addition of waste store leachate to the inputs, as described in section 2.7.6. This shows that the overall concentration measured at the borehole is increased by less than 0.5 mg/L. In the context of the much larger short term variations in nitrate concentrations this is considered not to be significant.

Figure 6.3 shows the effect of removing all the waste stores in the year 2000. As can easily be seen this has a negligible effect on predicted nitrate concentrations (less than 0.1 mg/L after 20 years). The results for the Chalk site are similar and are shown in Figure 6.4. In this case the effect of removing the stores is even smaller as a result of the dual porosity nature of the saturated Chalk aquifer.

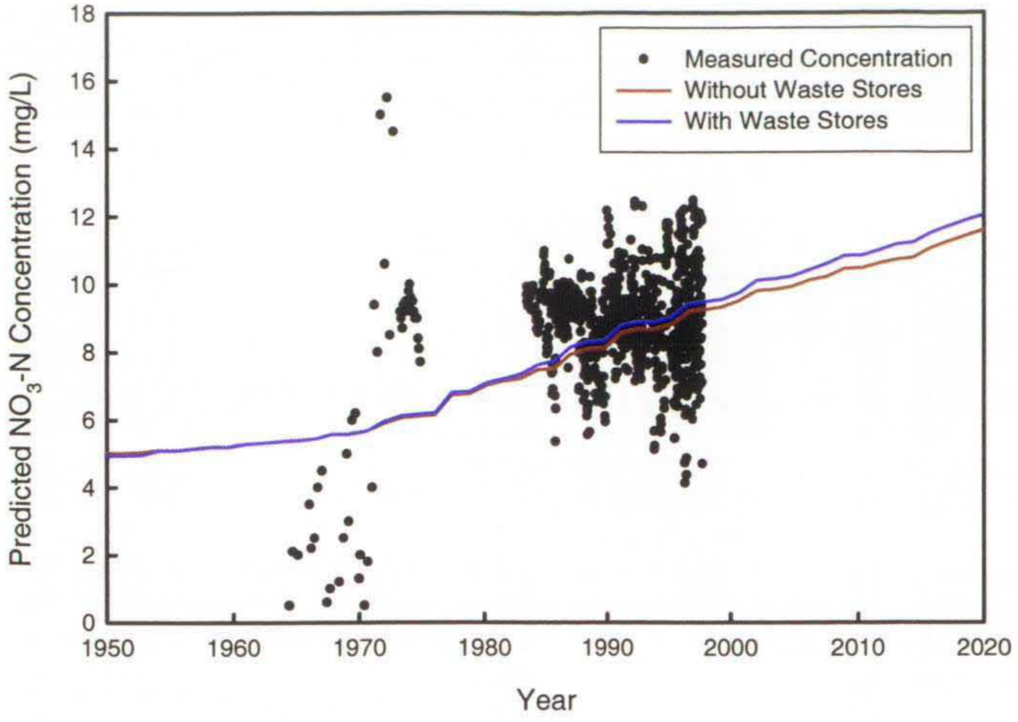


Figure 6.2 Best fit curves for a Sandstone site with and without waste stores.

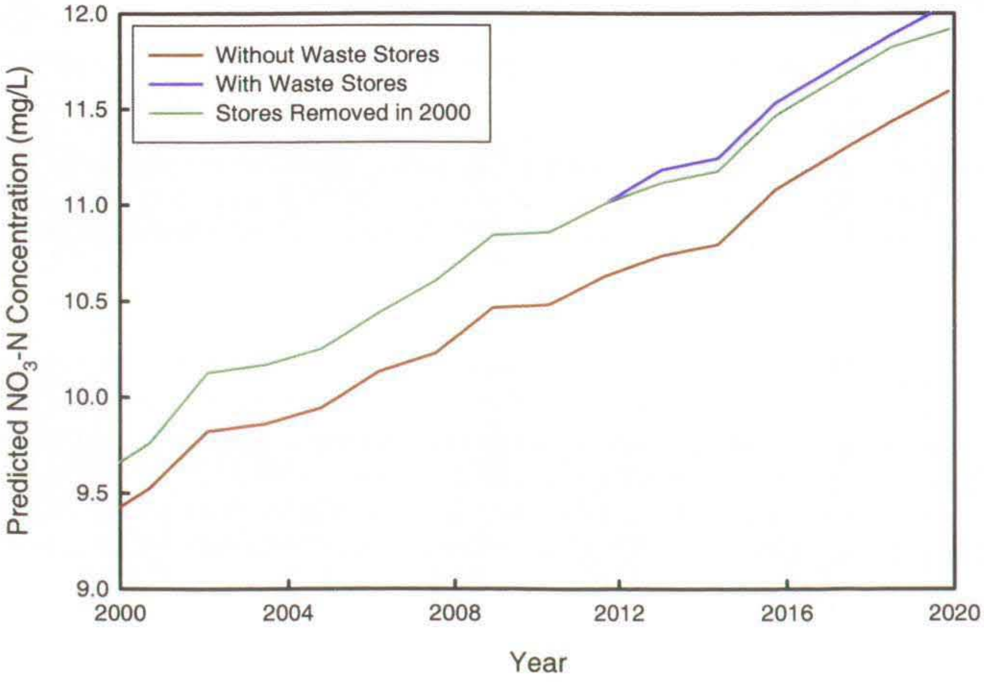


Figure 6.3 The predicted effect on groundwater nitrate concentration for a Sandstone site with farm waste stores removed in the year 2000

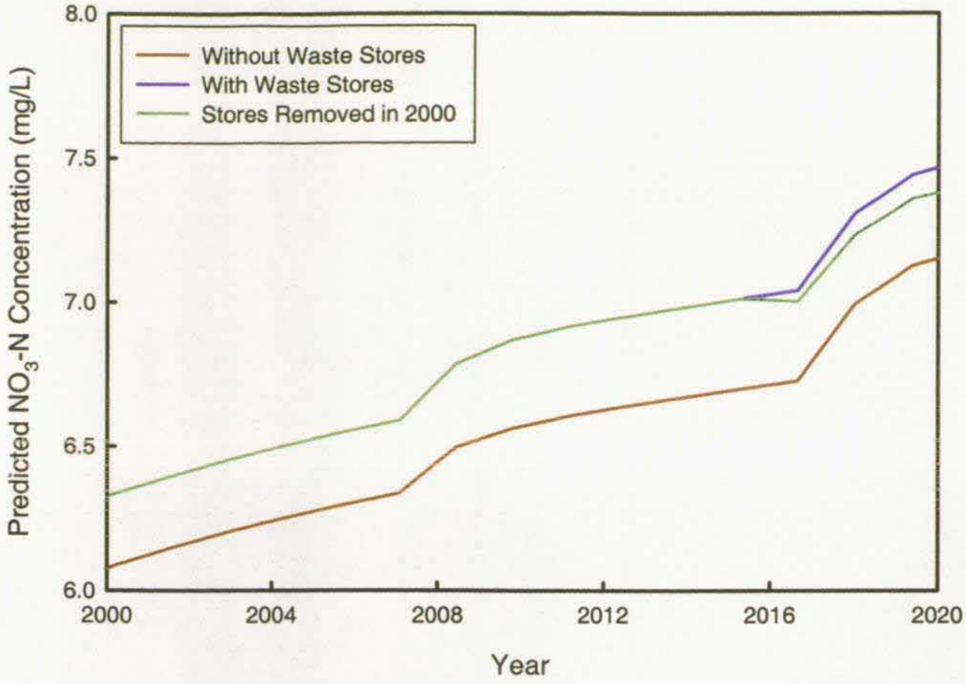


Figure 6.4 **The predicted effect on groundwater nitrate concentration for a Chalk site with farm waste stores removed in the year 2000**

6.6 Summary

A range of modelling techniques have been used to assess the possible impact of farm waste stores on abstracted groundwater. It has been shown that travel times within the aquifer system, from store to the groundwater table and then to an abstraction are relatively long. Where a seal has been formed, transport from the store to the water table is at a maximum velocity of around 1 m/a, which gives travel times of many years at most sites. Without the sealed layer the slurry pit can act as a soak-away because there is a hydraulic connection between the base of the pit and the water table. This may also occur where the unsaturated zone is very shallow. Within the aquifer itself the travel times from the water table to an abstraction point obviously depend on the distance, but are generally measured in years rather than days.

Consideration of the nitrate concentrations in the leachate from the stores leads to the conclusion that this poses little additional risk to the quality of abstracted water, unless the abstraction is small and/or is in the immediate vicinity of the store. However, the work has concentrated on consideration of nitrate which is present in the environment from many other agricultural sources.

The other possible pollutant from waste stores which has not been modelled is particulate pollutants such as *Cryptosporidium* parvum. Particles will travel in different pathways to dissolved pollutants as they are often too large to access all the pore space. From the modelling work reported here it is not possible to say whether farm wastes stores pose a significant pathogen hazard.

7. VULNERABILITY AND RISK MAPPING

7.1 Differences between classification approaches

The production of vulnerability maps was described in Section 2.8. Two maps were produced and compared, the first using the HOST classification of soils, and the second using a drift cover classification. The areas of Chalk or Permo-Triassic sandstones that are covered by soils belonging to the vulnerable or non-vulnerable HOST soil classes on a 1 km grid are shown in Figure 7.1. The areas of Chalk or Permo-Triassic sandstones that are covered by permeable drift (as defined in section 2.8) or no drift, and impermeable drift are shown in Figure 7.2.

In order to highlight areas of discrepancies between the HOST and drift approaches, the two maps were combined and a "difference" map produced (Figure 7.3). The areas where there were differences were then examined in detail by looking at more detailed geological and drift mapping (up to 1:50 000 scale) in order to try to identify the reasons for the divergence, and decide on the most accurate approach.

It should be taken into account that at least some of the "noise" in the difference map may be a result of discretisation of polygon data. Overall, the vulnerable areas calculated from each approach differed little, with the drift approach estimating a slightly greater area of vulnerable aquifer (Table 7.1). However, the areas that did not agree between the two maps were significant (Table 7.2).

Table 7.1 **Areas of vulnerable and non-vulnerable aquifer estimated by each approach**

	Area estimated by HOST approach (km^2)	Area estimated by Drift approach (km^2)
Vulnerable	17 429	17 884
Non-vulnerable	13 966	13 500

Table 7.2 **Areas where classification of the two approaches did not agree**

	Area (km^2)
HOST vulnerable/ drift non vulnerable	3 535
Drift vulnerable/ HOST non vulnerable	3 950[†]

[†] 1546 km^2 of this area classified as high leaching capacity on the groundwater vulnerability maps (NRA/EA, 1994-98)

In the south west a north-south strip of land was classified as not vulnerable under the HOST approach, but vulnerable according to the drift approach. The geology of this area on the 1:625,000 map shows it to be basal Permian Breccia; however, the 1:250,000 mapping differentiates the area into the Exeter Sandstone Group and the Aylesbeare Mudstone Group. The area that appears as vulnerable according to the drift approach closely coincided with the outcrop of the Aylesbeare Mudstone Group, and therefore did not represent a vulnerable aquifer. This area was corrected by assigning low permeability status to the areas covered by the Aylesbeare Mudstone outcrop.

Numerous other small areas that have been classed as not vulnerable by the HOST approach and vulnerable by the drift approach do appear to have no low permeability drift cover, and hence from the geological standpoint should be vulnerable. When compared to the soil leaching potential from the vulnerability maps (NRA/EA, 1994-1998), many of these areas do appear to have high leaching potential, further supporting the drift classification.

The other difference is where the drift approach has classed an area as not vulnerable, but the HOST approach classes it as vulnerable. Such areas include parts of Hampshire, East Anglia and eastern Yorkshire. In the south of England, these areas are almost entirely covered by clay-with-flints, and in East Anglia by boulder clay, both of which are assumed to confer a degree of groundwater protection. In eastern Yorkshire, the protection is offered by either till or lacustrine clays, silts and sands. Therefore for these areas, it appears that the drift classification is generally correct.

It is difficult to draw definite conclusions about which approach is most favourable. With both approaches, the coarse resolution of the data mean that conditions on a local scale may be different to those mapped at this scale.

7.2 Areas at Greater Risk

Figure 7.4 presents a map showing the estimated numbers of earth-banked slurry lagoons over the vulnerable area of the aquifers based on the HOST classification. This shows some clearly identifiable "hot spots" where the combination of high cattle numbers and aquifer vulnerability lead to a higher potential for aquifer pollution. It is important to note that these are areas where there is the highest potential for pollution: they do not necessarily represent actual pollution, as this will also be the result of many variations in local practice.

The main areas of concern are to be found in the Chalk outcrop of Dorset, and more locally over the Permo-Triassic Sandstone in the West Midlands. These correspond to areas where there are high cattle numbers. The Chalk of North East England does not appear to have a high risk. There are many pigs in the area, but the anecdotal feedback from all the approaches to find sites for this investigation suggested that there are very few "old" (pre-1991) unlined stores. This is in contrast to the dairying areas. It is likely that a larger proportion of pig slurry lagoons are lined, as they are often emptied by pumping, which unlike the use of mechanical buckets and excavators (common with thicker cattle slurry) does not damage a synthetic liner.

The Chalk aquifer of most of East Anglia and the North Downs also has a relatively low risk, reflecting the lower incidence of stock farming in these areas.

Although the modelling studies indicate that the flux of water through the base of a slurry pit is not principally a reflection of the climate, but of the mean depth of slurry, there nevertheless remains a climatic constraint on the vulnerable areas – as these are located in the higher rainfall areas, where livestock production is more important than in the drier east.

In all cases the thickness of the unsaturated zone has not been taken into account. In general, unsaturated zones in the Chalk are much thicker than those in the sandstone although the depth to water can vary considerably over a given catchment so lagoon siting would need to be carefully assessed for each site. Where a thin unsaturated zone exists the potential risk to groundwater is greater than for a thicker unsaturated zone since direct hydraulic connectivity between the base of the lagoon and the water table is more likely to be made. For pathogens which might have relatively short lifespans in the subsurface this could be of great significance since transit times from lagoon to well would be greatly reduced.

The other difference is where the drift approach has classed an area as not vulnerable, but the HOST approach classes it as vulnerable. Such areas include parts of Hampshire, East Anglia and eastern Yorkshire. In the south of England, these areas are almost entirely covered by clay-with-flints, and in East Anglia by boulder clay, both of which are assumed to confer a degree of groundwater protection. In eastern Yorkshire, the protection is offered by either till or lacustrine clays, silts and sands. Therefore for these areas, it appears that the drift classification is generally correct.

It is difficult to draw definite conclusions about which approach is most favourable. With both approaches, the coarse resolution of the data mean that conditions on a local scale may be different to those mapped at this scale.

7.2 Areas at Greater Risk

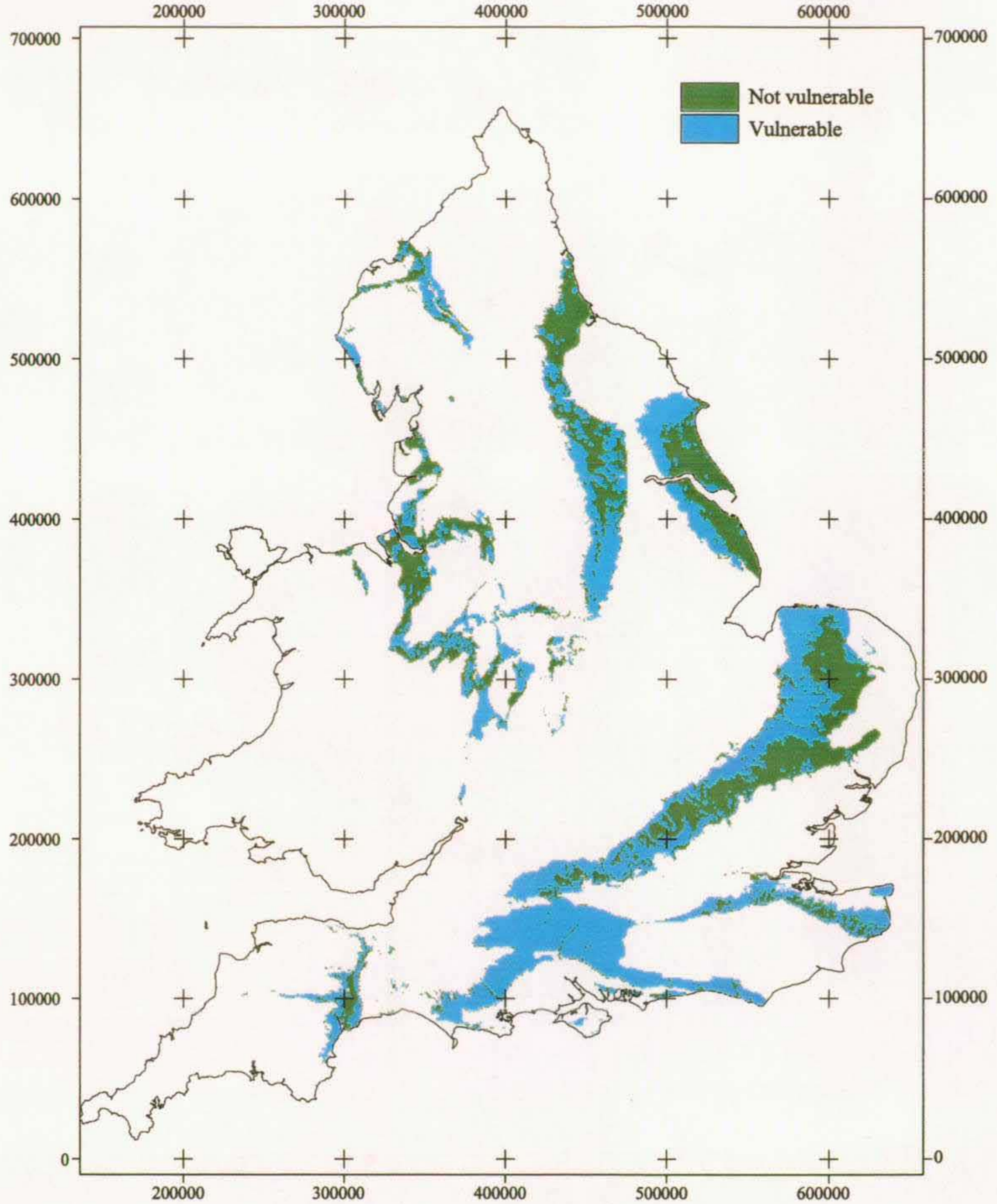
Figure 7.4 presents a map showing the estimated numbers of earth-banked slurry lagoons over the vulnerable area of the aquifers based on the HOST classification. This shows some clearly identifiable "hot spots" where the combination of high cattle numbers and aquifer vulnerability lead to a higher potential for aquifer pollution. It is important to note that these are areas where there is the highest potential for pollution: they do not necessarily represent actual pollution, as this will also be the result of many variations in local practice.

The main areas of concern are to be found in the Chalk outcrop of Dorset, and more locally over the Permo-Triassic Sandstone in the West Midlands. These correspond to areas where there are high cattle numbers. The Chalk of North East England does not appear to have a high risk. There are many pigs in the area, but the anecdotal feedback from all the approaches to find sites for this investigation suggested that there are very few "old" (pre-1991) unlined stores. This is in contrast to the dairying areas. It is likely that a larger proportion of pig slurry lagoons are lined, as they are often emptied by pumping, which unlike the use of mechanical buckets and excavators (common with thicker cattle slurry) does not damage a synthetic liner.

The Chalk aquifer of most of East Anglia and the North Downs also has a relatively low risk, reflecting the lower incidence of stock farming in these areas.

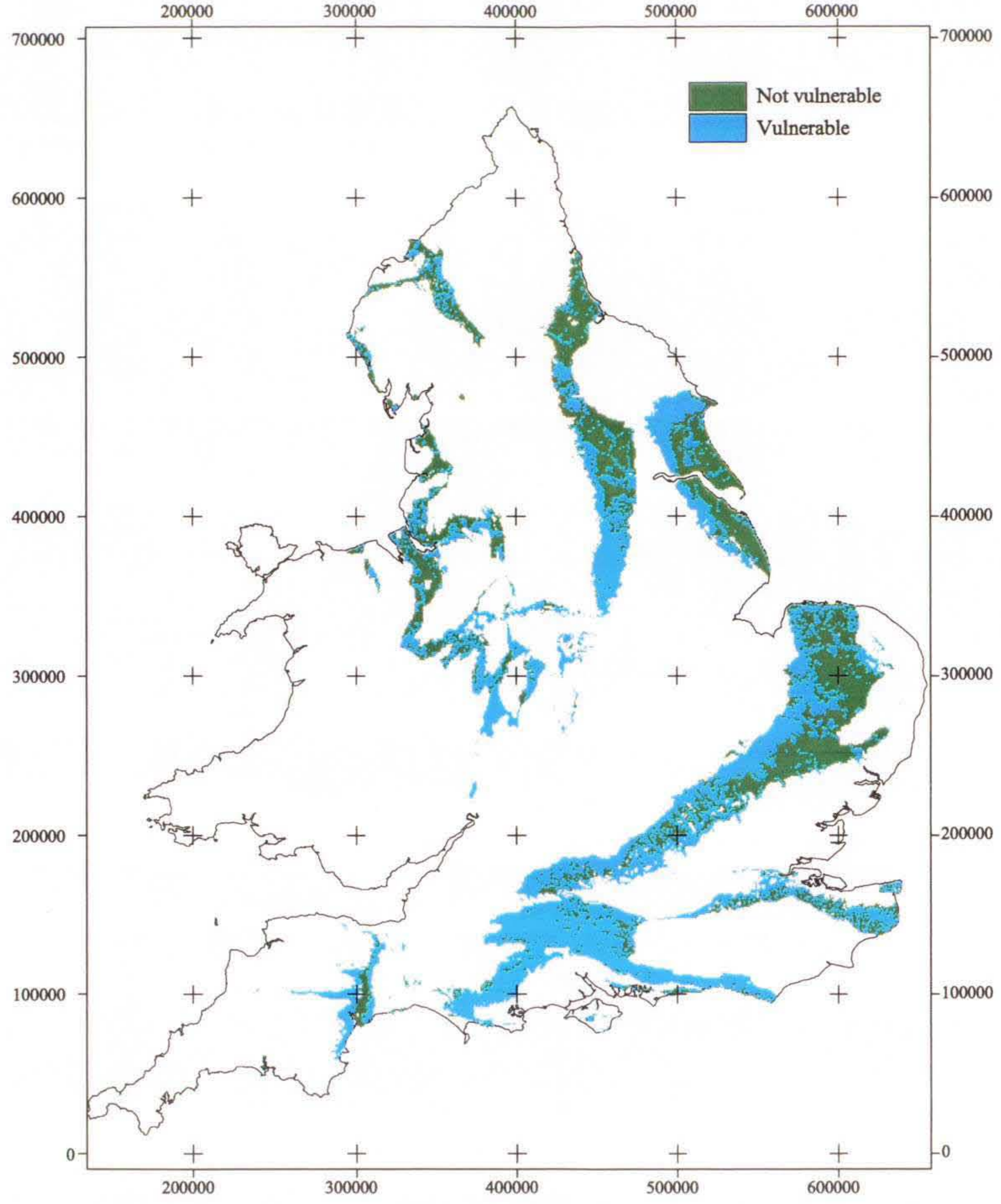
Although the modelling studies indicate that the flux of water through the base of a slurry pit is not principally a reflection of the climate, but of the mean depth of slurry, there nevertheless remains a climatic constraint on the vulnerable areas – as these are located in the higher rainfall areas, where livestock production is more important than in the drier east.

In all cases the thickness of the unsaturated zone has not been taken into account. In general, unsaturated zones in the Chalk are much thicker than those in the sandstone although the depth to water can vary considerably over a given catchment so lagoon siting would need to be carefully assessed for each site. Where a thin unsaturated zone exists the potential risk to groundwater is greater than for a thicker unsaturated zone since direct hydraulic connectivity between the base of the lagoon and the water table is more likely to be made. For pathogens which might have relatively short lifespans in the subsurface this could be of great significance since transit times from lagoon to well would be greatly reduced.



Geological linework is © NERC

Figure 7.1 Chalk or Permo-Triassic sandstones covered by areas of soils belonging to the vulnerable and non-vulnerable HOST soil classes



Geological linework is © NERC

Figure 7.2 **Chalk or Permo-Triassic sandstones covered by areas of impermeable drift and areas where the drift is permeable drift or does not exist.**

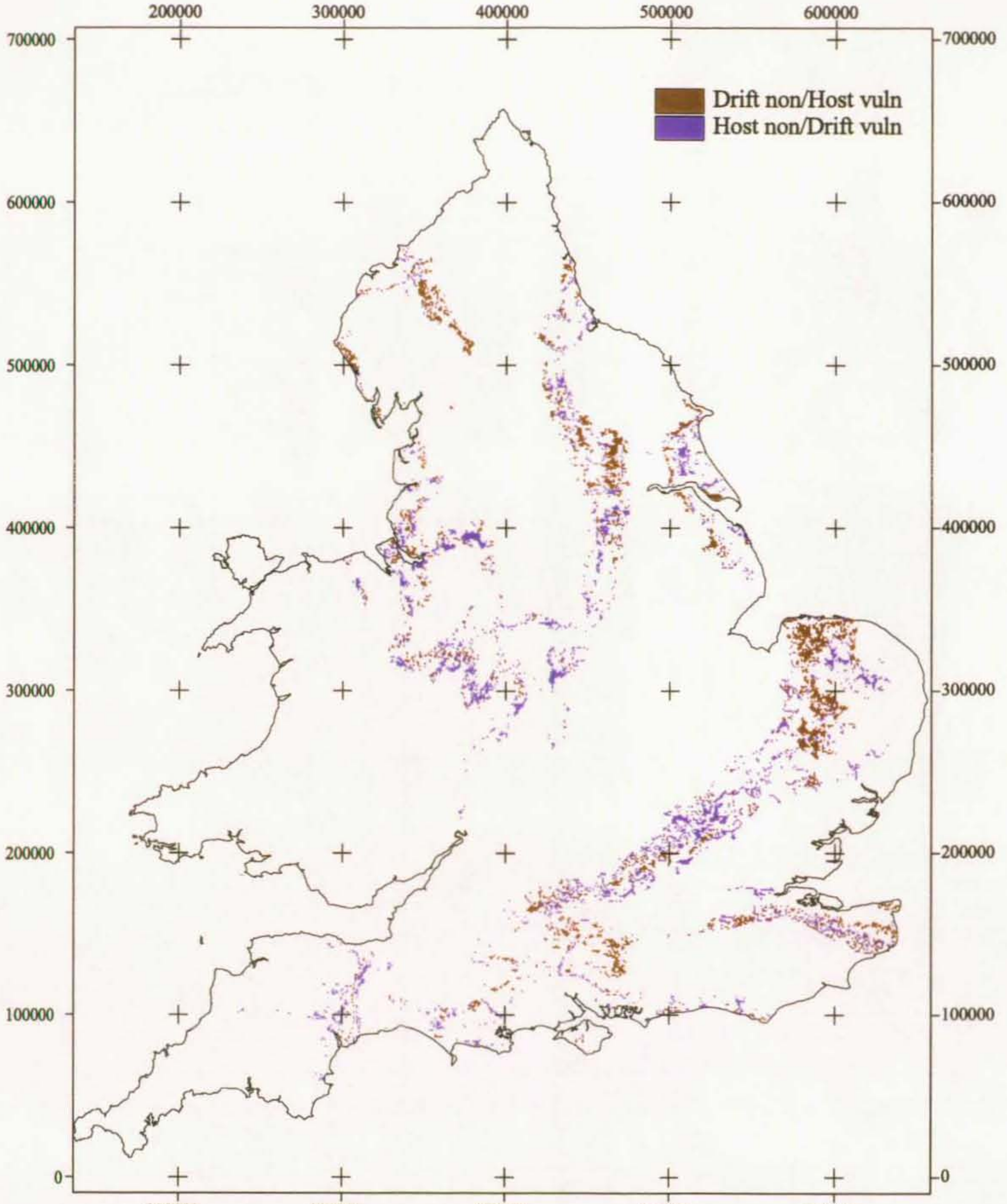
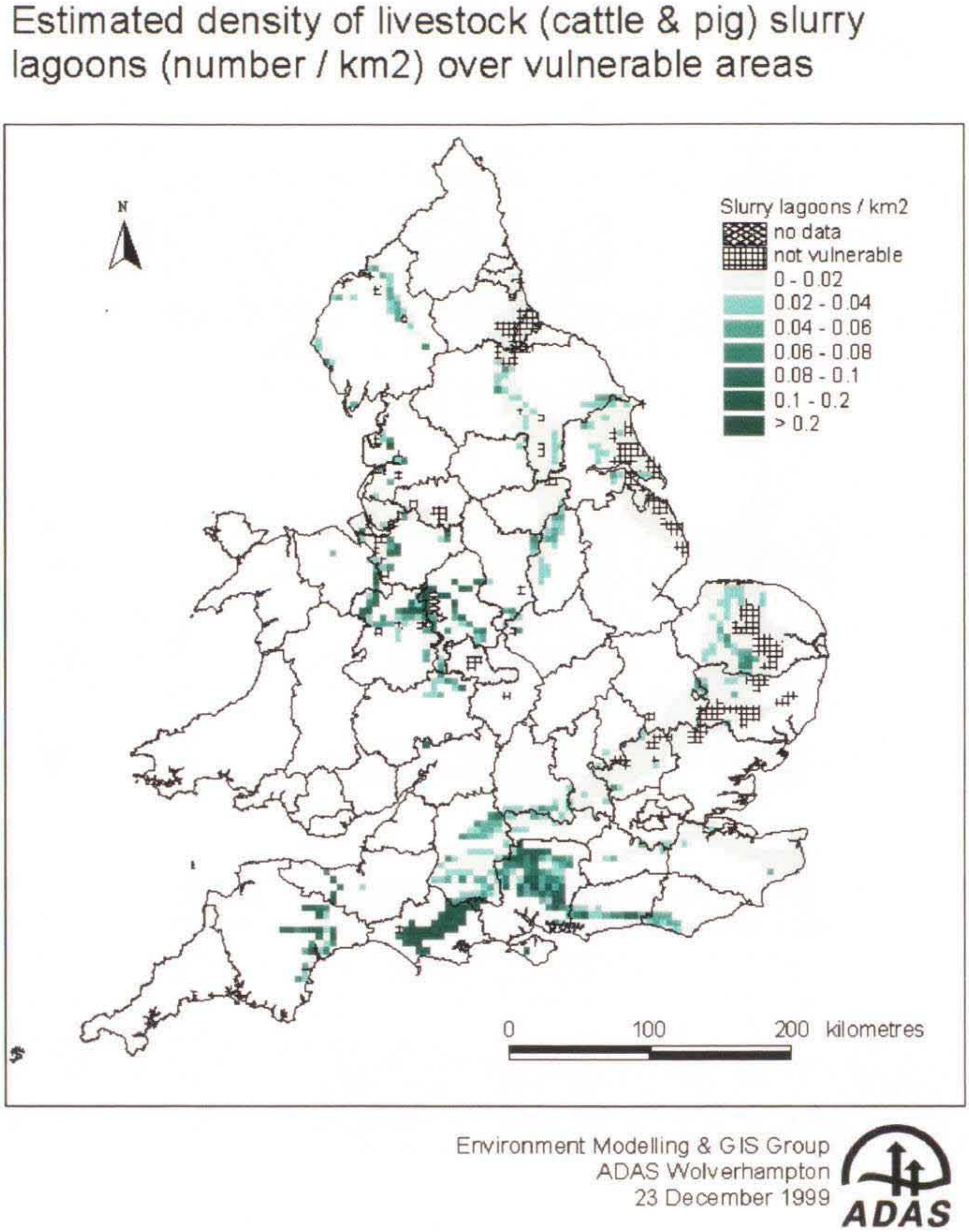


Figure 7.3 Difference map showing areas of discrepancies between the HOST and drift approaches



Estimated density of livestock (cattle & pig) slurry lagoons (number / km2) over vulnerable areas

Agricultural data adapted from the 1995 Parish Summaries of the Agricultural Census for England and Wales.
Crown Copyright. Reproduced by permission of the Controller of Her Majesty's Stationery Office.
Dataset provided by Edinburgh University Data Library.

Aquifer data provided by British Geological Survey.

Soil series data provided by Soil Survey and Land Research Centre.

Figure 7.4 **Estimated density of slurry stores over vulnerable areas based on HOST classification**

7.3 Summary

Vulnerability of UK aquifers has been assessed through using data from the HOST classification of soils and overlying this with data for Chalk and Permo-Triassic Sandstone aquifer coverage in England and Wales. This has been compared with an assessment using the same aquifer data with geological drift coverage. Some differences between the two approaches are observed. To assess the risk to these aquifers from farm waste stores, a further layer has been added with data relating to farm waste store density. Areas of highest farm waste store density over the most vulnerable aquifers can therefore be observed. The main areas of concern highlighted are the Chalk outcrop of Dorset, and more locally over the Permo-Triassic Sandstone in the West Midlands. Depth to water table was not considered in the risk analysis but may be of particular significance for pathogen transport.

8. CONCLUSIONS AND RECOMMENDATIONS

This three year study has focused on the impacts of earth-banked slurry stores which are unlined and overlying the two principal aquifers in the UK, the Chalk and Permo-Triassic Sandstone. Stores thus situated are generally accepted as the farm waste facilities most likely to pose a threat to groundwater quality. Few resources have been directed at solid manure heaps and these are not governed by regulations in the same way as unlined slurry lagoons. However, it is felt that the risk of solid heaps to groundwater is minimal due to the relative impermeability and high dry matter content of the manure. Further work would need to be undertaken to fully assess this impermeability and its likely impact on subsurface processes.

Results from field studies and contaminant modelling suggest that under the majority of situations, unlined slurry stores pose little threat to potable groundwater drinking supplies. The farm waste store represents a relatively small point source of contamination in the very large water body of a groundwater catchment. However, the potential for contamination of a farm borehole is much greater than that of a public drinking supply, and siting of wells for drinking and other agricultural purposes should be up groundwater gradient from the lagoon source. Public supply wells should not be sited in the near vicinity of a farm waste store. Contaminant modelling has also shown that discontinuing use of an unlined farm waste store will make little difference to the increase in a given solutes' concentration over the short to medium term. Therefore closing down an unlined farm waste store may not palliate the relatively small pollution threat.

The self-sealing of unlined slurry and manure stores by solids present in the leachate is seen as a crucial step in minimising leakage and consequently groundwater contamination. It is important for unlined facilities that good practice is carried out during emptying so that any seal is not broken. Where it appears a seal has formed, early on in the lifetime of a slurry store, sufficient oxygen is present in the unsaturated zone of the aquifer to allow the oxidation of ammonia to nitrate and the efficient oxidation of organic carbon. Where a store fails to seal or the seal is poor, the ammonia remains unoxidised and migrates in this form. Field data tend to suggest that stores do not form such good seals on the side walls and some seepage is able to occur through this route.

At the Chalk sites where a good seal is believed to have occurred, subsurface environmental conditions are suitable for denitrification to occur with the subsequent removal of a large component of the nitrate. The nitrate loading to groundwater is therefore considerably reduced although further detailed study would be required to more accurately determine denitrification rates. Where no seal or a poor seal has formed, conditions become increasing reducing with high concentrations of organic carbon and ammonia persisting. At the Chalk sites, the geochemical reactions taking place can often be buffered by the calcium carbonate based Chalk matrix. However, in many sandstones little calcium carbonate is present, leading to a lowering in pH as ammonia is oxidised. This combined with a reducing environment can lead to the mobilisation of metals present in the sandstone matrix.

Although some microorganisms were detected in the unsaturated zone beneath many of the stores investigated, none of these were pathogens, although pathogens were found to be present in the slurry lagoons themselves. This is an encouraging finding although should be taken in the context that this is a small subsample of the number of unlined slurry lagoons nationally.

The field studies provided evidence for slurry movement along fractures in the Chalk. Dark staining along fracture faces were observed to depths of at least 15 m below ground level. The age of the slurry on these fractures was not determined and so it is unclear as to whether or not this is an artefact of a lagoons' inception and these fractures are indeed effectively sealed, or represents a continual source of raw slurry throughout the unsaturated zone and beyond. This is another issue which requires further work to resolve.

Consideration of the nitrate concentrations in the leachate from the stores leads to the conclusion that this poses little additional risk to the quality of abstracted water, unless the abstraction is small and is in the immediate vicinity of the store. Modelling studies using a worst-case scenario estimate a 0.5 mg/L rise in nitrate-nitrogen concentration in groundwaters within a catchment containing a farm waste store. In the context of the much larger short term variations in nitrate concentrations this is considered not to be significant. Discontinuing the use of old stores which may be leaking has a negligible effect on predicted nitrate concentrations.

It has been identified that groundwater is most at risk where the water table is shallow. In this case there could be direct hydraulic connectivity between the lagoon base and the water table which would considerably reduce the travel times for contaminants to reach groundwater and thence potable water supplies. This is of greatest significance for pathogens which are thought to be relatively short lived in the subsurface. It is therefore deduced that the highest risk category for an unlined farm waste store would be in an area where the Chalk aquifer has no drift and the water table is shallow.

In summary:

- The project has focused on unlined cattle slurry lagoons and the Chalk and Permo-Triassic Sandstone aquifers
- Unlined lagoons pose minimal threat of contamination to public water supplies where abstraction wells are not in the immediate vicinity . Farm boreholes may be more vulnerable
- There is a low risk from solid manures (although more work needs to be done on this) with rates of solute transport much slower
- No pathogens were found in the cores taken from beneath 3 Chalk Sites and 5 Sandstone Sites studied although they were present in the lagoon slurry
- Good practice should be followed in filling and emptying unlined lagoons to avoid disrupting the sealing bottom layer
- Very high concentrations of nitrate, ammonia and organic carbon were measured in the porewaters under 2 sites on the Chalk and 1 site on the Permo-Triassic Sandstone
- Denitrification is a major process that, under appropriate conditions, has been observed to substantially reduced nitrate concentrations in porewaters
- Modelling studies estimate a 0.5 mg/L rise in nitrate-nitrogen concentration in groundwaters within a catchment containing a farm waste store
- Discontinuing the use of old stores which may be leaking has a negligible effect on predicted nitrate concentrations. Control of Pollution Regulations should ensure that recently constructed stores are safe
- The physical and chemical properties of the aquifer can influence contaminant movement and attenuation both in terms of the degree of fracturing and the geochemical reactions that can take place
- Groundwater would be at greatest risk of contamination from cattle slurry in areas where dairy farming is widespread, there is little drift or soil cover, and the water table is shallow

9. 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 the major aquifers in England and Wales. British Geological Survey Technical Report WD/97/34

Barker J A 1982. Laplace transform solutions for solute transport in fissured aquifers. *Advances in Water Resources* 5, 98-104

Barrington S F, Jutras P J and Broughton R S 1987. The sealing of soils by manure. I. Preliminary investigations. *Canadian Agricultural Engineering,* 29, 2, 99-103

Barrington S F, Denis J and Patni N K 1991. Leakage from two concrete manure tanks. *Canadian Agricultural Engineering*, 33, 1, 137-141.

Bell D F, McDonald A M, Morris B L and Lilly A 1997. Scotlands Minor Aquifers: A Scoping Study to Assess Groundwater Source Protection. BGS Technical Report WD/97/63.

Boorman D B, Hollis J M and Lilly A 1995. Hydrology of soil types: a hydrologically-based classification of the soils of the United Kingdom. Report No 126, Institute of Hydrology, Wallingford, UK, 137 pp.

Chilton P J, Williams A T, Marks R J, Buckley D K, Coleby L M, Gibbs B R and Bird M J 1997. Trends in nitrate concentrations in the Yorkshire Chalk aquifer. British Geological Survey Report WD/97/8C.

Chilton P J, Williams A T, Marks R J Smedley P L, Buckley D K and Merrin P D 1999. Groundwater nitrate concentrations in the Sherwood sandstone aquifer of South Yorkshire. British Geological Survey Report WD/99/38C.

Cho J-C and Kim S-J 2000. Increase in bacterial community diversity in subsurface aquifers receiving livestock wastewater input. *Applied and Environmental Microbiology*, 66, 3, 956-965.

Ciravalo T G 1979. Pollutant movement to shallow ground water tables from anaerobic swine waste lagoons. *Journal of Environmental Quality*, 8, 126-130.

Control of Pollution (Silage, Slurry and Agricultural Fuel Oil) Regulations 1991. S1 1991 No 324. HMSO (ISBN 0 11 133242).

Culley J L B and Phillips P A 1989. Groundwater quality beneath small-scale, unlined earthen manure storages. Transactions of the American Society of Agricultural Engineers, 32, 1443-1448.

Darling W G, Kinniburgh D G and Gooddy D C 1997. Gas compositions and processes in the unsaturated zone of the Chalk and Triassic Sandstone aquifers, England. In 'Isotope techniques in the Study of Environmental Change'. Proceedings IAEA Symposium, 14-18 April 1997, 265-274.

DETR 1997. Digest of Environmental Statistics. Department of the Environment, Transport and the Regions. London: TSO.

Edmunds W M, Cook J M, Kinniburgh D G, Miles D L and Trafford J M 1989. Trace element occurrence in British Groundwaters. British Geological Survey Research Report SD/89/3.

Farm Waste Storage - Guidelines for Construction 1992. CIRIA Report 126. Construction Industry Research and Information Association, London.

Feast N A, Hiscock K M, Dennis P F and Bottrell S H 1997. Controls on stable isotope profiles in the Chalk aquifer of north-east Norfolk, UK, with special reference to dissolved sulphate. *Applied Geochemistry*, 12, 803-812.

Fetter C W 1994. Applied hydrogeology (3rd ed). Prentice-Hall, Inc.

Gooddy D C, Shand P, Kinniburgh D G and Van Riemsdijk W H 1995. Field-based partition coefficients for trace elements in soil solutions. *European Journal of Soil Science*, 46, 265-285.

Gooddy D C, Withers P J A, McDonald H G and Chilton P J 1998a. Behaviour and impact of cow slurry beneath a storage lagoon: II. Chemical composition of chalk porewater after 18 years. *Water, Air and Soil Pollution*, 107, 51-72.

Gooddy D C, Armstrong A C, Williams J R, Moore A, Chilton P J, Bird M J and Williams A T 1998b. Impact of farm waste stores on groundwater quality: First annual report April 1997-March 1998. British Geological Survey Technical Report WD/98/32.

Gooddy D C, Bird M J, Williams P J, Armstrong A C, Williams J R and Chilton P J 1999. Impact of farm waste stores on groundwater quality: Second annual report 1998-1999. British Geological Survey Technical Report WD/99/34.

Hancock D D, Besser T E, Kinsel M L, Tarr P I, Rice D H and Paros M G 1994. The prevalence of *Escherichia coli* O157:H7 in dairy and beef cattle in Washington State. Epidemiology and Infection, 113, 199-207.

Harvey R W, Kinner N E, Bunn A, MacDonald D and Metge D 1995. Transport behaviour in groundwater protozoa and protozoan sized microspheres in sandy aquifer sediments. *Applied and Environmental Microbiology*, 61, 1, 209-217.

Inskeep W P and Bloom P R 1986. Kinetics of calcite precipitation in the presence of water-soluble organic-ligands. *Soil Society of America Journal*, 50, 5, 1167-1172.

Jenkins M B, Bowman D D and Ghiorse W C 1998. Inactivation of *Cryptosporidium parvum* oocysts by ammonia. *Applied and Environmental Microbiology*, 64, 2, 784-788.

Jones D L 1999. Potential health risks associated with the persistence of *Eschericia coli* O157 in agricultural environments. *Soil Use and Management*, 15, 76-83.

Kanazawa K, Miyaji N, Kusaba T, Ban K, Hayakawa Y and Hatano R 1999. Groundwater pollution by cattle slurry stored in unlined lagoon. *Japan Agriculture Research Quarterly*, 33, 1, 7-13.

Kinniburgh D G, Gale I N, Gooddy D C, Darling W G, Marks R J, Gibbs B R, Coleby L M, Bird M J and West J M 1999. Denitrification in the unsaturated zones of the British Chalk and Sherwood Sandstone aquifers. British Geological Survey Technical Report WD/99/2.

Kinniburgh D G and Miles D L 1983. Extraction and chemical analysis of interstitial water from soils and rocks. *Environmental Science and Technology*, 17, 362-368.

Kudva I T, Blanch K and Hovde C J 1998. Analysis of *Escherichia coli* O157:H7 survival in ovine or bovine manure and munure slurry. *Applied and Environmental Microbiology*, 64, 9, 3166-3174.

MAFF 1998 Code of Good Agricultural Practice for the Protection of Water (The Water Code). Ministry of Agriculture, Fisheries and Food. London, UK.

McDonald M G and Harbaugh A W 1988. A modular three-dimensional finite-difference ground-water flow model. USGS TWRI Chapter 6-A1, 586pp.

Miller M H, Robinson J B and Gillham R W 1985. Self-sealing earthen liquid manure storage ponds:I. A case study. *Journal of Environmental Quality*, 14, 4, 533-538.

Mariotti A, Landreau A and Simon B 1988. 15N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. *Geochimica et Cosmochimica Acta*, 52, 1869-1878.

National Rivers Authority 1992. Policy and Practice for the Protection of Groundwater. Bristol:NRA.

National Rivers Authority/Environment Agency, 1994 to 1998. Policy and practice for the protection of groundwater: Groundwater vulnerability 1:100 000 series, Maps 1 to 53.

Nicholson R J and Brewer A J 1997. Estimates of volumes and exposed surface areas of stored animal manures and slurries in England and Wales. *Journal of Agricultural Engineering Research*, 66, 4, 239-250

Oliver J O, Fairbank W C, Meyer J L and Rible J M 1974. Subfloor monitoring of Shady Grove liquid manure holding pond. *Californian Agriculture*, 28, 4, 6-7.

Owens, J. (no date) Site compliance criteria for earth banked slurry stores. ADAS Final report on MAFF Experiment WA 0502, ADAS Bridgets.

Pollock D W 1989. Documentation of computer programs to compute and display pathlines using results from the U S Geological Survey modular three-dimensional finite-difference gound-water flow model. USGS Open File Report 89-391, 188pp

Ritter W H and Chirnside A E M 1983. Influence of animal waste lagoons on ground-water quality. *American Society of Agricultural Engineers*, paper 83-4573, 34pp.

Robinson F E 1973. Changes in seepage rate from an unlined cattle waste digestion pond. *Transactions of the American Society of Agricultural Engineers*, 16, 95-96.

Rowsell J G, Miller M H and Groenevelt P H 1985. Self sealing of earthen liquid manure storage ponds: II. Rate and mechanism of sealing. *Journal of Environmental Quality*, 14, 4, 539-543.

Sewell J I, Mullins J A and Vaigneur H O 1975. Dairy lagoon system and groundwater quality. In 'Managing livestock wastes', pp286-288. Proceedings of the Third International Symposium on Livestock Wastes, Urbana-Champaign, IL. 21-24 April 1975. American Society of Agricultural Engineers, St. Joseph, MI.

Spalding R F and Parrott J D 1994. Shallow groundwater denitrification. *Science of the Total Environment*, 141, 17-25.

Strebel O, Bottcher J and Fritz P 1990. Use of isotopic fractionation of sulphate-sulphur and sulphate oxygen to assess bacterial desulphurication in a sandy aquifer. *Journal of Hydrology*, 121, 155-172.

Tiedje J M 1982. Denitrification. In 'Methods of Soil Analysis', A L Page, R H Miller and D R Keeney (eds.), pp1011-1026. American Society of Agronomy and Soil Science Society of America, Madison.

Williams A T, Hughes A G, Armstrong A C and Griffiths K J 2000. Details of the Numerical Modelling Work Undertaken to Study the Impact of Farm Waste Stores on Groundwater Quality. British Geological Survey Technical Report WD/00/13.

Withers P J A, McDonald H G, Smith K A and Chumbley C G 1998. Behaviour and impact of cow slurry beneath a storage lagoon: I. Groundwater contamination 1975 – 1982. *Water, Air and Soil Pollution*. 107, 35-49.

Zielinski R A, Simmons K R and Orem W H 2000. Use of 234U and 238U isotopes to identify fertilizer derived uranium in the Florida Everglades. *Applied Geochemistry*, 15, 3, 369-385.

WD/00/09