

Redox-driven changes in porewater chemistry in the unsaturated zone of the chalk aquifer beneath unlined cattle slurry lagoons

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Abstract

Farm waste stores such as cattle slurry lagoons are widespread in the UK and many overly important aquifers. Stores can be serious risks to water quality because they are important sources of nitrogen species, organic carbon and pathogenic microbes. At two sites on the Chalk aquifer of southern England, inclined boreholes were drilled and cored to obtain aquifer material from directly beneath unlined slurry stores. Vertical boreholes were also drilled adjacent to the slurry stores to determine any lateral movement of contaminants. Interstitial porewaters were analysed for major and minor ions and sulphur isotopes. At the second site, unsaturated zone gases were sampled from the inclined hole. Infiltration of slurry into the unsaturated zone caused significantly elevated concentrations of metals such as copper and nickel at both sites. Sulphate reduction was occurring at Site 1, as evidenced by sulphate concentrations decreasing from 150 mg/L to 50 mg/L and enhanced ratios of $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$. Ammonium-N also leaches along with dissolved organic carbon which were found 17 m below ground surface at concentrations up to 400 mg/L and 260 mg/L respectively. Contaminant concentrations were similar in the porewaters from both the inclined and vertical boreholes. At Site 2, higher contaminant concentrations were found in the inclined borehole compared with the vertical borehole. Organic carbon concentrations were considerably lower than at Site 1, ranging from 10-70 mg/l. Ammonium-N concentrations reached a maximum concentration of 25 mg/l, however nitrate-N concentrations were up to 500 mg/L and sulphate concentrations were generally higher than Site 1. Data for N_2/Ar and $\delta^{15}\text{N-N}_2$ from the gas samplers show a peak of 102 and 2.2‰ respectively at 14 m below ground level indicating denitrification was taking place. Evidence from $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ suggest that some sulphate reduction was taking place simultaneously. From methane and ammonia detected at depth it is suggested that slurry contamination, emanating from early use of the store, has passed through the top 18 m of the unsaturated zone at Site 2. The presence of high concentrations of nitrate and lower concentrations of organic carbon suggests that this lagoon has formed a relatively impermeable seal at its base within the first few years of its lifetime. The anoxic conditions at both sites may have mobilised uranium from nitrogen-phosphate-potassium fertilisers. Both sites are continuing to impact on the porewater chemistry and pose a risk of groundwater contamination.

1. INTRODUCTION

Groundwater provides over 30% of all water abstracted in England and Wales and accounts for more than 80% of the total public supply in south-east England. Both industry and agriculture rely on groundwater in many areas and it is the predominant source for private water supplies. The Chalk is

the major United Kingdom (UK) aquifer and its groundwater flow regime is well documented (Price, 1987). The Chalk is a soft microporous fractured limestone and has three components of porosity and permeability: 1) the Chalk has high intergranular porosity (25-45%) but only low intergranular permeability from pore-neck sizes of less than 1 μ m (Price et al., 1976); 2) joint components that have low porosity (0.1-1%) but depending on frequency, can increase the hydraulic conductivity by two or three orders of magnitude; 3) fissures that result from the solution and enlargement of joints can account for the bulk of flow in the saturated zone.

Although storage of livestock manure can present a serious potential risk of surface water pollution, there has not been the same concern about potential pollution to groundwater possibly because of the greater dilution and less immediate impact expected in groundwater systems (Goody et al., 2001). The majority of livestock slurry storage structures generally only pose a risk of water pollution because of structural or operator failure. Only in the case of unlined earth-based slurry lagoons, which were unregulated before 1991, and field heaps of solid manure, is there risk that pollutants can leach to groundwater (Withers et al. 1998; Goody 2002). There are about 10,000 earth-based slurry lagoons constructed prior to 1991 in England and Wales (Nicholson & Brewer 1997) many of which could be overlying aquifers.

There is conflicting evidence with regard to the risks from unlined cattle slurry lagoons (Kanazawa et al., 1999; Ritter and Chirnside, 1983). Monitoring around large-scale structures (Miller et al., 1984; Rowsell et al., 1985) in Canada has shown no adverse effects on groundwater, even when constructed on sandy material. The self-sealing effects of slurry at the lagoon base is believed to be the mechanism that protects the underlying unsaturated zone. Monitoring of slurry constituents in groundwater beneath lagoons in the United States has shown that the infiltration rate of lagoon contents decreases with time (Oliver et al., 1974; Robinson, 1973; Sewell et al. 1975; and Barrington et al., 1983), although there is little consensus as to the rate or degree of this decrease. In the UK, data from a single site on the Chalk of south-east England indicated that the organic-carbon-rich slurry and its constituents had leached from the bottom of recently decommissioned unlined slurry lagoon and contaminated an observation well sited 80 m down groundwater gradient (Goody et al. 1998; Withers et al., 1998). Similarly, a study from Japan (Kanazawa et al., 1999) showed evidence of groundwater pollution 75 m away from an unlined slurry lagoon just 4 days after the lagoon was first filled.

1.1 Biochemical Redox Processes and Calcite Dissolution

Decay of organic matter in cattle slurry occurs in the chalk matrix via aerobic and anaerobic respiration. The distinction between these processes is important in that they proceed along of decreasing energy efficiency with declining rates of organic matter decay.

Organic matter is primarily degraded by oxidation reactions (the removal of electrons) mediated by bacteria that derive energy in the process. During bacterially mediated oxidation, proteins in the slurry break down into their constituent amino acids, which contain both nitrogen and sulphur compounds. These compounds are ultimately broken down into inorganic species such as ammonia, nitrate, and sulphate and cations such as sodium and potassium. This form of oxidation is predominantly via dissimilative metabolism by chemoheterotrophic bacteria that can utilise a range of potential Terminal Electron Acceptors (TEAs) in the reaction. The range of TEA species are characterised by differences in their energy yield. Aerobic respiration is the most energy productive process and is followed by anaerobic respiration processes that yield successively less energy; the order of energy yield on reduction is $\text{NO}_3^- > \text{Mn}^{4+} > \text{Fe}^{3+} > \text{SO}_4^{2-} > \text{CO}_2$. The reactants and products from these reactions are commonly used to define identifiable geochemical zones that can be used to identify the thermodynamic TEA progression (Lawrence et al., 2000).

Chalk in the UK contains more than 99% CaCO_3 (Murphy, 1998). The matrix content of redox sensitive elements such as Fe^{2+} and Mn^{4+} is very low, (<0.05%) and therefore they are unlikely to participate in any redox related reactions. Reactions 1-4 demonstrate that in a calcium carbonate

environment, redox reactions all result in the production of HCO_3^- and or CO_2 . The relative contribution of HCO_3^- or CO_2 results from hydrogen ion concentration of the porewater and the interplay between aerobic and anaerobic respiration processes. In an aerobic environment calcite will be dissolved but in aerobic environments calcite is precipitated.



Oxidation (aerobic respiration)



Bacterial Nitrate Reduction (denitrification)



Bacterial Sulphate Reduction



1.2 Sulphate Stable Isotopes

Stable isotopes help understand redox processes by elucidating both reduction and re-oxidation of TEA species. Re-oxidation of TEA cannot be determined by chemical data alone because only net reduction can be determined. The fractionation of $^{18}\text{O}/^{16}\text{O}$ and $^{34}\text{S}/^{32}\text{S}$ can be used to identify bacterial sulphate reduction (BSR) and subsequently re-oxidation of the reduction products. Sulphur is a useful isotopic indicator because it is present in cattle slurry and can exist in a wide range of oxidation states.

During BSR the light ^{32}S isotope is preferentially metabolised due to its weaker bond strength, producing a kinetic isotopic fractionation (Nakai and Jensen 1964). As ^{32}S reacts more quickly to form hydrogen sulphide there is an enrichment of ^{34}S in the remaining sulphate. BSR also causes exchange of oxygen isotopes between sulphate and water, resulting in enrichment of ^{18}O in remaining sulphate (Fritz et al. 1989). Reoxidation of sulphide can form new sulphate with an oxygen isotopic composition distinct from that of the original sulphate and thus provide an isotopic tracer for this process.

1.3 Determining denitrification in the unsaturated zone using N_2O , N isotopes and N_2/Ar

Denitrification occurs under anaerobic conditions when nitrate is used as a TEA leading to the stepwise production of nitrogen with nitric oxide and nitrous oxide as gaseous intermediate products (5).



Detection of nitrous oxide should therefore be a good indicator that denitrification is taking place. However, nitrous oxide can also be produced under aerobic conditions as an intermediate product during the oxidation of ammonia in nitrification (6-8), therefore detection on its own cannot provide unequivocal evidence for denitrification.



During denitrification, the nitrate that remains becomes progressively enriched in ^{15}N because ^{14}N is concentrated in the gas phase. Under closed conditions there is an exponential increase in $\delta^{15}\text{N}$ 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. Other processes, such as volatilisation of ammonia, also result in the preferential loss of ^{14}N and therefore ultimately in ^{15}N rich residual nitrate-N.

Since the end product of denitrification is nitrogen gas, an obvious way of detecting denitrification is

by measuring the evolved nitrogen. However, due to the very high atmospheric concentration measuring an excess of nitrogen is problematic. It is possible to correct for this problem by high precision measurement of N_2/Ar ratios. In atmospheric air this ratio is fixed at 83.6 and any increase in nitrogen due to denitrification will increase in the ratio (Darling et al., 1997).

By combining these methods it should be possible to obtain unequivocal evidence for denitrification in the unsaturated zone even in an environment that contains very high concentrations of ammonia such as a farm waste store.

2. SITE DESCRIPTIONS

2.1 Site 1

Site 1 is situated about 5 km from Salisbury, Wiltshire, UK (exact location withheld for farmer confidentiality). Slurry is stored in a pit roughly 15 m long, 6 m wide and 2 m deep. The pit is flush to ground level and was constructed in 1978 (Figure 1).

The farm is situated on the Upper Chalk high above a river valley and so is missing any possible alluvium or gravel sequences. A borehole situated on the farm, drilled in 1973, provides water for the cattle and for washing the milking sheds. The log for this borehole states that the top 10 metres of drilling was into Pebble Beds. Drilling carried out in 1997 as part of the current study revealed pebbles occurred down as far as 7 metres below ground level (m bgl). The water table was measured at the farm borehole in 1973 as 44 m bgl. The farm has a herd of roughly 160 dairy cows.

2.2 Site 2

Site 2 is situated about 8 km from Salisbury, Wiltshire, UK (exact location withheld for farmer confidentiality). Slurry is stored in a pit roughly 20 m long, 8 m wide and 2.5 m deep. Solid and liquid wastes are disposed of together in the same lagoon. The lagoon is earth walled and constructed on a hill. It has been built up to counter the incline, reaching a height of roughly 4 m above ground level at its southerly end (Figure 2a). The lagoon was constructed in 1983.

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 therefore free of the gravel layer. By extrapolation between boreholes at the top and bottom of the hill, the water table is estimated to be between 35 and 40 m bgl. The farm has a herd of roughly 200 dairy cows

3. METHODS

3.1 Borehole Construction

As the slurry stores were still active, it was necessary to construct inclined boreholes (at an angle of 45°) so as to obtain chalk core from directly underneath the lagoon. Continuous core was obtained throughout the unsaturated zone by rotary coring. In addition to the inclined holes, vertical holes were drilled adjacent to the lagoons to identify whether or not there was any lateral movement of slurry components. The inclined holes were drilled to a depth below ground level of 17 metres and 18.4 metres respectively for Sites 1 and 2. The vertical holes were both drilled to a depth of 15 m bgl. Boreholes at Site 1 were constructed at the opposite end of the lagoon to the farm sheds where the herd is housed and milked. The inclined borehole at Site 2 was angled so as to sample from beneath the entire width of the slurry lagoon. After construction of the inclined hole at Site 2, 6 specially designed gas samplers were installed at discrete depths throughout (see 3.4). Boreholes were only drilled in the unsaturated zone to avoid direct contamination of the saturated zone from the slurry lagoons.

3.2 Unsaturated Zone Porewater Extraction and Chemical Analysis

Porewater was extracted from the cored material by the high speed centrifuge 'drainage' method (Edmunds and Bath, 1976). Briefly, core crushed in a polythene bag to fragments of roughly 5 mm diameter are placed into the buckets of a fixed angle rotor refrigerated centrifuge. Delrin liners with collection cups and pre-filters hold the rock fragments in the centrifuge rotor. The samples are centrifuged at 14000 rpm for 35 minutes. The supernatant porewater is then split into three fractions; one filtered and acidified for cations; a second filtered and unacidified for anions; and a third unfiltered and unacidified for dissolved organic carbon. Typically a minimum of 30 ml of extracted porewater was required to carry out all the chemical measurements required.

Filtered acidified porewaters are analysed using an ARL 34000C Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) which is calibrated for the following 16 elements: Na, K, Ca, Mg, B, Ba, Li, P_{total}, SO₄, Si, Sr, Be, Ba, Y, Fe_{total} and Al. All analyses are blank corrected and detection limits defined as 6 times the standard deviation of the blank.

Filtered acidified samples from each borehole were also analysed for Mn, Mo, Cr, Co, Ni, Cu, Zn, Cd, Rb, Pb and U, using a VG Plasma Quad Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Internal standards of In and Pt (at 50 µg L⁻¹) are used to compensate for instrument drift and matrix effects caused by the relatively high total dissolved solids (TDS) likely in some of the samples. Calibration is carried out for each element using aqueous standards in the range 1-100 µg 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 Goody et al. (1995).

The filtered unacidified water fraction is analysed for Nitrate-nitrogen (NO₃-N), ammonium-nitrogen (NH₄-N), molybdate-reactive phosphorus (MRP) and Cl using standard Auto Analyser II colorimetric methods (Kinniburgh and Miles, 1983). Organic phosphate is assumed to be the difference between total phosphate and molybdate-reacting phosphate (MRP). To overcome interference problems with the yellow/brown colour of some of the porewaters, samples are run with and without the colour reagent for Cl analysis and the difference between the two taken as the actual concentration. NO₃-N is determined by the cadmium column reduction method since the high organic carbon content of the samples caused suppression of the baseline when the hydrazine/copper reduction method was used. pH is measured with a glass micro electrode and bicarbonate (HCO₃) 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.

3.3 Sulphur and Oxygen Isotopes

Sulphate from filtered acidified porewaters was precipitated as BaSO₄ for gravimetric and isotopic analysis on SO₂ prepared by the method of Halas et al. (1982). As concentrations of sulphate were low, several samples from a composite depth range were required to provide sufficient water for the isotopic analysis. Consequently the resolution of this data is poor relative to the other porewater data.

Samples of raw cattle slurry were collected from the storage lagoons at each farm. Three separate aliquots of each sample were treated to extract total sulphur, inorganic sulphate and inorganic sulphides. Organically bound sulphur was calculated by difference.

Sulphate extraction from slurry was done with a dilute nitric acid leach under a nitrogen atmosphere (Louie et al., 1995; Poulton et al., 1996) and precipitated as BaSO₄ for gravimetric and isotope analysis. Reduced inorganic sulphur was determined by a modified chromous chloride reduction method (Newton et al 1995). This method reacts chromous chloride with inorganic sulphides in the sample to form hydrogen sulphide which is then trapped as a copper sulphide precipitate (CuS) for isotopic analysis. The residual copper chloride was then back titrated with EDTA to determine the amount of inorganic sulphur present in the samples. Total sulphur was obtained by chemical oxidation

of all sulphur species with a hot mixture of nitric acid, brominated water and potassium chlorate and subsequent precipitation as BaSO₄ for gravimetric and isotope analysis.

Sulphate-oxygen isotopic compositions were determined by reduction with graphite in an induction furnace at approximately 1000°C to produce CO₂ and CO. Carbon monoxide was then disproportionated to CO₂ by sparking of platinum electrodes in a discharge bulb. A residual of BaSO₄ within the furnace crucible was reacted with silver nitrate to produce silver sulphide precipitates. These were combusted with CuO₂ to yield SO₂ for isotopic analysis.

Sample gases were cryogenically purified and analysed on a VG SIRA 10 Mass Spectrometer. Results are reported in standard delta (δ) notation as parts per thousand deviations relative to the international standards Canyon Diablo Troilite (V-CDT) for sulphur and Standard Mean Ocean Water (V-SMOW) for oxygen. Accuracy of the isotopic analysis determined from analysis of standards is $\pm 0.4\%$ for $\delta^{18}\text{O}$ and $\pm 0.2\%$ for $\delta^{34}\text{S}$.

3.4 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 sand fill around the pipes. 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. Samplers were installed at 3.5 m, 5.5 m, 7.5 m, 10.5 m, 14.3 m and 17.7 m below ground level (Figure 2b). Each section was isolated from its neighbour by 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 about 12 months after installation to ensure equilibration with the unsaturated zone environment based on the experience of Kinniburgh et al. (1999).

Free gases were collected from the installed samplers by connecting an evacuated 300 ml glass bulb to the extraction tube of each sampler. Each bulb had a built-in 'T' allowing a hand pump to be attached at the same time as the bulb was connected to the extraction tube. At each sampling, the toggle valve at the end of the extraction tube was opened and the system pumped enough to extract more than three times the volume of the tubing to purge the system. At this stage, the tap on the glass bulb was opened and the bulb allowed to fill with gases from the sampler.

Gas from these bulbs was admitted to the gas chromatograph (GC) through a three way valve with a sampling loop. Nitrogen and oxygen were analysed on an MS5A column at room temperature, using argon as a carrier gas and a thermal conductivity detector (TCD). Carbon dioxide and methane were analysed on a Porapak-Q column at room temperature using a helium carrier gas and TCD and flame ionisation detectors. Nitrous oxide was analysed on a Porapak-Q column using a nitrogen carrier gas and an electron capture detector. Certified gas standards were run with the samples to calibrate the results.

Samples for N₂/Ar measurement were prepared by gas-pipetting an aliquot of gas into a 'finger'-type vessel containing approximately 0.5g of copper flakes. Atmospheric air was sampled in the same way to produce 'air spikes' against which to calibrate the results. The sealed fingers were then heated at 450°C for 1 hour in order that all O₂ could be removed by the copper. After cooling, the fingers were attached to a VG Optima Mass Spectrometer and analysed by simultaneous measurement of the mass 28 (N₂) and 40 (Ar) peaks using the approach of Martin et al. (1995). This allows analysis on a dynamic (i.e. constant flow) mass spectrometer, which is an improvement on static mass spectrometry because of the absence of 'cracking' effects in the ion source. A higher precision is therefore possible. Ratios of N₂/Ar were calculated by reference to the results obtained for air samples. Precision is $\pm 0.2\%$.

Samples for $\delta^{13}\text{C}$ measurement on CO₂ were prepared by extracting the CO₂ in the gas remaining after GC and N₂/Ar analysis by pumping the gas through a liquid nitrogen trap. This caused both CO₂ and water vapour to remain after the permanent gases had been pumped away. Water was retained in the trap by substituting a 'slush bath' (-60 to 70°C) for the liquid N₂ trap, while the liberated CO₂ was

refrozen into finger-type vessels using liquid N₂. The fingers were then attached to a VG Optima mass spectrometer and their ¹³C/¹²C ratios measured. A carbonate standard was used for calibration purposes. Results are expressed with respect to the PeeDee Belemnite (PDB) standard. Precision of the combined extraction and analysis steps is ±0.1‰.

Samples for δ¹⁵N-N₂ analysis were prepared in a similar way to that for N₂/Ar, with the addition of passing the aliquot of gas through a CO₂ absorbent ('Carbosorb') between the sample bulb and finger vessel containing the copper flakes (the presence of CO₂ interferes with the mass spectrometer measurement of the N₂ mass 29 minor peak). Precision is ±0.2‰.

4. RESULTS

Chemical parameters of groundwater within Chalk aquifers in the UK have been determined by Edmunds et al (1989) and are shown in Table 1. The study in Berkshire is of an unconfined aquifer, whereas the London Basin is confined. The two have been compared to provide a spectrum of values for UK Chalk groundwaters in southern England. Although there is a good deal of variation between the two, clear water quality trends can be seen. A 'baseline' chalk groundwater would 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.

4.1 Site 1

4.1.1 Porewater Chemistry

Porewater data from both vertical and inclined boreholes for Site 1 are shown in Table 2a and Table 2b. All depths are expressed in terms of metres below the ground surface. Observation of the core showed visible slurry along fractures within the chalk matrix. Visual observation of the pore waters showed them to be significantly coloured, with the most contaminated samples dark brown in colour and the lesser contaminated samples a pale yellow. Table 2a and Table 2b demonstrate that the porewaters are grossly contaminated throughout the depth of the two profiles with highest concentrations occurring below 10 m. Bicarbonate and chloride are roughly 10 times baseline concentrations (Table 1) and potassium nearly 2 orders of magnitude greater than baseline. Calcium concentrations are nearly a factor of 10 lower than baseline for the deeper porewaters from both boreholes. Dissolved organic carbon (DOC) and ammonia concentrations are both very high, 2 and 3 orders of magnitude above a typical baseline value.

Porewater profiles of nitrate-N, ammonium-N, DOC, pH, calcium and bicarbonate, chloride, copper and nickel at Site 1 display very similar trends (Figure 3a-i) for boreholes drilled beneath the slurry lagoon and those adjacent to the lagoon. Nitrate-N concentrations are initially between 20-70 mg/l in the top 3-4 m but then quickly decline to be below the detection limit. Calcium follows a similar trend to nitrate-N with concentrations rapidly declining to 5-10 mg/l below 6 m. Ammonium-N, DOC and bicarbonate all follow a similar trend showing a rapid rise in concentration below 3-4m. The ammonia-N and bicarbonate both show a sudden dip in concentration in the inclined hole around 12 m whereas pH (Figure 3d) shows a sudden increase.

Concentrations of heavy metals such as nickel and copper are all very high and follow the same increasing concentration with depth as DOC (Figures 3h&i) probably due to the formation of strong organo-metallic complexes.

4.1.2 Sulphate and Sulphur Isotopes

Porewater profiles for sulphate, δ³⁴S-SO₄ and δ¹⁸O-SO₄ are shown in Figure 4. For both boreholes, sulphate concentrations are about 50 mg/L or less below 3 m with a narrow rise in sulphate to about 100 mg/l in the inclined hole around 12 m. Both the inclined and vertical boreholes show a slight increasing trend with depth for sulphate. There are few data for δ³⁴S although the range is 9.3‰ (-0.7

– 8.6‰). Shallow porewaters in the vertical and inclined holes have slightly higher $\delta^{34}\text{S}$ values than the slurry, whereas the opposite is true in samples below 4.0 m. A relatively large enhancement of $\delta^{34}\text{S}$ occurs at the same depth as the increase in sulphate at 12 m in the inclined hole. More data exists for $\delta^{18}\text{O}$ which shows a steadily increasing trend in both boreholes with depth. Values range from 2.1‰ in the shallowest sample to about 12‰ in the deepest samples.

4.2 Site 2

4.2.1 Porewater Chemistry

Porewater data from both inclined and vertical boreholes for Site 2 are shown in Table 3a and Table 3b. Cores from Site 2 also contain slurry along fracture planes of the chalk matrix although to a lesser extent than Site 1. Porewaters were again coloured but less so than at Site 1 with the most contaminated samples exhibiting a pale yellow colour. Porewater profiles (Figure 5) define different trends in the inclined and vertical boreholes, which suggests that the boreholes intersect different parts of the contaminant plume. Generally, concentrations of chloride, bicarbonate, sulphate, DOC and ammonium-N are all highest in the inclined borehole in contrast to the vertical borehole where concentrations of nitrate and calcium are higher. Relative to baseline (Table 1) mean chloride concentrations are 5 times higher in the vertical borehole and an order of magnitude higher in the inclined borehole. DOC and bicarbonate both show a trend of increasing concentration with depth in the inclined borehole, reaching a peak at around 16 m before concentrations start to decline. Concentrations of DOC and bicarbonate in the vertical borehole are considerably lower than the inclined hole and remain fairly constant through out the profile. Nitrate-N in the inclined borehole shows a rapid increase in concentration to a peak around 8 m before showing a rapid decline in concentration. In the vertical borehole, nitrate-N has a higher initial concentration, rising to a peak at about 4 m before also rapidly decreasing and following a fairly constant concentration throughout the rest of the profile. Ammonium-N is detected in the inclined borehole at depths beyond 12 m but is only found in the vertical borehole in the top 50 cm.

Trace metal concentrations of copper and nickel also high with highest concentrations found in porewaters from the inclined borehole (Figures 5h&i).

4.2.2 Sulphate and Sulphur Isotopes

Porewater profiles for sulphate, $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ are shown in Figure 6. Sulphate shows a rising concentration trend in both holes. In the inclined borehole sulphate concentrations peak around 10 m and then show a slight decrease in concentration down to 16 m. Concentrations in the inclined borehole then continue to increase to the bottom of the borehole. Values for $\delta^{34}\text{S}$ range by 15.5‰ (-2.5 – 13‰) although values in the inclined borehole fall very close to the slurry composition (3.9‰) between 7 – 16 m and show a slight increasing trend. The vertical borehole generally exhibits lower $\delta^{34}\text{S}$ values than the inclined borehole. Values for $\delta^{18}\text{O}$ range by 7.5‰ (1.9 – 9.3‰), with a decreasing trend down to 8 m and then an increasing trend to the borehole base. Inclined and vertical boreholes generally follow the same trend.

4.2.3 Gas Analysis

Baseline gas sampling data has been prepared by Darling et al. (1997) and this is summarised in Table 4. Site 2 exhibits a radically different gas chemistry relative to baseline and also took considerably longer to equilibrate than samples taken below agricultural grassland (Kinniburgh et al., 1999). Profiles for gas samples taken after 428 and 569 days are shown in Figure 7. 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, showing a marked increase with depth from 6 m and below. Concentrations of methane at 17 m depth increased by five orders of magnitude from the first sampling to the second (>10% methane), with the concentration of methane found being of the same

order of magnitude as that found in landfill sites. By the second round of sampling, this methane concentration has reduced considerably to below 1%. The $\delta^{13}\text{C-CO}_2$ ratio did not change during the large change in methane concentrations.

A 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, coincident with a minimum of N_2O and a maximum of $\delta^{15}\text{N}$.

5. DISCUSSION

The porewater chemistry displays clear indications of slurry infiltrating the Chalk at both sites. Unpolluted groundwaters in the Chalk are predominantly a calcium carbonate type and slurry infiltration is readily identified by high concentrations of sulphate, nitrogen species (nitrate or ammonium), chloride, organic carbon and much greater concentrations of bicarbonate. These constituents correspond with those associated with cattle slurry by previous studies (Gooddy et al., 1998; Hooda et al., 2000).

The similarity between inclined and vertical borehole concentrations at Site 1 indicates a large component of the slurry is migrating through the side of the pit walls and causing considerable contamination in porewaters adjacent to the pit. At Site 2, the pit is still impacting the adjacent porewaters but to a lesser degree as reflected by a 50% difference in chloride concentration between the inclined borehole and the vertical borehole.

A major component of the slurry is organic matter as indicated by high dissolved organic carbon values. Within the slurry/chalk matrix system, the primary TEA's available for microbial degradation comprise dissolved oxygen, nitrate and sulphate. By examining the profiles at Sites 1 and 2, distinct geochemical processes can be seen associated with degradation of the slurry and the consumption of available TEA's. The region of aerobic respiration is apparent by the presence of nitrate and sulphate at high concentrations, which are removed by anaerobic respiration in the sub-oxic section of the profiles. In both cases, the aerobic zone is considerably thinner than normally found in a pristine chalk aquifer as this would usually extend throughout the depth of the unsaturated zone to the water table.

5.1 Aerobic and Anaerobic Zones – Site 1

At Site 1, a rapid reduction in nitrate-N concentrations and rise in ammonium-N concentration begins just below the ground surface. This is likely to be due to the ingress of ammonium-N from the mineralisation of organic nitrogen in the slurry rather than nitrate reduction. Depletion of sulphate concentrations occurs at a similar depth to the increase in ammonium-N. The $\delta^{34}\text{S-SO}_4$ shows a clear enrichment relative to the slurry composition at 12 m although this occurs in the same zone where an increase in sulphate is observed. It is unclear why sulphate and pH increases at 12 m whilst ammonium-N and bicarbonate decrease. In a previous study (Gooddy et al., 1998) similar behaviour was encountered and explained in terms of the dual porosity of the aquifer, with contaminated porewater intercepting a relatively oxygen rich fracture in the chalk. However, with the decline in ammonium-N and bicarbonate concentrations pH also decreased, whereas nitrate-N and calcium concentrations increased. In the current study no such rise in calcium or nitrate concentrations is found. It is suggested therefore that at 12 m in the inclined borehole, conditions are less reducing than in the 8 m above and the 4 m below, but the reason is unresolved. The steady shift in the enrichment of both $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ with depth strongly suggests BSR is taking place, although the paucity of $\delta^{34}\text{S-SO}_4$ data makes it hard to confirm from this measurement alone. Enrichment in the $\delta^{18}\text{O-SO}_4$ occurs despite a slight increase the sulphate concentration. This may infer that sulphate concentrations were initially higher and the approximately 50 mg/l concentration that occurs below 3 m represents a threshold level for the viability of BSR in this system. Alternatively it is possible that the isotopic

composition of the stored cattle slurry has changed markedly over the 20 year period that the pit has been in operation, indeed the difference between the cattle slurry at chalk Site 1 and chalk Site 2 is some 2‰.

5.2 Aerobic and Anaerobic Zones – Site 2

Gas samplers located in the inclined hole show unsaturated zone oxygen gas concentrations between 13 – 17% in the top 7.5 m of the borehole (Figure 7a). Sufficient oxygen is able to diffuse into the top of the profile to facilitate the oxidation of ammonium derived from the mineralisation of the slurry. The vertical hole appears to remain relatively aerobic throughout its depth but is characterised by high concentrations of nitrate. These possibly arrive through dispersion of ammonia from the contaminant plume and its consequent oxidation, or from dispersion and dilution of nitrate from beneath the pit.

In the inclined borehole, nitrate-N concentrations decrease four fold over a distance of roughly 6 m between 8 – 14 m. The higher concentrations of DOC (Figure 5c) and absence of oxygen (Figure 7a) demonstrate that this region is anaerobic and data from the gas samplers (Figures 7b,c and g) indicates denitrification occurs over this depth range. The concurrence of a maximum in the N₂/Ar ratio and the $\delta^{15}\text{N-N}_2$ and a minimum in the N₂O concentration at 14 m suggest most denitrification is occurring at this point in the profile.

A slight decrease in sulphate concentration in the inclined borehole occurs between 8 and 16 and this is accompanied by a slight shift in $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ over the same depth range. This suggests that BSR is taking place and occurs at the same time as denitrification.

A high in $\delta^{34}\text{S-SO}_4$ occurs at the base of the inclined borehole where concentrations of ammonium-N start to rise and a very high concentration of methane was observed in the gas sampler (Figure 7e). It is suggested that during the evolution of the profile, conditions at depth may have been more reducing. This is consistent with the concept of an initial contaminant pulse migrating through the profile in the early years of the slurry lagoon operation, prior to the lagoon base sealing.

5.3 Degradation of Organic Carbon

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 aerobic and anaerobic regions. In practice this can be seen, with a large increase in bicarbonate immediately below the aerobic zone associated with anaerobic respiration. The predominance of bicarbonate corroborates the evidence that anaerobic respiration is prevailing over both profiles for Site 1 and the inclined profile for Site 2. The degradation of organic carbon is well demonstrated at Site 2 by comparing the inclined borehole profile for DOC with that of a conservative element such as chloride. Chloride remains fairly constant in concentration from 4 m bgl to the profile base but a dramatic rise is seen in DOC concentrations between 12 and 14 m bgl which indicates considerable degradation between 4 and 12 m bgl. Anaerobic respiration 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 an aerobic zone were present. DOC increases inversely with depth in the anaerobic profile as more organic matter survives microbial attack. The greater efficiency of aerobic oxidation over denitrification is demonstrated by the lower DOC concentrations in the vertical borehole at Site 2 compared with the inclined borehole. Similarly, the greater efficiency of denitrification over BSR is demonstrated by the considerably lower DOC concentrations found in the inclined borehole at Site 2 compared with Site 1.

With the small pore-neck size of the chalk aquifer matrix, it must be inferred that the microbes responsible for degradation of organic carbon reside in the fractures and the microbial population is largely derived from the slurry material.

5.4 Carbonate Dissolution and Precipitation

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 Chatelier'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 promoting saturation and precipitation of calcite. There is evidence to suggest calcite dissolution in the aerobic portion of the profiles as shown by the presence of calcium, formed by dissociation of chalk. However, over the majority of the profiles bicarbonate is generated leading to calcite precipitation. As would be expected based upon carbonate equilibria, bicarbonate and calcium are inversely related. The cross over between aerobic and anaerobic boundaries is evidenced by the rapid depletion of calcium and increased concentrations of bicarbonate.

Data for calcite and dolomite saturation are shown in Figure 8. Saturation indices have been calculated by using PHREEQC (Parkhurst and Appelo, 1999). The temperature has been assumed as 10°C as no data is available for the temperature of the extracted porewaters and this is assumed a reasonable average for UK groundwaters (Edmunds et al., 1989). The porewaters are supersaturated with respect to both calcite and dolomite. Supersaturation of calcite has been observed previously for waters where high concentrations of organic matter are present (Amrhein and Suarez, 1987; Inskeep and Bloom, 1986).

Gas sampler data from Site 2 (Figures 7d and f) shows rising concentrations of CO_2 and $\delta^{13}\text{C}\text{-CO}_2$ becoming less negative. As the $\delta^{13}\text{C}\text{-CO}_2$ of organic matter tends to be around -24‰ and the mean $\delta^{13}\text{C}\text{-CO}_2$ of chalk in southern England is $+1.9\text{‰}$ (Downing et al., 1979), a positive shift suggests some carbonate dissolution. This could have happened early in the life of the slurry lagoon when the sub-surface environment was aerobic throughout and migrating ammonium could be oxidised to nitrate.

5.5 Uranium in Porewaters

A cross plot of uranium and bicarbonate is shown in Figure 9. For all but the vertical borehole at Site 2, where oxygen appears to be freely available, a reasonable positive correlation is observed. Uranium forms strong complexes with bicarbonate which helps to keep it in solution (Elless and Lee, 1998). 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 correlation is best for boreholes where conditions are reducing and calcite is being precipitated. It has previously been postulated by Gooddy et al. (1998) 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). Although originating from phosphate, no clear relation is observed between uranium and total phosphate. The uranium could be released by mineralisation from any complex formed with phosphate in the slurry store or in the upper part of the contaminant plume prior to transport through the profile as a soluble carbonate.

6. CONCLUSIONS

A combination of geochemical techniques have been used to determine plume development and attenuation beneath two unlined slurry lagoons on the chalk. These techniques have eluded to a deep zone of sulphate reduction beneath Site 1 and a deep zone of denitrification with some sulphate reduction beneath Site 2. The sites differ significantly in design with the fully submerged design of Site 1 producing a larger contaminant footprint than Site 2. This is concluded from the similar concentrations found in porewater chemistry for the inclined and vertical boreholes at Site 1.

The large contaminant loading beneath Site 1 suggests that it is continuing to leach contaminants into the aquifer as an impermeable seal has not been formed. Site 2 is still exhibiting a contaminant loading on the aquifer but this is substantially less than Site 1. It is possible that the raised design has allowed greater ingress of oxygen and more degradation of the slurry has been able to occur in the pit itself. The presence of methane, elevated ammonia concentrations and an enhancement of $\delta^{34}\text{S-SO}_4$ at depth however, suggest that a large pulse of contamination has already passed through the unsaturated zone and what is observed now is the unsaturated zone in a state of recovery. The lagoon has formed a sealed base relatively early in its lifetime and the contaminant plume originates from the early operation of the store.

Trace elements present in the slurry have been transported through the unsaturated zone as organo-metallic complexes. In addition, it has been suggested that uranium originating from NPK fertilisers used in cattle feedstocks, has been transported through the unsaturated zone as carbonate complexes due to the formation of bicarbonate produced in the reduction process.

In the absence of a significant aerobic zone it seems unlikely that the cattle slurry will be fully degraded in the chalk. The other available redox drivers have all originated from the slurry itself. There is a significant risk of effluent migration to the water table from both sites.

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Table 1. Mean concentrations of groundwater sampled from Chalk of England (Data from Edmunds et al, 1989)

Site	SEC μS/cm	pH	Cl	HCO ₃	SO ₄	NO ₃ -N mg/L	Na	K	Ca	Mg
Berkshire (<i>n</i> =26)	320	7.9	40	304	33	3.1	23	5.3	86	13
London Basin (<i>n</i> =21)	931	7.2	65	340	118	1.5	100	8.1	74	21
Combined (<i>n</i> =47)	676	7.6	51	326	71	1.9	57	6.1	82	17

Table 2a. Porewater data from vertical borehole at Site 1

Depth m	SEC mS/cm	pH	DOC mg/l	HCO ₃ mg/l	Cl mg/l	NO ₃ -N mg/l	NH ₄ -N mg/l	SO ₄ mg/l	P-tot mg/l	P-org mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Si mg/l	Fe-tot μg/l	Al μg/l	B μg/l	Sr μg/l	Ba μg/l	Cr μg/l	Mn μg/l	Co μg/l	Ni μg/l	Cu μg/l	Zn μg/l	Cd μg/l	Pb μg/l	Rb μg/l	Y μg/l	Mo μg/l	U μg/l
1.8	2.76	8.13	42.2	877	248	21	62	200	2.3	1.8	70.2	431	137	26.4	6.8	10	7.8	162	364	235	0.41	116.4	8	25	21	70	0.17	0.55	92	0.16	12	1.39
3.4	1.76	8.70	61.0	842	75	2.6	45	34.6	4.4	3.7	28.4	346	53.9	13.5	9.23	13	12.6	192	206	254	0.41	12.0	15	71	10	45	0.15	0.55	98	0.07	33	0.87
4.1	2.39	7.96	80.4	1040	138	12	94	48.9	7.7	6.1	43.1	465	31.6	12.5	8.56	49	31.4	147	110	187	0.90	9.6	20	77	19	87	0.34	1.46	103	0.15	30	1.08
4.9	4.44	8.07	125.9	2330	287	1.0	220	28.4	11.6	11.1	84.3	798	58.8	38.4	14.4	83	7.7	205	241	185	0.37	3.8	23	132	47	48	0.20	2.50	110	0.05	11	1.40
5.6	4.51	8.16	166.6	2190	314	0.7	240	30.5	12.3	8.3	87.7	800	28.1	29.8	12.8	99	18.4	156	109	278	0.89	5.7	22	116	32	67	<0.40	2.87	235	0.10	5.7	2.13
6.3	4.99	8.14	129.8	2480	333	0.5	270	28.5	16.7	14.5	95.2	878	21.1	29	13.5	95	23.2	188	102	329	0.90	2.9	29	147	38	84	<0.40	1.39	284	0.07	11	2.02
6.8	5.20	8.17	133.8	2630	344	0.6	300	27.5	14.4	17.6	101	949	14.9	30.1	11.4	80	13.4	162	58	176	0.88	3.3	25	142	32	53	<0.40	2.21	315	0.20	10	2.40
7.3	5.54	8.11	166.1	2860	348	0.7	330	34.5	13.6	15.3	108	905	19.8	40.4	11.5	142	22.7	165	90	197	1.18	5.3	54	252	26	69	<0.40	3.02	362	0.16	2.9	2.46
7.8	5.28	8.25	161.4	2710	344	0.6	350	32.3	6.5	5.0	110	859	9.93	32.8	8.27	191	22.7	151	39	174	1.02	3.8	55	193	19	63	<0.40	1.91	318	0.11	5.4	3.35
8.5	5.33	8.27	153.0	2780	344	0.7	370	34	7.3	6.1	115	837	13.1	29.5	6.32	202	30.8	156	44	185	1.18	6.3	59	267	33	65	<0.40	2.43	280	0.15	2.1	3.75
9.3	5.66	8.12	172.6	2980	333	2.5	380	33	4.9	3.9	117	872	14.8	36.8	6.05	262	40.9	205	86	265	2.49	7.6	57	272	44	104	<0.40	3.19	308	0.11	3.9	3.03
9.9	5.59	8.21	184.4	2910	339	0.8	390	37.7	1.6	0.6	117	820	8.9	29.6	3.48	334	19.3	164	38	178	1.11	3.5	66	543	71	57	<0.40	1.81	252	0.19	4.8	4.55
10.5	5.79	8.13	215.9	3030	337	3.8	400	34.2	2.7	1.6	118	889	11.5	33.4	3.78	403	24.9	149	42	159	1.33	4.7	57	267	34	86	<0.40	1.71	249	0.15	6.0	3.56
11.1	5.81	8.22	232.3	3070	344	0.7	390	38.2	4.6	3.5	123	903	6.59	32.1	4.02	476	38.7	184	46	204	1.89	2.2	110	508	66	85	<0.40	3.41	245	0.15	1.1	3.74
11.7	5.72	8.26	221.6	3000	351	0.6	390	42.4	2.1	1.0	124	912	5.42	29.1	3.37	652	40.7	166	33	113	1.98	2.5	107	535	73	62	<0.40	2.53	228	0.14	5.4	4.29
12.8	5.13	8.37	200.0	2620	344	0.6	350	46.3	1.6	0.7	112	871	4.71	15.3	1.03	323	14.5	163	15	137	1.14	2.1	79	555	105	50	0.76	3.45	171	0.16	4.9	6.98
14.3	5.24	8.37	164.8	1640	403	3.5	250	69.1	1.6	0.3	90.1	817	6.25	6.0	2.9	83	21.3	148	29	161	0.97	2.1	26	156	220	35	1.00	1.79	202	0.07	330	2.41

Table 2b. Porewater data from inclined borehole at Site 1

Depth m	SEC mS/cm	pH	DOC mg/l	HCO ₃ mg/l	Cl mg/l	NO ₃ -N mg/l	NH ₄ -N mg/l	SO ₄ mg/l	P-tot mg/l	P-org mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Si mg/l	Fe-tot μg/l	Al μg/l	B μg/l	Sr μg/l	Ba μg/l	Cr μg/l	Mn μg/l	Co μg/l	Ni μg/l	Cu μg/l	Zn μg/l	Cd μg/l	Pb μg/l	Rb μg/l	Y μg/l	Mo μg/l	U μg/l
0.4	2.11	7.82	26.8	345	212	67.0	<0.01	96.8	<0.2	0.0718	42	349	140	12.3	2.4	<6	6.8	94	380	254	0.41	3.3	2	11	12	44	0.10	<0.22	12	0.07	0.6	0.96
1.1	2.05	7.81	14.7	293	326	37.0	0.1	144	<0.2	0.0783	49.4	56.8	310	14.5	1.3	<6	6.0	120	835	175	0.32	10.5	2	24	6	48	<0.10	0.44	11	0.04	1.2	0.87
1.8	2.00	7.92	24.5	473	222	20.9	2.5	139	0.9	0.431	59.7	323	118	17.4	3.2	<6	6.5	137	320	161	3.23	22.6	7	33	12	41	<0.10	0.23	61	0.03	5.9	0.98
2.5	3.18	7.96	85.4	1310	199	19.2	152	120	7.7	6.36	91	423	75.4	20.1	11.7	39	15.5	154	191	195	0.59	77.8	8	26	13	52	<0.10	0.95	108	0.09	15.9	1.58
3.2	2.11	8.11	65.6	961	102	1.0	71	61.1	6.7	6.17	40.3	323	78.7	17.5	11.3	14	17.8	163	238	180	0.35	22.3	8	36	8	29	<0.10	0.36	95	0.05	8.0	0.84
3.9	2.32	8.18	86.6	1140	90	2.2	88	28.8	8.4	7.57	34.4	437	45.8	17.2	11.5	20	11.5	192	164	168	0.46	11.3	13	52	8	43	0.14	1.05	110	0.09	8.0	1.11
4.5	4.72	8.12	169.6	2280	288	1.1	255	38.2	12.9	10.6	83.7	834	23.1	29.1	12.5	134	21.1	173	92	215	1.04	4.8	18	91	14	56	<0.40	1.81	256	0.07	28.1	2.56
4.8	5.40	8.17	190.5	2660	334	0.8	303	36.6	20.0	11.7	97.4	948	18.4	32.9	13.3	176	31.8	186	74	209	1.30	4.6	20	110	16	62	<0.40	2.15	313	0.11	8.1	2.84
5.1	5.86	8.10	168.7	2910	373	0.6	335	34.8	16.6	13.7	105	990	23.9	40.7	12.8	141	23.2	191	96	218	1.14	5.4	33	212	18	51	<0.40	1.81	358	0.10	6.8	2.48
5.5	5.97	8.09	165.9	2950	381	1.0	347	30.6	13.9	13.3	107	1010	20.9	41.4	13.2	119	22.8	181	82	172	1.21	4.2	25	213	8	70	<0.40	1.39	364	0.13	3.1	2.47
5.8	5.91	8.21	168.3	2840	402	0.6	329	30.2	20.6	15.1	110	947	17.9	42.2	14.7	112	18.9	168	73	148	1.10	3.8	28	181	21	49	<0.40	1.71	345	0.12	2.9	2.13
6.2	5.71	8.04	152.5	2770	392	1.0	342	26.5	20.1	13.3	101	905	23.2	44.0	13.7	101	23.4	192	108	170	1.22	5.4	32	175	18	49	<0.40	1.70	359	0.08	1.1	2.15
6.7	5.40	8.23	169.5	2510	373	0.8	329	35.6	21.8	10.4	105	849	9.14	28.3	9.6	170	29.6	175	39	120	1.66	2.8	81	252	66	42	<0.40	1.87	319	0.09	12.0	2.75
7.4	5.69	8.24	204.3	2690	352	0.7	366	57.2	16.0	10.8	107	848	10.8	27.5	7.6	250	24.5	176	41	172	1.38	5.0	87	276	35	50	<0.40	1.97	309	0.06	20.8	4.01
8.1	4.95	8.24	154.2	2410	271	0.6	321	33.9	17.7	12.6	91.5	725	9.52	26.6	9.4	158	21.8	132	36	153	1.12	2.6	83	240	35	66	<0.40	1.47	233	0.09	4.2	2.24
8.7	3.98	8.24	111.1	1870	229	<0.5	244	25.8	2.2	1.33	72.5	600	11.0	21.0	4.8	54	8.3	147	34	152	0.53	2.7	28	139	17	28	<0.40	0.71	183	0.10	3.1	3.26
9.0	4.00	8.32	131.5	1890	219	0.5	248	35.5	5.9	5.09	73.6	577	9.09	17.2	5.7	95	13.8	151	35	180	1.11	4.0	49	202	26	45	<0.40	0.92	170	0.10	14.7	2.71
9.4	4.18	8.32	141.0	2010	240	0.6	256	39.3	8.0	6.85	77.9	667	11.0	23.3	6.9	86	13.1	148	41	205	0.99	3.3	52	178	21	41	<0.40	1.23	237	0.09	5.7	2.36
9.7	3.99	8.14	125.1	1880	234	1.2	250	28.5	6.7	6.36	67.5	618	11.6	25.1	7.8	92	18.6	119	49	200	0.96	3.5	70	279	27	59	<0.40	1.07	197	0.14	3.2	2.07
10.3	4.41	8.22	134.4	2190	229	0.7	280	30.3	2.5	1.86	78.3	659	7.19	18.3	3.9	128	17.5	153	29	161	0.97	3.7	64	267	54	45	<0.40	1.08	204	0.14	2.4	4.26
10.9	4.94	8.15	185.2	2360	268	0.6	299	42.1	2.3	1.20	94	526	8.54	23.6	6.8	404	38.0	207	47	181	1.69	3.0	40	239	50	54	<0.40	1.78	213	0.13	33.2	4.16
11.4	4.92	8.28	200.3	2340	275	0.6	310	55.6	4.5	3.20	97.7	742	10.3	21.4	4.4	264	19.4	165	35	131	1.27	4.1	34	448	27	41	<0.40	1.67	190	0.13	6.5	4.91
11.9	3.40	8.80	213.6	861	425	0.6	171	103	2.2	0.24	78.9	594	4.54	0.93	1.6	39	8.3	294	24	263	1.07	1.0	9	89	29	19	2.76	0.55	157	0.07	1000	0.40
12.5	3.24	8.89	207.1	508	519	1.7	117	104	1.8	0.16	90.5	599	4.97	0.80	1.3	22	13.1	253	32	197	1.47	2.0	12	71	450	32	1.66	0.59	138	0.04	470	1.04
13.0	4.46	8.22	187.4	2140	260	1.1	271	35.1	7.4	5.29	82.9	708	7.93	20.7	5.4	224	26.5	146	37	165	2.85	5.3	71	288	34	49	<0.40	1.34	154	0.10	7.4	3.20
13.5	5.44	8.24	202.7	2690	272	0.6	338	38.8	6.0	4.31	102	853	6.24	24.8	5.2	437	43.5	149	34	110	2.15	2.5	128	469	51	54	<0.40	2.41	178	0.11	2.5	4.05
14.1	6.34	8.21	236.8	3190	320	0.6	411	39.7	2.8	2.02	118	1020	5.43	28.4	4.5	773	55.8	184	32	151	2.32	3.0	105	492	72	68	<0.40	3.41	190	0.19	1.1	4.42
14.6	6.14	8.24	220.7	3080	329	1.0	400	37.1	1.2	0.44	114	984	5.56	21.6	2.2	602	25.8	189	23	137	1.56	2.8	63	318	81	66	0.66	3.50	171	0.14	3.2	6.20
15.1	5.73	8.13	236.6	2830	311	0.6	352	45.7	1.6	0.74	111	915	6.6	22.6	3.7	496	44.2	173	47	156	1.98	2.3	73	412	55	71	<0.40	2.32	135	0.15	57.1	4.54
15.6	6.45	8.20	263.3	3260	345	0.8	400	48.1	2.0	1.14	122	1050	5.42	22.7	3.0	670	48.9	183	34	125	2.20	3.2	131	664	126	82	<0.40	3.71	141	0.13	2.3	5.34
16.2	5.99	8.25	229.0	2890	354	0.6	389	38.7	1.2	0.54	111	964	4.33	14.1	2.4	430	34.0	153	26	170	1.63	2.1	72	279	82	95	<0.40	3.80	99	0.13	1.4	4.98
16.7	6.64	8.18	259.1	3330	371	0.7	433	43.8	1.2	0.51	124	1090	5.82	20.4	2.9	594	37.0	174	32	174	2.02	3.3	42	333	57	82	<0.40	3.13	126	0.14	1.1	4.97

Table 3a. Porewater data from vertical borehole at Site 2

Depth m	SEC mS/cm	pH	DOC mg/l	HCO ₃ mg/l	Cl mg/l	NO ₃ -N mg/l	NH ₄ -N mg/l	SO ₄ mg/l	P-tot mg/l	P-org mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Si mg/l	Fe-tot µg/l	Al µg/l	B µg/l	Sr µg/l	Ba µg/l	Cr µg/l	Mn µg/l	Co µg/l	Ni µg/l	Cu µg/l	Zn µg/l	Cd µg/l	Pb µg/l	Rb µg/l	Y µg/l	Mo µg/l	U µg/l
0.8	4.27	7.98	27.9	279	387	273	2.5	147	0.6	0.20	182	479	239	69.3	3.56	<6	5.2	178	644	353	0.94	7.9	5	30	19	55	0.27	<0.22	56	0.03	52.9	0.88
1.5	4.70	7.86	21.8	188	365	358	<0.01	117	0.3	0.14	216	495	253	88.4	4.73	7	12.6	183	839	382	0.81	2.9	4	23	14	58	0.22	0.62	76	0.03	4.2	1.01
2.5	4.86	7.91	26.9	186	430	349	0.05	111	0.4	0.14	232	639	199	74.2	5.2	7	20.6	191	711	296	7.25	18.0	7	33	24	53	0.18	0.39	99	0.07	8.3	0.94
3.5	5.01	7.78	16.2	199	414	384	<0.01	82.8	0.3	0.09	203	636	209	105	3.12	7	6.8	173	807	319	0.48	2.6	5	21	14	46	<0.10	2.33	40	0.03	2.8	0.66
4.5	4.46	7.95	12.7	235	349	317	<0.01	97.4	0.2	0.09	157	629	171	88.3	3.38	130	4.5	211	818	328	0.26	3.1	4	17	16	43	<0.10	<0.22	34	0.03	1.9	0.65
5.5	4.09	7.99	13.8	225	320	279	<0.01	111	0.2	0.09	132	617	115	80.4	2.86	<6	3.3	189	590	272	0.27	2.2	4	17	24	46	0.17	0.40	34	0.02	1.2	0.64
6.5	3.81	7.93	13.9	129	301	261	0.17	120	<0.2	0.07	121	591	102	67.0	2.3	<6	8.6	165	609	233	0.48	4.7	4	20	21	44	<0.10	<0.22	37	0.03	4.0	0.48
7.5	3.50	7.92	11.1	131	267	233	<0.01	125	<0.2	0.06	103	562	123	52.0	2.16	<6	5.7	210	723	222	0.41	3.4	4	16	17	34	<0.10	0.54	21	0.01	0.7	0.46
8.5	3.50	7.87	12.5	119	275	239	<0.01	143	<0.2	0.05	111	613	118	57.4	1.98	<6	3.0	157	625	215	0.31	2.9	4	18	20	35	<0.10	0.28	23	0.03	0.6	0.51
9.4	4.03	7.97	12.7	158	329	265	<0.01	164	0.2	0.06	120	673	138	61.7	1.84	7	3.5	137	719	220	0.37	3.3	4	21	23	56	<0.10	<0.22	15	0.02	0.9	0.60
10.1	4.12	7.89	13.5	130	332	264	<0.01	170	<0.2	0.06	124	700	136	61.3	1.79	170	20.4	145	663	205	0.50	3.3	5	22	25	51	0.26	<0.22	14	0.04	0.7	0.45
10.9	4.21	7.98	12.6	145	347	274	0.02	171	0.2	0.07	124	681	165	61.2	2.36	<6	4.0	183	901	224	0.25	3.3	4	20	20	40	<0.10	<0.22	13	0.04	1.8	0.63
11.6	4.10	7.93	12.8	133	338	264	<0.01	172	<0.2	0.06	119	658	166	56.0	1.96	<6	5.4	210	902	253	0.27	3.3	5	21	22	44	<0.10	0.28	13	0.02	0.6	0.63
12.5	4.12	7.92	11.9	124	355	264	0.68	169	<0.2	0.06	118	651	181	46.7	1.95	340	50.8	140	943	192	0.56	3.4	5	23	21	38	0.22	<0.22	11	0.03	8.4	0.47
13.5	4.19	7.91	10.8	132	364	270	<0.01	183	0.2	0.07	119	645	205	45.2	2.08	350	16.9	221	1120	254	1.09	5.8	5	24	21	48	0.17	0.36	10	0.03	2.1	0.66
14.5	4.18	7.85	11.4	115	366	262	<0.01	189	<0.2	0.06	120	663	203	42.2	1.83	9	5.2	177	1000	213	0.33	3.4	5	20	18	39	0.27	<0.22	8.0	0.03	0.3	0.60

Table 3b. Porewater data from inclined borehole at Site 2

Depth m	SEC mS/cm	pH	DOC mg/l	HCO ₃ mg/l	Cl mg/l	NO ₃ -N mg/l	NH ₄ -N mg/l	SO ₄ mg/l	P-tot mg/l	P-org mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Si mg/l	Fe-tot µg/l	Al µg/l	B µg/l	Sr µg/l	Ba µg/l	Cr µg/l	Mn µg/l	Co µg/l	Ni µg/l	Cu µg/l	Zn µg/l	Cd µg/l	Pb µg/l	Rb µg/l	Y µg/l	Mo µg/l	U µg/l
0.35	0.83	8.11	21.9	186	29.1	36.8	<0.01	38.1	0.9	0.82	21	63	78	13	4.3	<6	20.2	336	183	445	1.41	6.3	2	10	12	49	<0.10	<0.22	7	0.07	6.2	0.40
1.1	1.02	8.08	12.7	208	43	42	<0.01	60.7	0.5	0.47	28	98	95	9	4.27	<6	6.6	93	214	167	0.27	2.7	2	7	8	37	<0.10	<0.22	6	0.05	4.5	0.37
1.80	1.79	7.85	7.3	154	195	92	<0.01	44.8	<0.2	0.18	57	133	175	19	3.81	<6	4.0	138	527	242	0.24	3.9	2	8	6	32	<0.10	<0.22	13	0.03	1.6	0.31
2.50	2.72	7.85	5.9	139	226	201	<0.01	57.7	<0.2	0.09	81	191	267	38	3.94	6	4.5	151	859	277	0.27	5.6	3	18	8	50	<0.10	<0.22	25	0.04	1.9	0.38
3.20	3.44	7.58	5.6	135	293	257	0.01	53.1	<0.2	0.08	101	234	293	42	3.06	<6	5.2	109	1027	381	0.43	5.3	3	18	6	53	<0.10	<0.22	26	0.04	0.7	0.40
3.90	4.52	7.69	10.0	134	380	347	<0.01	66.2	<0.2	0.09	166	418	362	54	3.13	<6	9.4	116	1385	368	0.43	5.8	5	23	10	52	<0.10	<0.22	38	0.04	0.6	0.44
4.60	4.03	7.92	19.7	202	340	254	0.15	128	0.3	0.11	197	578	148	40	3.32	<6	6.5	401	707	292	0.49	11.1	5	22	34	81	0.88	0.31	30	<0.01	57.7	0.56
5.30	5.11	8.05	18.3	173	417	354	<0.01	152	0.3	0.08	218	868	145	70	2.36	<6	4.8	175	690	251	0.28	4.4	5	19	23	57	0.65	0.38	50	0.04	2.0	0.64
5.80	5.33	8.27	16.6	266	448	330	<0.01	214	0.2	0.08	177	1050	84	87	2.4	<6	3.3	173	495	204	<0.22	2.7	5	27	26	40	0.25	0.56	70	0.01	2.4	0.68
6.20	5.59	8.04	24.4	236	480	339	<0.01	260	<0.2	0.07	174	1130	85	96	2.13	<6	81.3	169	574	195	0.40	3.5	7	41	39	56	0.40	1.99	55	0.03	1.3	0.78
6.60	5.32	8.08	18.6	204	453	333	1.52	186	0.4	0.07	139	1020	91	68	2.35	<6	3.1	185	724	181	0.24	8.5	5	31	32	50	0.50	0.41	47	0.03	34.4	0.60
7.20	5.82	8.09	21.8	292	476	365	<0.01	239	0.3	0.07	169	1170	107	95	2.72	<6	4.6	252	671	327	0.33	4.4	6	33	31	52	<0.10	0.36	78	0.03	2.9	0.76
7.70	5.75	8.05	20.3	223	480	366	<0.01	262	0.2	0.06	168	1130	113	96	2.13	<6	11.7	171	613	231	0.44	2.8	6	31	31	61	0.23	0.88	46	0.02	2.2	0.78
8.20	5.98	8.03	25.3	235	491	378	<0.01	223	0.3	0.09	160	1230	70	82	2.87	8	7.8	261	622	193	1.32	5.3	8	44	35	39	0.25	0.38	145	0.04	3.9	1.11
8.70	6.13	8.15	33.0	409	504	342	0.03	306	0.6	0.32	207	1300	55	99	4.64	<6	6.2	275	447	185	0.38	3.9	10	67	44	48	0.39	0.25	220	0.06	9.7	1.34
9.00	6.06	8.24	38.5	439	521	317	0.13	296	0.9	0.57	211	1270	46	87	5.17	440	19.2	299	272	179	0.84	3.6	15	188	72	62	1.03	28.49	110	0.06	8.6	1.86
9.40	5.92	8.11	38.0	550	524	285	<0.01	291	1.1	0.78	223	1250	45	86	5.44	<6	13.4	233	388	231	0.40	3.3	14	96	47	57	0.79	1.42	244	0.06	11.6	1.42
9.70	5.78	8.24	40.1	614	539	252	0.06	269	0.8	0.53	225	1220	41	77	5.91	<6	9.0	269	293	243	0.40	5.1	30	189	69	57	0.31	2.36	177	0.08	27.6	2.09
10.1	5.63	8.21	43.2	640	550	238	<0.01	246	1.7	1.04	239	1130	39	68	6.08	<6	8.6	236	326	149	0.65	5.0	14	158	75	51	0.37	0.87	67	0.06	11.3	1.55
10.4	5.61	8.37	45.9	734	567	217	0.05	221	0.8	0.36	254	1180	35	70	6.76	<6	10.2	293	393	407	0.76	7.1	11	93	52	40	1.67	1.19	145	0.03	299.5	1.45
10.8	5.22	8.35	43.6	836	573	147	<0.01	191	0.8	0.42	192	1110	28	48	3.94	260	31.1	266	303	365	1.18	17.7	21	128	21	115	0.46	2.55	322	0.16	4.9	2.17
11.1	5.17	8.24	47.7	758	558	168	<0.01	209	1	0.54	240	1080	33	57	4.96	<6	4.5	197	275	184	<0.22	8.4	16	96	44	72	0.60	0.71	187	0.03	7.2	1.45
11.5	5.02	8.34	43.1	825	597	98.0	<0.01	279	0.7	0.18	210	1150	23	50	3.61	<6	11.9	166	280	134	0.30	2.7	10	74	38	45	0.13	0.47	190	0.03	10.7	1.00
11.8	4.76	8.29	39.7	628	624	77.0	<0.01	265	0.6	0.12	174	1070	20	34	2.58	87	7.9	178	201	133	0.90	1.5	8	119	47	39	<0.40	0.87	70	0.06	6.4	1.28
12.2	4.95	8.32	57.0	1020	543	90.0	0.17	205	3.5	2.47	249	1050	34	52	7.31	27	5.2	201	155	238	0.50	4.1	20	118	52	42	<0.40	1.42	172	0.02	41.0	2.45
12.6	5.06	8.41	67.7	1070	560	65.0	15.4	315	0.8	0.25	248	1060	21	52	3.85	<6	7.6	217	184	240	0.70	2.4	16	314	72	66	<0.40	1.24	128	0.05	14.5	2.21
12.9	4.68	8.31	45.0	630	586	75.0	8.0	326	1	0.14	210	970	30	35	3	340	4.7	178	241	140	0.23	4.5	18	87	48	35	0.60	0.47	175	0.03	12.3	1.48
13.3	4.73	8.38	41.4	614	592	97.0	0.1	306	0.8	0.28	203	964	46	42	3.35	330	13.8	216	311	137	0.30	3.9	10	108	52	42	<0.10	0.57	73	0.05	7.3	1.49
13.6	4.7	8.36	51.4	642	597	78.0	0.06	301	0.8	0.15	218	1020	16	40	4.7	<6	7.0	200	134	191	0.58	1.7	15	182	56	39	<0.40	0.65	128	0.08	12.8	2.55
14.0	4.77	8.38	55.0	743	594	74.0	<0.01	291	0.7	0.28	217	1020	15	43	4.86	<6	9.0	225	138	196	0.59	1.7	15	193	55	42	<0.40	0.94	137	0.04	11.5	2.97
14.3	4.57	8.36	65.5	1010	560	44.8	10.3	183	3.3	2.35	202	927	24	44	4.69	58	4.9	167	156	230	0.42	3.0	17	123	48	33	<0.40	0.54	145	0.02	49.5	2.38
14.7	3.83	8.21	23.1	337	503	107	14.1	122	1.3	0.33	142	757	23	15	2.16	10	4.1	169	213	190	0.22	2.7	19	93	36	41	0.22	0.75	135	0.02	9.7	1.27
15.0	4.96	8.4	67.0	890	586	19.6	5.7	257	4.3	0.59	219	1150	18	60	6.4	8	6.2	199	103	238	0.77	2.5	21	92	45	44	<0.40	1.09	194	0.04	15.5	2.70
15.38	5.03	8.45	74.6	1240	600	25.0	23.8	265	1.9	1.01	233	1110	10	54	7.05	26	7.3	209	72.0	199	0.44	0.9	27	148	80	40	<0.40	0.89	181	0.05	8.2	4.39
15.73	4.93	8.35	70.0	1090	605	53.0	0.74	166	1	0.46	173	1100	13	50	4.27	56	8.0	165	124	164	0.57	2.4	25	248	72	54	<0.40	0.77	139	0.04	20.7	2.54
16.08	4.75	8.42	68.2	1000	582	53.0	<0.01	199	1.5	0.91	205	1050	12	59	4.42	<6	4.5	170	100	199	0.46	2.2	16	257	72	42	<0.40	0.84	135	0.06	11.3	2.55
16.44	4.74	8.38	57.7	1020	561	64.0	0.33	207	1.2	0.56	211	1030	24	52	7.79	24	6.6	271	183	197	0.61	3.6	29	186	67	36	<0.40	0.97	157	0.02	34.7	2.36
16.79	4.95	8.31	43.9	1110	587	64.0	<0.01	222	0.8	0.20	206	1090	26	65	5.19	99	6.5	325	264	204	0.42	3.0	15	195	54	38	0.27	0.90	116	0.06	5.3	1.51
17.14	3.77	8.26	40.1	716	475	18.4	1.77	274	0.7	0.35	155	734	50	39	5.38	45	7.9	288	325	162	0.39	7.5	11	98	24	33	<0.10	1.24	58	0.01	4.5	1.06
17.50	3.92	8.36	35.7	648	561	11.1	6.7	274	0.8	0.14	188	775	42	29	4.78	<6	12.8	336	407	141	0.52	3.1	12	117	43	33	<0.10	0.83	52	0.03	2.8	0.96
18.03	3.19	8.15	28.8	540	416	15.4	1.44	240	0.6	0.15	133	595	58	24	4.57	43	5.4	238	354	127	0.64	5.1	8	82	27	35	0.23	<0.22	43	0.03	4.6	0.91

**Table 4 Mean concentrations of gases found in the unsaturated zone atmosphere of the Chalk
(Data from Darling et al., 1997)**

	N ₂ —— volume %	O ₂ —— volume %	CO ₂ ——	CH ₄ ppmv	N ₂ O ppmv	N ₂ /Ar
Chalk	77.69	19.49	1.52	<0.1	4.24	83.9
Atmospheric	78.08	20.95	0.035	1.8	0.3	83.6