ABSTRACT

Farm waste stores are widespread in the UK, with many overlying the principal aquifer the Chalk. The stores pose a threat to groundwater quality through the infiltration of high concentrations of nitrogen species and organic carbon together with pathogenic microbes. Two cored boreholes have been drilled into the unsaturated chalk to depths of 15 and 20 metres respectively through a site which has been used to store turkey litter for in excess of 20 years. Porewaters were extracted from the cores and analysed for a range of chemical elements. In addition, chalk core material was also taken for microbial examination. Both boreholes showed very high concentrations of nitrate-N (3000 mg/L), ammonia (5000 mg/L), organic carbon (3000 mg/L) and potassium (10000 mg/L) in the top 5 metres of the profile. Below this depth concentrations declined dramatically. Highest concentrations were found in the borehole constructed in the middle of the site. The borehole constructed at the edge of the store showed much lower concentrations but did show a peak of nitrate around 10 metres below ground level. The apparent lack of movement beneath the centre of the store suggests the turkey litter is relatively impermeable and most leaching occurs where the covering of litter is thin or when the litter is annually cleared. If the leachate continues to migrate at this apparent rate, it will take more than 100 years to reach the water table.

Key Words: Waste storage, Chalk, groundwater pollution, microorganisms

INTRODUCTION

Groundwater provides over 30% of all water abstracted for public water supplies in England and Wales, 8% in Northern Ireland and 5% in Scotland. The regional differences reflect the distribution of aquifers and the more favourable geological and meteorological conditions for surface water resource development in Northern Ireland and Scotland. Over 70% of the total public supply in south-east England is derived from groundwater. 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 60% is pumped from the largest aquifer, the Chalk. This is a soft, microporous fractured limestone with a well documented flow regime (Foster and Milton, 1974; Price, 1993).

Storage of farm wastes presents a serious potential risk of surface water pollution. In the past, serious pollution incidents to surface waters have led to prosecutions by the UK 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 chalk 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 km². 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 in Table 1. 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 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 will occur and cause pollution of groundwater (Gooddy et al., 1998). Several studies have dealt with the issue of slurry lagoons (Culley and Phillips, 1989; Withers et al., 1998; Gooddy et al., 1998; Kanazawa et al., 1999; Gooddy et al., 2001) but relatively few have examined solid manure stores (Zhu et al., 2000), this study has therefore concentrated on a field heap of turkey litter.

The large nitrogen (ammonium and nitrate) load carried in solid turkey litter presents a serious potential impact to the groundwater beneath. 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. Most microbial contaminants die off in passage through the soil however, where by-passing of the sub-soil occurs, the role of the unsaturated zone is especially important.

The unsaturated chalk may provide an effective zone for pathogen removal. Like the soil zone, the chalk unsaturated zone exhibits aerobic conditions and provides a good medium for the degradation of many organic compounds. However, soil and vadose zones can become overloaded. Furthermore, microorganisms may percolate through most soils and rock pores, except in fine-grained strata where pore diameters are small (Harvey et al, 1995).

Nevertheless the effects of fractures may be very important in allowing the transmission of chemical and particulate pollution to groundwater by largely bypassing the unsaturated zone. Bypass flow velocities in the Chalk are large compared to typical intergranular velocities and can be seen in fractures after major recharge events. Recent discussions of this topic are provided in Price et al. (1993) and Price et al. (2000). It is unclear how important these processes are for long term groundwater quality beneath solid manure stores.

MATERIALS AND METHODS
Site Details
The site is in southern England 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 below ground level (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. In the fall of each year the site is cleared and the litter applied to the surrounding farmland.
Sample Extraction and Analysis
Continuous, undisturbed core samples from the unsaturated zone of the Chalk were obtained during the fall of 1999 (after the annual litter removal had just taken place) using a lightweight rig of the Pilcon Wayfarer type. The undisturbed samples were retrieved by driving a steel tube, 100 mm in diameter and 0.45 m long, into the Chalk. This method has the advantage over other drilling techniques in that no lubricating fluids are used. The core was retained in the tube within an inner PVC liner. When full, the steel tube was brought to the surface, capped and taped securely with the top and bottom depths recorded. 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 respectively.

Porewater was extracted from the Chalk core material as soon as possible after drilling. This was carried out using the high speed centrifuge 'drainage' method (Edmunds and Bath, 1976). 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 was 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.

Filtered acidified porewaters were analysed using an ARL 34000C Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) which is calibrated for the following 11 elements: Na, K, Ca, P$_{\text{total}}$, SO$_4^{2-}$, Mn, Fe$_{\text{total}}$, Zn, Cu, Co and Ni. All analyses are blank corrected and detection limits defined as 6 times the standard deviation of the blank.

Nitrate-nitrogen (NO$_3^{-}$-N), ammonium-nitrogen (NH$_4^{+}$-N), 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 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 high organic carbon content of the samples can cause suppression of the baseline when the hydrazine/copper reduction method is 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.

Microbiological Determinations
Core material from the boreholes was selected at approximately 5 m vertical intervals. These samples were disaggregated (comminuted) and suspensions were prepared in maximum recovery diluent 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)
• *Campylobacter* presence/absence by selective enrichment using Park Sanders broth and selective plating using Nutritive Blood Gelatine agar and Modified Charcoal Cefoperazone Deoxycholate agar.

**RESULTS AND DISCUSSION**
A study by Gooddy et al. (2000) showed the dry matter content of 7 cattle slurries to vary between 0.2-13.9% (median 2.5%), and the total N vary from 0.25-5.7 kg/m$^3$ (median 1.4 kg/m$^3$). Analysis of the turkey litter from this site showed a dry matter content of 62.3% and total N as 27.1 kg/m$^3$ which is considerably drier than cattle slurries and also displays a much greater fraction of N by weight.

Borehole 1
Porewater concentrations for the borehole constructed through the centre of the litter store are presented in Figure 1. It can clearly be seen that in the top part of the profile solute concentrations are very high, up to 50 times a baseline Chalk groundwater (Gooddy et al., 1998) 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 by approximately 15 metres. 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 (Table 2). Solutes appear to decline in concentration and then peak at 3.5 metres 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. Recharging rainwater would be expected to migrate at a rate of roughly 1 m/a for the Chalk unsaturated zone (Darling and Bath, 1988). Beneath the top 1 metre little ammonia is present in the porewater suggesting that conditions are highly oxidising. Nitrate concentrations also peak at around 3000 mg/L at 3.5 metres and decline rapidly after this suggesting both limited movement of a contaminant plume and maybe rapid rates of denitrification. Copper, nickel, zinc and cobalt are all found in the upper 5 metres of the profile. They are associated with the turkey litter as all three of these elements form strong organo-metallic complexes and would not be expected at these concentrations in uncontaminated porewaters.

Borehole 2
Porewater concentrations for the borehole constructed through the edge of the litter store are presented in Figure 2. Over the length of the profile, solute concentrations decrease by an order of magnitude to end in levels close to baseline (Table 3). The chloride profile again shows a peak in concentration at around 3.5 metres (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 with maxima of 70 mg/L and 25 mg/L respectively. Higher moisture contents (generally 5-10% higher than borehole 1) support the possibility that litter coverage was less dense at the edges and may explain the 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. Concentrations of copper, nickel, zinc and cobalt are lower than in borehole 1 which reflects the generally lower organic loading at this part of the store.

Microbiology
Microbiological data have been tabulated in Table 4. With the exception of the top 0.5 metres, 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 and suggest the chalk matrix is acting as an efficient filter, greatly restricting the downward migration of microbial contaminants.

Geochemical Processes
From the porewaters extracted from borehole 1 an inverse relationship exists between oxidised and reduced nitrogen species (nitrate and ammonia) corresponding with the crossover between aerobic and anaerobic conditions (Figure 1). The presence of iron and manganese in the top metre supports this observation. For borehole 2 this cross-over is less clear with the two species co-existing (Figure 2) which suggests considerably greater availability of oxygen consistent with the much thinner litter cover on the edge of the manure store. 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 2. This reaction also generates protons which require buffering.

$$\text{NH}_4^+ + 2\text{O}_2 (\text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}) \quad (1)$$

These protons can lead to the dissolution of Ca$^{2+}$ from the calcite chalk matrix, producing high concentrations of Ca$^{2+}$ in solution (2).

$$\text{CaCO}_3 + 2\text{H}^+ (2\text{HCO}_3^- + \text{Ca}^{2+}) \quad (2)$$

The top few metres of borehole 1 indicate that nitrate, in the absence of oxygen, is acting as the terminal electron acceptor for organic carbon degradation (3) as all the available oxygen has been consumed in the initial formation of nitrate.

$$5\text{CH}_2\text{O} + 4\text{NO}_3^- (2\text{N}_2 + 4\text{HCO}_3^- + \text{CO}_2 + 3\text{H}_2\text{O}) \quad (3)$$

In the case of borehole 1, the upper 2 to 3 metres is anaerobic, while for borehole 2 the aerobic zone extends throughout the profile. The extent of the aerobic zone is significant in terms of organic degradation, which occurs most efficiently by aerobic respiration (4).

$$\text{CH}_2\text{O} + \text{O}_2 (\text{CO}_2 + \text{H}_2\text{O}) \quad (4)$$

In a closed system this reaction forms bicarbonate and a proton and so also requires buffering leading to more dissolution of the calcite matrix. However, it is apparent that in the aerobic zone below 5 metres, the system is open allowing for the exchange of CO$_2$ with the atmosphere, and calcium concentrations decline to values comparable with pristine chalk porewaters.
SUMMARY AND CONCLUSIONS
Core from both boreholes drilled beneath the turkey litter store showed elevated concentrations of organic carbon, nitrate and ammonia in just the top few metres of the porewater profile, with ammonia only present in the top 2 metres below which it is oxidised. Most of the organic carbon has been oxidised below the top 5 metres. There appears to be limited movement of the contaminants and this is most likely due to the substantially reduced recharge that occurs beneath a dry matting of turkey litter. Movement has occurred where the covering of litter is less consistent or possibly during the few weeks in the year after the litter has been cleared. 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. No faecal microorganisms were observed beneath the turkey litter and no preferential routes for contaminant transport were observed. Both boreholes suggest that the majority of contamination has moved no further than 5 m over a period of 20 years and at this rate of transport it would take more than 100 years for the leachate to reach groundwater.

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