# A review of ammonium attenuation in soil and groundwater

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## Abstract

Ammonium attenuation in subsoils and groundwater is predominantly due to cation exchange and/or nitrification (biological oxidation) processes. These processes have been little studied in UK formations and this relative lack of information can result in reduced consistency and robustness in the assessment of risks posed by ammonium contamination arising from landfills, effluent soakaways, contaminated sites and other sources. A review of ammonium fate and transport in the subsurface has been completed and guidance developed on the key processes that contribute to attenuation. The amount of relevant literature is small but sufficient to provide indicative ranges of partition coefficients and biological nitrification rates for ammonium in UK subsoils and aquifers. Ammonium attenuation was found to be highly sensitive to the clay mineralogy and pore size of the strata, the availability of oxygen and the chemical composition of the contaminated fluid. The values derived may have application in the initial (screening) phases of risk assessment where the conceptual model for the site under consideration matches that from which the presented data originate.

*Keywords: environmental protection, groundwater contamination, ion exchange, risk assessment*

Inorganic nitrogen in the form of ammonia ($NH_3$) and the ammonium ion ($NH_4^+$) is recognized as one of the most common groundwater contaminants arising from waste disposal activities, fertilizer use and contaminated land (Environment Agency 1996). (In this paper, $NH_4^+$ is used when referring to the ammonium ion, $NH_3$ when referring to ammonia, and $NH_4$-N when presenting concentration data, which are reported throughout as ammonium measured as N.) In drinking water supplies $NH_4^+$ can reduce disinfection efficiency, lead to nitrite formation, and cause taste and odour problems (World Health Organization 1993). In surface water, un-ionized ammonia ($NH_3$) can cause fish mortality at very low concentrations (National Rivers Authority 1992; Environment Agency 1998).

Ammonium is a List II substance under both the Groundwater Directive (80/68/EEC) and the Dangerous Substances Directive (76/464/EEC). As such, its entry into groundwater and surface waters must be controlled to prevent pollution. The principal environmental drivers for limiting $NH_4^+$ discharges to the aquatic environment are its effect on ecology (particularly fish), and potable use of water. In addition, the Water Framework Directive (2000/60/EC) requires Member States to achieve good chemical status for groundwater bodies and good ecological status in surface water bodies. Furthermore, EU Member States must reverse significant and sustained upward trends in the concentration of pollutants in groundwater. The impact of $NH_4^+$ within a surface water body, and the effects of polluted groundwater discharging into surface waters are important factors that need to be assessed as part of the river basin characterization process.

Ammonium is typically present in landfill leachates, wastewater discharges and other industrial liquors, such as quench waters at coking plants and gasworks sites, at very high concentrations relative to relevant standards for drinking water or environmental quality (Table 1). Under certain conditions it is also a relatively mobile contaminant. For these reasons, it is common to use $NH_4^+$ as a key contaminant species in risk assessments for landfills, effluent soakaways and contaminated sites (Environment Agency 2003*a*).

## Attenuation of ammonium

The transport of dilute aqueous contaminants in groundwater is generally represented by the advection–dispersion equation, which assumes that the contaminants neither decay nor interact with other aqueous species or mineral phases (Domenico & Schwartz 1998). However, reactive processes will be critical in determining the transport of the majority of contaminants. For $NH_4^+$, the key reactive processes controlling subsurface transport are sorption as a result of cation exchange processes and biological degradation.

Although cation exchange processes have been widely studied, particularly with respect to nitrogen cycling in topsoils (Brady & Weil 2002), there has been relatively little research on the effects of cation exchange on $NH_4^+$ transport in subsoils and groundwater, particularly under the conditions prevailing in UK aquifers. Similarly, there are relative few field data on biological attenuation of $NH_4^+$, as most research has focused on

**Table 1.** *Typical concentrations of sources of dissolved $NH_4^+$ to groundwater.*

| Occurrence | Reference | Typical concentration $(mg(NH_4\text{-}N)\,l^{-1})$ |
| --- | --- | --- |
| Pumped urban groundwater (Birmingham) | Ford & Tellam 1994 | <0.01– 0.93 |
| Sewage effluent (tertiary treatment) | Horan 1990 | 1–5 |
| Sewage effluent (secondary treatment) | Horan 1990 | 15–25 |
| Untreated sewage | Horan 1990 | 20–40 |
| Typical landfill leachate (recent wastes) | Department of the Environment 1995 | 800 |
| Typical gasworks soil | CL:AIRE 2003 | up to $1000\ mg\ kg^{-1}$ [1] |
| Groundwater at cemeteries or graveyards | Environment Agency 1999a | up to 400 |
| Foot and mouth epidemic mass burial leachate | Environment Agency 2003c | 1000–7000 |

For comparison, the current UK Environmental Quality Standard (for ammonia) for freshwater salmonid fisheries is $0.015\ mg(NH_3\text{-}N)\,l^{-1}$ and the Drinking Water Standard (for ammonium) is $0.39\ mg(NH_4\text{-}N)\,l^{-1}$.

[1] Soil concentration; no reported data on representative groundwater concentrations.

$NH_4^+$ fate in wastewater and topsoils (USEPA 1993; Brady & Weil 2002).

The lack of data on $NH_4^+$ behaviour in the subsurface limits consistency and robustness in the assessment of risks posed by $NH_4^+$ contamination arising from landfills, effluent soakaways, contaminated sites and other sources. Some of these data were reviewed by Erskine (2000), who considered $NH_4^+$ attenuation at different scales in subsoils and aquifers and suggested parameter values for application in risk assessments.

To address the requirement for field-relevant data on $NH_4^+$ attenuation, the Environment Agency has undertaken a review of $NH_4^+$ fate and transport in the subsurface and developed guidance on the key processes that contribute to $NH_4^+$ attenuation in subsoil and groundwater under UK conditions (Environment Agency 2003b). This paper summarizes the findings of that literature review.

## Attenuation of ammonium by sorption

Sorption is the process by which a contaminant partitions between the solid and aqueous phases in a porous media. It includes all surface-related reactions such as adsorption, absorption, surface complexation, surface precipitation and ion exchange (Stumm 1992). The effect of sorption is to slow or retard the rate of migration of the contaminant relative to the average (advective) groundwater flow velocity.

Sorption of $NH_4^+$ is primarily controlled by cation exchange reactions occurring at negatively charged mineral surfaces. In aqueous solutions of low to neutral pH, cation exchange occurs primarily on clay surfaces, but at pH values above neutral sorption to iron oxyhydroxides also makes a significant contribution (Sverjensky & Sahai 1996). This is because metal oxides have a variable negative charge as a function of pH. The extent of sorption to metal oxide surfaces depends on the ambient pH, amount of oxide present and point of zero charge (PZC) of the specific oxyhydroxide mineral.

Metal oxides are negatively charged at pH values above the PZC. Manganese oxides (e.g. $MnO_2$) with a PZC of *c.* 4–4.5 are likely to contribute more exchange capacity for $NH_4^+$ sorption than Fe oxides (e.g. FeOOH), with PZC around 6–7 (Parks 1965). Sorption to metal oxides may be an important contribution to the attenuation of $NH_4^+$ in aquifers or geological materials containing these minerals as surface coatings on particles (e.g. Triassic sandstone).

The relative strength with which cations bond to a charged mineral surface is determined by their selectivity coefficients, which are a function of both the mineral surface and solution composition (Appelo & Postma 1993). The following series of relative selectivity has been presented in order of decreasing affinity for cation exchange sites (Domenico & Schwartz 1998), although other schemes have been proposed: $Al^{3+} > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > H^+ > Na^+$.

In many contaminant plumes, $NH_4^+$ is not the most abundant cation. For example, sodium is usually the dominant cation in domestic landfill leachate (Department of the Environment 1995) and competes, along with potassium, calcium and magnesium, with $NH_4^+$ ions for exchange sites. Cations retained electrostatically are easily exchangeable with other cations in the groundwater with a high selectivity coefficient for the sorbent.

Estimates of sorption and retardation for the same geological formation, using different test methods (and especially different solution compositions), may vary by more than two orders of magnitude (e.g. Lower Chalk, Environment Agency 2000; Lias Clay, Cave & Taylor 2002). Factors that contribute significantly to this variability are:

- non-linear sorption isotherms, which apply at higher concentrations but can be measured by appropriately designed experiments;
- composition of the aqueous phase and solid exchanger material;
- non-equilibrium behaviour, which can be measured by longer duration column experiments (although flow velocities in such tests are generally higher than expected in the field);

● non-ideal behaviour, which has been observed in laboratory and field experiments; this is thought to be predominantly due to field-scale heterogeneity in hydraulic conductivity and partition coefficients, $K_d$;

● method, precision and validity of experimental testing procedures (e.g. the use of single solute solutions to represent competitive sorption in multi-solute field systems).

## Sorption models

*Theory.* The simplest sorption model relates the sorbed mass to the solute concentration by a constant of proportionality, termed the partition coefficient, $K_d$:

$$K_d = \frac{C^*}{C} \qquad (1)$$

where $K_d$ is the partition coefficient ($l\,kg^{-1}$), $C^*$ is concentration of the sorbed contaminant ($mg\,kg^{-1}$) and $C$ is aqueous concentration ($mg\,l^{-1}$). Although this formulation should strictly use activities rather than concentrations, $K_d$ tends in practice to be based upon measured concentrations without correction for ionic strength (e.g. Environment Agency 2000).

The principal limitation of the linear sorption model is that the substrate is assumed to have infinite sorption capacity, irrespective of solute concentration. This is unrealistic for natural materials and several alternative sorption models have been proposed that account for a maximum sorption limit.

The Langmuir isotherm (Appelo & Postma 1993) assumes that there are a finite number ($\beta$) of surface sites that have identical sorption characteristics. It is commonly written as

$$C^* = \beta \frac{\alpha C}{1 + \alpha C} \qquad (2)$$

where $\alpha$ is the partition coefficient ($l\,kg^{-1}$) and $\beta$ is the maximum amount of solute that can be sorbed by the solid ($mg\,kg^{-1}$). At low concentrations the Langmuir isotherm becomes linear with $K_d = \alpha\beta$.

Neither the linear nor the Langmuir model accounts for sorption heterogeneity in the substrate, although these models are additive if there are multiple homogeneous substrates. Taken to the limit of a continuous Gaussian-like distribution of $\alpha$ and $\beta$ to represent a heterogeneous exchanger, Langmuir isotherms may be integrated to give the Langmuir–Freundlich isotherm (Sposito 1984):

$$C^* = \beta \frac{(\alpha' C)^N}{1 + (\alpha' C)^N} \qquad (3)$$

where $\alpha'$ is the mean value of $\alpha$ in the distribution and $N$ is a constant between zero and one that describes the degree of heterogeneity in the substrate. With $N = 1$ the

distribution becomes the Langmuir isotherm. At small values of $C$, the Langmuir–Freundlich isotherm can be approximated by the Freundlich equation:

$$C^* = KC^N \qquad (4)$$

where $K$ is a constant of proportionality. With $N = 1$, the Freundlich isotherm becomes the linear isotherm.

Both the Langmuir and Freundlich isotherms are non-linear but tend to linearity at low concentrations or over a limited concentration range. It is particularly important to note that the ratio $C^*/C$ decreases at higher concentrations for the Langmuir and Freundlich isotherms. Therefore, if $K_d$ values are determined from $C^*/C$ ratios at low concentrations, the partition coefficients may be overestimated. This will overestimate the retardation factor and breakthrough time of $NH_4^+$ at a receptor, and underestimate the predicted length of a pollutant plume in an aquifer.

In this paper, when a partition coefficient is derived only for a given concentration (i.e. there is no evidence for a linear isotherm), the symbol $K_d^*$ is used to denote the ratio $C^*/C$. The symbol $K_d$ is therefore reserved for a partition coefficient that describes the slope of a linear isotherm. It should be noted that many publications reviewed did not make this distinction.

*Experimental observations.* Both linear and non-linear isotherms have been observed in studies where sufficient data were collected to derive sorption isotherms. In general, linear isotherms are obtained where $NH_4^+$ concentrations were relatively low. Ceazan *et al.* (1989) obtained linear isotherms for $NH_4^+$ in spiked uncontaminated groundwater at concentrations up to $25\ mg(NH_4\text{-}N)\,l^{-1}$. In contrast, DeSimone *et al.* (1996) obtained linear isotherms for groundwater containing $NH_4^+$ at concentrations up to $2\ mg(NH_4\text{-}N)\,l^{-1}$ whereas the Freundlich model best represented the sorption relationship at higher concentrations, up to $22\ mg(NH_4\text{-}N)\,l^{-1}$.

Cave & Taylor (2002) fitted a Freundlich isotherm to experimental data for which the $NH_4^+$ concentration was as low as $2\ mg(NH_4\text{-}N)\,l^{-1}$, although data obtained at much higher concentrations, up to $280\ mg(NH_4\text{-}N)\,l^{-1}$, were required to fully define the shape of the isotherm. Colley (1991) used both Freundlich and Langmuir isotherms to fit experimental data from three different lithologies at concentrations in landfill leachate between 35 and $185\ mg(NH_4\text{-}N)\,l^{-1}$, whereas Jackson (1989) used Langmuir isotherms only to describe sorption for four lithologies at concentrations in landfill leachate between 316 and $575\ mg(NH_4\text{-}N)\,l^{-1}$.

$K_d$ values from column experiments are obtained by assuming that a linear isotherm applies, but there is often insufficient evidence for the validity of linear isotherms. However, Thornton *et al.* (1996) showed that, at least for the system examined (landfill leachate in

Sherwood Sandstone), a linear sorption isotherm for $NH_4^+$ could be used to reproduce the results of detailed cation exchange modelling using a numerical reactive transport code. The $K_d$ values obtained for $NH_4^+$ by Thornton *et al.* (1996) are appropriate only for the leachate–aquifer systems studied. Moreover, the range of conditions under which complex multi-component ion-exchange reactions involving $NH_4^+$ can be described by a simple linear isotherm model remain poorly understood. Predictions of $NH_4^+$ transport under such conditions (e.g. landfill leachate plumes in geological media) should be undertaken using appropriate reactive transport codes. For example, PHREEQC or other models with comparable functionality use ion-exchange selectivity coefficients, which more correctly describe $NH_4^+$ exchange as a function of solution composition and exchanger properties (Appelo & Postma 1993; Tellam *et al.* 1997).

However, there is evidence that $NH_4^+$ sorption does not always occur by an exchange mechanism. Sorption of $NH_4^+$ to illite and other 2:1-type clay minerals may be an effectively irreversible process because the $NH_4^+$ ion fits into the intra-layer clay lattice. In soils with considerable illite content, interlayer-fixed $NH_4^+$ can typically account for 20–40% of the total nitrogen (Brady & Weil 2002). Discussing the data presented for Burntstump and Gorsethorpe landfills, Lewin *et al.* (1994*a*, *b*) and Harris (1988) noted that sorption of $NH_4^+$ is not accompanied by release of base cations as would be expected with ion exchange. Ceazan *et al.* (1989) obtained only 80% recovery of the $NH_4^+$ used to determine the sorption isotherm for a clay-poor sand and gravel.

## Solution composition

There is abundant evidence that $K_d$ values obtained in tests with $NH_4^+$ spiked artificial solutions (e.g. distilled or de-ionized water) can be significantly higher than $K_d$ values obtained when real landfill leachate is used. The use of artificially spiked solutions therefore causes greater uptake of $NH_4^+$ by mineral surfaces than that which would be observed using real landfill leachate. This observation is generally ascribed to the effects of competition for exchange sites by other cations that are present in the landfill leachate but absent from a spiked solution.

This effect was clearly observed in both Chalk and Mercia Mudstone by the Environment Agency (2000). For Chalk, $K_d^*$ values for an artificial $NH_4^+$ solution (10 mg($NH_4$-N) l$^{-1}$; pH 8) and leachate (4.24 mg($NH_4$-N) l$^{-1}$; pH 6.3) were 1.43 and 0.03 ml g$^{-1}$, respectively. This effect was, in part, probably due to the acidic leachate dissolving calcium from the rock matrix to compete with the $NH_4^+$ ions. In tests using Mercia Mudstone, artificial $NH_4^+$ solution and leachate (but at pH 7), $K_d^*$ values of 7.78 and 5.24 ml g$^{-1}$, respectively, were obtained.

Similar effects were observed by Freewood *et al.* (2001) in colliery spoils and by DeSimone *et al.* (1996) in sand and gravel. Cave *et al.* (2002) noted the opposite effect with leachate in which the $NH_4^+$ ion was in excess; these concentrations significantly affected the ability of the rock to adsorb potassium. These results indicate that either real landfill leachate or artificial solutions with the same ionic composition as the leachate or leachate-affected groundwater should be used to estimate $NH_4^+$ sorption if the techniques being used to predict transport do not account for multi-species competition.

## Lithology

Sorption of cations in aquifers primarily occurs at clay surfaces (and metal oxide surfaces, depending on conditions). The degree of sorption can often be explicitly related to the proportion of clay minerals in the aquifer material. Both Griffin *et al.* (1976) and Thornton *et al.* (2001) used column experiments to measure the attenuation of $NH_4^+$ in mineral landfill liners using landfill leachate. Griffin *et al.* (1976) tested mixtures of sand and montmorillonite, whereas Thornton *et al.* (2001) used mixtures of sand and Oxford Clay or Coal Measures Clay. In both cases the $K_d$ values varied linearly with clay content, within the concentration range of $NH_4^+$ in the leachates tested.

With regard to clay mineralogy, it has generally been found that mixed-layer clays (e.g. montmorillonite–smectite, including bentonite) adsorb $NH_4^+$ more strongly than two-layer clays, such as illite, which in turn adsorb $NH_4^+$ more strongly than single-layer clays, such as kaolinite (Stumm 1992). As such, partition coefficients of $NH_4^+$ to aquifer materials are implicitly related to their lithology and/or mineralogy. The Environment Agency (2000) reported $K_d^*$ values for UK aquitards and the series of clay mineralogy that shows broadly decreasing $NH_4^+$ sorption is: smectite (Gault Clay) > illite (Mercia Mudstone) > kaolinite (Oxford Clay).

## Implications for modelling of subsurface ammonium transport

In most cases competitive cation exchange will control $NH_4^+$ transport in a subsurface flow system. Under these conditions accurate description of $NH_4^+$ transport and attenuation requires the simultaneous solution of coupled non-linear equations. Although this is relatively simple for systems where transport processes are not important, such as landfill liners (Environment Agency 2002), the non-linearity of the equations prevents their use in simple transport equations. If transport is significant, numerical codes, such as PHREEQC (Pankhurst 1995) or MINTEQA2 (Allison *et al.* 1991), need to be used.
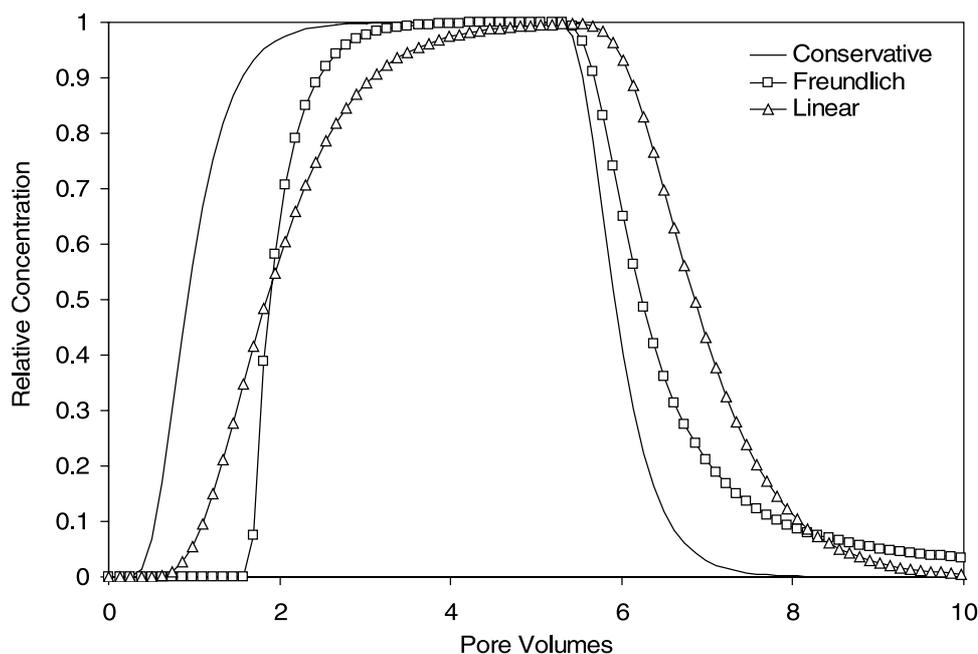
**Fig. 1.** Illustrative breakthrough and flushing curves for linear and Freundlich sorption models, generated using a model adapted from the column breakthrough model of Appelo & Postma (1993).

Modelling of column experiments shows that the sorption isotherm affects the shape of breakthrough curves (Appelo 1994). Because Langmuir and Freundlich isotherms adsorb relatively less at higher concentrations, they tend to have sharper initial breakthroughs and are shallower when approaching peak concentrations (Fig. 1). They also tend to have longer tails during flushing.

## Indicative partition coefficients for ammonium sorption in UK lithologies

Many of the studies quoted above show that the linear sorption model is appropriate for use in predicting $NH_4^+$ transport in dilute solutions. It is generally considered reasonable to expect the linear isotherm to be true at low concentrations under a very wide range of conditions, even when there are many substances adsorbed and when there is some heterogeneity (Milne *et al.* 2002). Table 2 presents a compilation of reported $K_d$ values from the reviewed literature, assuming that the linear sorption model is appropriate. They are considered relevant for screening risks associated with $NH_4^+$ transport and attenuation in different lithologies for dilute mixed solutions.

In Table 2, ranges are presented for probabilistic modelling purposes. Where two values for $K_d$ are given this indicates that a uniform distribution is suggested. If three are presented, the data are of sufficient quality to justify the use of a triangular distribution. Where there is uncertainty in the lower bounding value, a value of zero has been assumed. The exception is where knowledge of the lithology suggests that there will always be some

attenuation, in which case a value of 10% of the upper bound is used. Where possible, Table 2 has been based solely on values derived for mixed solutions, such as dilute landfill leachate, as these are more representative of field conditions.

The values provided are unlikely to be valid (and will not be conservative) for the assessment of transport through landfill liners or the unsaturated zone where there is migration of high-strength $NH_4^+$ solutions. Under these conditions the use of a linear isotherm model is likely to overestimate the amount of sorption. Modelling fate and transport in these circumstances, or where the outcome of a risk assessment is critical, is better accomplished using modelling tools that incorporate ion exchange processes and can take into account the detailed site hydrochemistry.

## Microbial attenuation of ammonium

### Contributory processes

Nitrogen is an essential component of cells and significant quantities of $NH_4^+$, nitrite, nitrate and organic nitrogen compounds may be utilized by active microorganisms. With the exception of highly fertile topsoils, microbial growth in the subsurface is constrained by the supply of oxidants, essential nutrients, substrates and other growth factors (Bitton & Gerba 1984). Consequently, biomass production is small and removal of $NH_4^+$ by uptake and incorporation into biomass will generally make an insignificant contribution to $NH_4^+$ attenuation in the subsurface.

**Table 2.** *Estimated partition coefficients for ammonium reported for a selection of UK lithologies.*

| Lithology (and references)[1] | $K_d$ range (ml g$^{-1}$)[2] | Comments |
|---|---|---|
| Chalk (7, 10) | 0–0.03 | Low confidence as isotherms have not been identified |
| Triassic Sherwood Sandstone (1, 4, 5, 7, 8, 10, 12) | 0–0.2–0.6 | Reasonable confidence as there have been several independent tests, although most values are from one site only (Burntstump) |
| Lincolnshire Limestone (7) | 0.065–0.65 | Low confidence as isotherms have not been identified |
| Lower Greensand 'Hassock' (4, 10) | 0.18–1.8 | Low confidence as no isotherms have been found. Measurements have been on the 'Hassock' lithology only. A lower bound of zero should be used for Lower Greensand in general |
| Lower Greensand (undifferentiated) (4, 10) | 0–1.8 | |
| Red Crag (10) | 0.05–0.5 | Low confidence as isotherms have not been identified |
| Oxford Clay (7, 13) | 0.135–1.35 | Based on modelling of column experiments |
| Mercia Mudstone (7) | 0.5–5 | Low confidence as isotherms have not been identified |
| Gault Clay (7) | 0.65–6.5 | Low confidence as isotherms have not been identified |
| Lias Clay (2) | 1.2–2.6 | Low confidence as isotherms have not been identified. Cave & Taylor (2002) presented higher $K_d^*$ values for lower concentrations |
| Coal Measures Clay (13) | 0.18–1.8 | Based on modelling of column experiments, being derived from clay–sand mixtures. Value of 1.8 ml g$^{-1}$ obtained for 100% clay system |
| Sand and gravel, clean (3, 6, 8, 11) | 0–0.4–0.9 | Reasonable confidence as there have been several independent tests. However, this is naturally a very heterogeneous lithology so a full site characterization should be made if the 'clayey' range of values is used |
| Sand and gravel, clayey (3, 6, 8, 11) | 0.4–0.9 | |
| Cohesive Boulder Clay (2) (Glacial Till) | 2–4 | Low confidence as isotherms have not been identified. Glacial Till is naturally a very heterogeneous lithology so a full site characterization should be made and the risk assessor must be very confident that there are no sandy sequences in the Till |
| Engineered clay landfill liners (9, 13) | 0.1–0.5–5 | Reasonable confidence as there have been a number of independent tests that yield seemingly consistent results. $K_d$ has been shown to correlate with clay content and/or CEC so less conservatism might be permissible with suitable testing and justification. Consideration should be given to the dominant clay mineral present |

References cited: (1) Butler *et al.* (2003); (2) Cave & Taylor (2002); (3) Ceazan *et al.* (1989); (4) Colley (1991); (5) Davison & Lerner (1998); (6) DeSimone *et al.* (1996); (7) Environment Agency (2000); (8) Erskine (2000); (9) Griffin *et al.* (1976); (10) Jackson (1989); (11) Kjeldsen & Christensen (1984); (12) Thornton *et al.* (2000); (13) Thornton *et al.* (2001).
[1]Values are considered to apply equally to both the unsaturated and saturated zones.
[2]Where two values for $K_d$ are given this indicates that a uniform distribution is suggested for probabilistic modelling; where three are presented then a triangular distribution is suggested.

Ammonium can also be oxidized by certain bacteria to generate energy, a process known as nitrification. Nitrification is generally a two-stage process; each stage is performed by different microorganisms, collectively known as nitrifiers:

$$NH_4^+ + 1.5 O_2 \rightarrow NO_2^- + H_2O + 2H^+$$
$$NO_2^- + 0.5 O_2 \rightarrow NO_3^-.$$
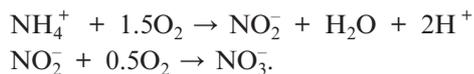
Carbon for biosynthesis in nitrifying bacteria is provided by dissolved $CO_2$ (as bicarbonate). Representing the chemical composition of microbial biomass as $C_5H_7NO_2$, the two stages of nitrification can be combined to give an overall reaction (Horan 1990):

$$NH_4^+ + 1.83 O_2 + 1.98 HCO_3^- \rightarrow 0.021 C_5H_7NO_2 + 1.041 H_2O + 0.98 NO_3^- + 1.88 H_2CO_3.$$
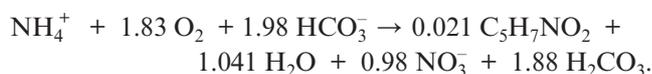
The process is aerobic (i.e. it requires oxygen) and oxygen consumption is *c.* 3.3 kg $O_2$ for each kilogram of $NH_4$-N degraded (i.e. 3.3 kg kg($NH_4$-N)$^{-1}$). This means that nitrification requires a continuous supply of oxygen. Biomass yield from nitrification is also low, *c.* 0.13 kg kg($NH_4$-N)$^{-1}$, which suggests that the growth of nitrifying bacteria will be slow.

Nitrification can also take place under anaerobic (i.e. oxygen-free) conditions with nitrate or manganese oxides acting as the oxidant, for example:

$$5NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 9H_2O + 2H^+$$
$$2NH_4^+ + 3MnO_2 + 4H^+ \rightarrow N_2 + 6H_2O + 3Mn^{2+}.$$
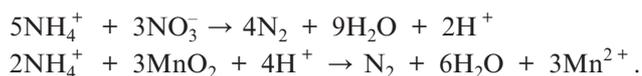
These reactions were originally observed in waste-water treatment processes (Mulder *et al.* 1995; Van de Graaf *et al.* 1995), but have more recently been demonstrated in soils and sediments and may play an important role in the natural nitrogen cycle (Schmidt *et al.* 2001; Thamdrup & Dalsgaard 2002). The contribution of anaerobic $NH_4^+$ oxidation to subsurface attenuation has not been significantly assessed to date.

The nitrite and nitrate generated by aerobic nitrification of $NH_4^+$ are susceptible to biological degradation (denitrification) to nitrogen ($N_2$) under anaerobic conditions. Further discussion of denitrification is beyond the scope of this review, except to note that this could consume nitrate that might otherwise be available for anaerobic $NH_4^+$ oxidation.

## The significance of nitrification in subsurface ammonium attenuation

There is clear evidence that nitrification can play a significant role in the attenuation of $NH_4^+$ in the unsaturated zone and groundwater (Erskine 2000). Such observations have been made for $NH_4^+$ contamination arising from contaminated sites (e.g. Torstensson *et al.* 1998), landfills (e.g. Bjerg *et al.* 1995) and effluent discharges to land (e.g. DeSimone *et al.* 1996; Lee & Bennett 1998). Under conditions where attenuation by cation exchange is limited, for example in clay-poor aquifers, nitrification can be the main process limiting development of an $NH_4^+$ plume (Christensen *et al.* 2000, 2001).

Most research has evaluated nitrification under aerobic conditions. Most studies have not determined the significance of anaerobic $NH_4^+$ oxidation under anoxic and anaerobic conditions. This is not surprising, as anaerobic $NH_4^+$ oxidation has only recently been recognized, but the study of Bjerg *et al.* (1995) had already highlighted the potential importance of anaerobic $NH_4^+$ oxidation before it had been directly demonstrated in soils and sediments. These workers reported that nitrification was an important process controlling the attenuation of $NH_4^+$ in a landfill leachate plume in a Danish sand–gravel aquifer, and demonstrated a major contribution from anaerobic $NH_4^+$ oxidation, possibly linked to microbial manganese-reduction. In contrast, other field studies have suggested that little or no anaerobic $NH_4^+$ oxidation occurs (e.g. DeSimone *et al.* 1996; Ptacek 1998; Torstensson *et al.* 1998; Gooddy *et al.* 2002). Consequently, it is not yet clear whether anaerobic $NH_4^+$ oxidation is an important attenuation process for many plumes or whether the process becomes important only under particular conditions.

## Environmental factors controlling subsurface nitrification

Nitrification is generally considered to be sensitive to environmental conditions and the presence of inhibitors, at least in wastewater treatment processes where most studies have been performed (USEPA 1993). Such inhibitory conditions may also arise in a contaminant plume and need to be taken into account when evaluating the behaviour of $NH_4^+$ pollution in the subsurface.

*Oxygen.* Aerobic nitrification in the subsurface will be limited by the supply of oxygen. This may be either the rate of oxygen (air) diffusion from the atmosphere or the infiltration of oxygenated recharge (Fetter 1999). As both nitrification and biodegradation of organic matter (either natural or contaminant compounds) consume oxygen, microbial activity in contaminated subsurface environments tends to consume oxygen more rapidly than it can be replenished and anaerobic conditions result (Christensen *et al.* 2001). In such cases, significant aerobic biological nitrification will be confined to the margins of the plume, where recharge by infiltration or mixing with uncontaminated, oxygenated groundwater by dispersion occurs. Furthermore, it should not be assumed that the unsaturated zone will contain oxygen, as monitoring at the Stangate East landfill indicated that the migration of methane could create anaerobic conditions in the subsoil beneath and around that landfill (Robinson 1989).

Anaerobic $NH_4^+$ oxidation is likely to occur only in the absence of oxygen, but the conditions that support this process in the subsurface are not known.

*Temperature.* Nitrification can be expected to occur at UK subsurface temperatures (groundwater typically around 11 °C). Rates used in assessing attenuation must be derived for ambient aquifer conditions.

*Acidity.* Nitrification is relatively sensitive to pH, in part because of the generation of ammonia ($NH_3$) under alkaline conditions and nitrous acid ($HNO_2$) under acidic conditions (USEPA 1993). Both substances inhibit nitrifying bacteria. The nitrification reaction itself generates acidity via the production of $H^+$ (see reaction above).

It is reasonable to infer that pH 6.5–8 is the optimum pH range for nitrification, but rates are likely to be significantly decreased below pH 6.0 or above pH 8.5 (USEPA 1993). However, Allison & Prosser (1993) have measured nitrification in natural environments at pH values as low as 3.7.

Soils are generally well-buffered systems but significant pH changes can be induced by alkaline or acidic contaminants present at contaminated sites. For landfill leachates containing a high proportion of putrescible organic matter, highly acidic leachate (e.g. pH 5–6) can

arise during the early period of leachate generation in domestic waste landfills (Department of the Environment 1995). Although not explicitly considering nitrification, a review by Mather (1989) provides pertinent information on microbial activity in the unsaturated zone of the Chalk and sandstone aquifers underlying landfills. Chalk and other calcareous formations appear to be sufficiently buffered to prevent detrimental pH changes, as are strata that contain a high proportion of clay minerals (as a result of ion exchange, although this capacity will ultimately become exhausted). However, in formations containing little clay and only a few per cent carbonate minerals (e.g. much of the Permo-Triassic sandstone) the pH may drop below 6.0 during the early period of landfill leachate generation. This can cause a significant decline in microbial activity (e.g. Thornton *et al.* 1996; Tellam *et al.* 1997). Older landfill leachates tend to have a neutral pH value and microbial inhibition as a result of pH changes is generally transient, although it may persist for a number of years (Department of the Environment 1995; Environment Agency 1999*b*).

*Ammonium concentration.* Except for the production of ammonia ($NH_3$) or nitrous acid at pH values outside the optimum range, nitrification in the subsurface does not appear to be sensitive to the $NH_4^+$ concentration. For topsoil, Malhi & McGill (1982) considered 400–800 mg($NH_4$-N) kg$^{-1}$ to be a reasonable upper concentration to ensure optimum nitrification under neutral conditions.

*Water content.* Nitrification does not take place in desiccated soils but is otherwise a viable process across the range of soil water contents normally found in the unsaturated zone in the UK (Malhi & McGill 1982; Flowers & O'Callaghan 1983). Rates of aerobic nitrification in unsaturated zone soils will tend to decrease at high water contents as a result of reduced oxygen availability.

*Presence of other contaminants.* Nitrification in wastewater treatment is often relatively sensitive to inhibition by organic and inorganic components (e.g. USEPA 1993), such as heavy metals and many organic contaminants that may also arise from industrially contaminated sites or landfills. However, there has been little research on their effects on nitrification in the subsurface.

Deni & Penninckx (1999) reported the effects of hydrocarbon contamination on the rate of nitrification in loamy sand topsoils obtained from an agricultural source and an oil refinery site. The addition to the soil of diesel fuel hydrocarbons at a concentration of 4000 mg kg$^{-1}$ had no detrimental effect on nitrification in the agricultural soil but inhibited nitrification in the refinery soil by *c*. 50%. It was demonstrated that this inhibition was not due to toxic effects but rather to competition for mineral nutrients by hydrocarbon-degrading bacteria stimulated by the addition of diesel.

Broholm & Arvin (2000) found no nitrification in laboratory microcosms constructed with samples from a coking waste-contaminated site on the Triassic Sherwood Sandstone aquifer, even after biodegradation had removed a significant proportion of the dissolved organic contaminants. Those workers noted that the lack of nitrification may have been due to the absence of aerobic nitrifying bacteria in the strongly anaerobic samples collected.

*Salinity.* Nitrifying bacteria appear to be relatively sensitive to changes in salinity. Many reports indicating nitrification inhibition at high concentrations of inorganic $NH_4^+$ have found that this was due to osmotic shock caused by the added salts (e.g. Malhi & McGill 1982; Flowers & O'Callaghan 1983).

Rapid changes in salinity can therefore affect nitrification rate. However, adaptation to elevated salinity occurs relatively readily (USEPA 1993) and dissolved salts in landfill leachates (Department of the Environment 1995) are not expected to have a significant detrimental long-term effect on nitrification.

## The significance of hydraulic flow paths

The majority of microbial biomass in the subsurface is attached to solid surfaces. Consequently, most microbiological metabolism in subsoils and aquifers occurs at the mineral surface–water interface (Fredrickson & Fletcher 2001). The nature of hydraulic flow in the subsurface will therefore play a significant role in determining the rate and ultimate capacity of nitrification and other biological attenuation processes.

Intergranular flow provides a high surface area to volume ratio for microbial growth and the pore space is the location of greatest biomass and metabolic activity (see data for the Chalk and sandstone of Blakey & Towler (1988) and the Environment Agency (1999*b*)). The exception to this is when the pore spaces are too small to permit the entry of microorganisms. For example, Rees (1981) noted the absence of microbial activity in the pore spaces of unfissured Lower Chalk beneath a landfill in Oxfordshire. Whitelaw & Rees (1980) confirmed the presence of nitrifying bacteria in the unsaturated zone, to a depth of at least 50 m, of the Middle and Upper Chalk underlying agricultural land but proposed that microbial activity was confined to fissures. Both studies concluded that penetration of microbial cells (typical diameter 1 μm) was precluded by the small pore sizes of the Chalk matrix (median diameter 0.22 μm for the Lower Chalk and 0.5–0.7 μm for the Middle and Upper Chalk; Rees 1981). Based on these studies it appears unlikely that a large microbial population can develop in the pore space of the Chalk matrix. Consequently, there could be a much lower capacity for

nitrification in poorly fissured Chalk aquifers. In general, the pore sizes of the matrix of other UK aquifers are larger (British Geological Survey & Environment Agency 1997, 2000) and therefore are likely to have the capacity to support an active microbial population for nitrification (Environment Agency 2001).

Conversely, where large fractures represent the predominant flow pathway in a formation, there will be a small surface area for microbial growth relative to the fracture volume, and a comparatively short hydraulic residence time within the fractures. Consequently, the rate of biodegradation activity in a fracture flow system will be low compared with an otherwise similar intergranular system (Mather 1989). The reduced biodegradation potential of organic contaminants in aquifers during fracture flow is well known (e.g. Wealthall *et al.* 2001) and the aquifer capacity for nitrification may similarly be significantly less in such systems. Selection of a model that adequately simulates conceptual model assumptions (relating to both hydrogeological and microbiological processes), including both flow and degradation within fracture and matrix environments, is essential. The common approach of simulating flow and attenuation in fractured aquifers by assuming a low effective porosity value within a porous medium model is unlikely to be sufficiently robust to accurately represent pollutant behaviour in fractured aquifers.

## Measured rates of nitrification in subsurface environments

There is relatively little information on subsurface nitrification rates, except for topsoils. DeSimone *et al.* (1996) reported a long-term mass balance evaluation for contaminants arising from a rural sewage treatment plant soakaway in Massachusetts, USA. Ammonium was almost completely removed during transport through the unsaturated subsoil zone (sandy soil) with nitrification being the predominant attenuation mechanism. The estimated rate of nitrification was *c.* 0.017 kg(NH$_4$-N) day$^{-1}$, corresponding to a half-life of *c.* 13 days at the discharge NH$_4^+$ concentration of 27 mg(NH$_4$-N) l$^{-1}$. However, such rates are likely to occur only where high biological growth rates can be supported by other nutrients in the contaminant mixture. The assumption adopted by DeSimone *et al.* (1996) and many others is that NH$_4^+$ degradation is a first-order process, which requires estimation of a single parameter equivalent to a half-life.

The much slower rates of nitrification that can be expected under typical aquifer conditions were illustrated by Erskine (2000), who discussed nitrification rates obtained from field data for two landfill leachate plumes. At the Llwn Isaf landfill in North Wales,

aerobic nitrification in the shallow sand–gravel aquifer was calculated to result in an NH$_4^+$ half-life of *c.* 6 years. Data for the Sherwood Sandstone aquifer underlying the Burntstump landfill in Nottinghamshire (Lewin *et al.* 1994a) suggested a half-life close to 3.5 years, although more recent work at the same site by Butler *et al.* (2003) suggested a half-life of 2.2 years.

Where a high concentration of NH$_4^+$ exists, the rate of nitrification in deeper subsoils and aquifers may be inadequate for it to be distinguished from abiotic processes, except at the margins of a plume. A similar situation may result from the presence of high concentrations of biodegradable organic contaminants. For example, in a mixed organics–ammonium plume in the Triassic Sherwood Sandstone, Torstensson *et al.* (1998) were unable to determine the rates of nitrification, although geochemical evidence clearly indicated that it took place. This may have been due to the relatively high concentrations of dissolved NH$_4^+$, or to the preferential biodegradation of the organic contaminants (Broholm & Arvin 2000), or both.

## Nitrification kinetics

The kinetics of nitrification in wastewater biotreatment processes have been intensively studied and modelled, commonly using Monod kinetics (USEPA 1993). Readers are directed to Kovárová-Kovar & Egli (1998) for a fuller description of the principles of Monod and related kinetic expressions. In contrast, nitrification kinetics in subsoil and groundwater have received little attention.

Selection of an appropriate kinetic model (Bekins *et al.* 1998; Suarez & Rifai 1999) for subsurface nitrification will be complicated by a number of factors. Where NH$_4^+$ concentrations show significant spatial variation (e.g. within a groundwater plume), different kinetic models may be appropriate in different regions of the plume. First-order kinetics, which have been widely applied for modelling biodegradation of organic contaminants, are applicable for biological processes only when the substrate concentration is significantly below the reaction half-saturation constant ($K_s$). Such conditions may well apply towards the margins of a plume, as $K_s$ values for nitrifying bacteria are generally 0.2–5.0 mg(NH$_4$-N) l$^{-1}$ (USEPA 1993). However, a zero- or second-order model may be more appropriate at other NH$_4^+$ concentrations or where site data support its use. Monod and other kinetic expressions that incorporate microbial growth may be inappropriate in subsoil and groundwater where limiting conditions mean that net biomass growth of nitrifiers may be insignificant. Furthermore, a necessary input to these models is a number of biological parameters, few of which have been determined for nitrifying organisms growing under subsurface conditions. As a further complication, the greatest proportion of subsurface nitrification activity is

likely to result from biomass present on mineral surfaces (Fredrickson & Fletcher 2001), which may require special kinetic models.

In a study of biodegradation kinetics for groundwater contaminant fate and transport modelling, Davison & Lerner (1998) found that degradation rates were often relatively insensitive to the biological parameters applied in the Monod model. They concluded that it may be acceptable to assume that the degradation reaction is instantaneous relative to groundwater velocity. Based on a dataset from a column study, Davison & Lerner (1998) argued that the instantaneous reaction assumption could apply to aerobic nitrification, but noted considerable uncertainty as to when this assumption may be valid.

The selection and application of an appropriate kinetic model for nitrification is complicated and suffers from a lack of relevant parameter data. When the effect of biodegradation modelling plays a critical role in determining the impact of $NH_4^+$ contamination, the justification for the kinetic model applied ought to be carefully made on the basis of appropriate site-specific data, but for screening purposes a simpler approach may be used.

Of equal importance is the method used to simulate biodegradation of contaminants sorbed to aquifer minerals. Many contaminant fate and transport methods assume that degradation of contaminants can occur in both sorbed and aqueous phases. However, sorption may affect the bioavailability of contaminants (Bosma *et al.* 1997) and it may therefore be necessary to model biodegradation using different rate constants for the dissolved and sorbed contaminant fractions (Zheng & Bennett 1995). In the extreme case, degradation may be inhibited by sorption and although sorption may reduce the apparent velocity of a contaminant plume in an aquifer, it will not reduce the concentration eventually observed at the receptor.

## Indicative rates of nitrification under UK subsurface conditions

There are very few data on measured rates of nitrification in unsaturated subsoils and aquifers. It is evident from the literature that nitrification can play a significant role in controlling the concentrations of $NH_4^+$ in infiltrating water and contaminated groundwater. Aerobic nitrification is particularly important at plume margins, where the influx of oxygenated groundwater via dispersion is sufficient to support this process. However, the literature is contradictory on whether anaerobic $NH_4^+$ oxidation is a significant process in the subsurface, especially at high contaminant concentrations.

It is apparent from the literature that nitrification can occur in most formations, except where intergranular flow takes place through pore spaces too small to allow the access of microorganisms (an average pore diameter of <1 μm; Rees 1981). The dataset is insufficient to allow conclusions to be made on parameterization of kinetic models for nitrification in the subsurface. Estimated ranges for the first-order degradation half-life of $NH_4^+$ in UK subsoils and aquifers have been derived from the published literature (Table 3) but caution must be used in their application, as they are based on a very limited dataset and extrapolation from broader studies. With the present state of knowledge, it is not possible to provide more reliable guidance, and further research on subsurface nitrification under both aerobic and anaerobic conditions is essential. Although the rates of nitrification are slow, the long contaminant travel times that apply in many cases mean that indigenous nitrifiers may have the opportunity to achieve significant mass removal of $NH_4^+$ (Robinson 1992).

## Conclusions

Significant attenuation of $NH_4^+$ contamination in subsoils and groundwater is predominantly due to cation exchange and/or nitrification (biological oxidation) processes. A literature review (Environment Agency 2003*b*), of which this paper is a summary, has provided a moderate amount of data on $NH_4^+$ sorption for a number of UK geological strata and engineered landfill liners. The degree of $NH_4^+$ attenuation is strongly dependent on the clay mineralogy of the strata and the chemical composition of the contaminated fluid. However, sufficient evidence was available to provide a range of partition coefficients for $NH_4^+$ in UK lithologies. The literature indicates that nitrification can be a significant mechanism for $NH_4^+$ attenuation in unsaturated subsoils under both aerobic and anaerobic conditions. However, in aquifers nitrification may be limited by the relatively low aqueous solubility of dissolved oxygen (maximum $10 \text{ mg l}^{-1}$ at standard temperature and pressure) and physical mixing by dispersion of the anaerobic $NH_4^+$ plume with aerobic groundwater.

Based on the limited literature available, estimates of the typical degradation rate and attenuation capacity under both aerobic and anaerobic conditions have been derived (Tables 2 and 3). These values may be helpful in the initial (screening) phases of risk assessment for landfills, sewage effluent disposal to land, and potentially contaminated sites. However, the ranges provided are indicative and site-specific data will always be preferred and will be necessary for more detailed risk assessments or when the conceptual model for the site under consideration does not match that from which the presented data originate. In such cases, it is recommended that more sophisticated reactive transport modelling should be undertaken using codes that

**Table 3.** *Estimated half-lives for $NH_4^+$ biodegradation (nitrification) in different subsurface lithologies under aerobic and anaerobic conditions.*

| Lithology[1] | $NH_4^+$ half-life under aerobic conditions (years)[2] | $NH_4^+$ half-life under anaerobic conditions (years)[3] | Comments |
|---|---|---|---|
| Sands and gravels | 1–6 | ∞ | Based on range of literature-derived values (<1–6 years) in unsaturated subsoil and aquifers |
| Unfissured Chalk and other strata with mean pore size of <1 μm | ∞ | ∞ | No degradation; pore size excludes entry of bacteria |
| Strata with mean pore size of >1 μm or showing a significant degree of fissure flow[4] | 5–10 | ∞ | No kinetic data exist but attenuation has been demonstrated to take place. Suggested range (5–10 years) is considered reasonably conservative |
| Landfill liners | ∞ | ∞ | No data, but pore size may exclude entry of bacteria. Assume no degradation to ensure liner design suitably conservative |

Estimated half-lives are taken from literature and extrapolated to representative systems, which must be consistent with the conceptual model to which the data are applied during risk assessments.

[1]Values are considered to apply equally to both the unsaturated and saturated zones.

[2]Where a range is given a uniform distribution is recommended for probabilistic modelling.

[3]It is assumed that no anaerobic $NH_4^+$ oxidation takes place unless site-specific data indicate otherwise.

[4]Where mean pore sizes in the matrix of dual porosity media are less than 1 μm (e.g. fissured Chalk) care should be taken that only the fraction of contaminant flowing in the fractures is degraded by the model used.

describe the fundamental ion-exchange reactions controlling $NH_4^+$ transport in natural porous media. This approach will provide a more accurate and robust prediction of $NH_4^+$ fate in the subsurface than that which can be achieved at present using partition coefficients.

The literature review has shown that there are few data on $NH_4^+$ sorption by cation exchange in UK subsoils and aquifer solids, and there is even less information on nitrification. Further evaluation and quantification of these processes *in situ* under UK conditions would be of significant benefit.

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