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The role of humic non-exchangeable binding in the promotion of metal ion transport in groundwaters in the environment

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Metal ions form strong complexes with humic substances. When the metal ion is first complexed by humic material, it is bound in an 'exchangeable' mode. The metal ion in this fraction is strongly bound, however, if the metal–humic complex encounters a stronger binding site on a surface, then the metal ion may dissociate from the humic substance and be immobilised. However, over time, exchangeably-bound metal may transfer to a 'non-exchangeable' mode. Transfer into this mode and dissociation from it are slow, regardless of the strength of the competing sink, and so immobilisation may be hindered. A series of coupled chemical transport calculations has been performed to investigate the likely effects of non-exchangeable binding upon the transport of metal ions in the environment. The calculations show that metal in the non-exchangeable mode will have a significantly higher mobility than that in the exchangeable mode. The critical factor is the ratio of the non-exchangeable first-order dissociation rate constant and the residence time in the groundwater column, metal ion mobility increasing with decreasing rate constant. A second series of calculations has investigated the effect of the sorption to surfaces of humic/metal complexes on the transport of the non-exchangeably bound metal. It was found that such sorption may reduce mobility, depending upon the humic fraction to which the metal ion is bound. For the more weakly sorbing humic fractions, under ambient conditions (humic concentration *etc.*) the non-exchangeable fraction may still transport significantly. However, for the more strongly sorbed fractions, the non-exchangeable fraction has little effect upon mobility. In addition to direct retardation, sorption also increases the residence time of the non-exchangeable fraction, giving more time for dissociation and immobilisation. The non-exchangeable dissociation reaction, and the sorption reaction have been classified in terms of two Damkohler numbers, which can be used to determine the importance of chemical kinetics during transport calculations. These numbers have been used to develop a set of rules that determine when full chemical kinetic calculations are required for a reliable prediction, and when equilibrium may be assumed, or when the reactions are sufficiently slow that they may be ignored completely.

1. Introduction

Over the past decade, models have been developed that are able to predict the humate-mediated transport of metal ions in laboratory column experiments (*e.g.* Warwick *et al.*¹ Schuessler *et al.*,^{2,3} Artinger *et al.*,⁴ Bryan *et al.* 2005⁵). At the same time, there have been a number of batch experimental studies that have improved our knowledge of the metal ion–humate system. These studies have shown that humic substances bind metal ions in two different modes.⁶ It seems that initial uptake is to an 'exchangeable' fraction, where the metal ion is bound strongly, but may be removed instantaneously if a stronger

competing sink is encountered. Over time, the metal may transfer to the 'non-exchangeable' fraction(s). In this state, the metal is not more strongly bound, but it may not dissociate instantaneously, rather its release is kinetically controlled. It is effectively isolated from all direct contact with solution and mineral surface chemistry, and the rate at which it dissociates from the humic substance is fixed and independent of the concentration or strength of any competing sink. While it is effectively 'trapped' within the non-exchangeable fraction, the metal ion takes on the characteristics of its humic host. Further, recent column experiments and associated modelling have shown that the interaction of humic material, and hence also metal–humic non-exchangeable complexes, with mineral surfaces (sorption) may affect metal ion transport significantly.⁵ Moreover, the interaction between the humic substance and surface may also be slow.^{7,8}

Clearly, humic-derived kinetics may have implications for field-scale migration studies. However, although the influence

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of non-exchangeable binding in laboratory experiments has been studied, as yet the implications for pollutant metal ion migration in the environment have not been determined. Given that humic interactions can affect the transport behaviour of metal ions, including radionuclides, there are potential implications for the post-closure radiological performance assessment (RPA) of nuclear waste repositories. However, calculations that include chemical kinetics are computationally expensive. Current approaches to RPA calculations assume equilibrium, and to include kinetics directly would be inconvenient. Therefore, it is important to identify exactly when it is necessary to include them explicitly in transport calculations.

1.1 Metal ion–humate kinetics

King *et al.*⁶ analysed the dissociation of Eu^{3+} from fulvic and humic acid complexes. They found that although a significant fraction was exchangeably bound, and could be removed from the humic substance either instantaneously or within a few minutes, there were also a series of progressively more slowly dissociating fractions. Amongst those, there was a distinct, most long-lived component, which was the slowest desorbing, and could be described with a single rate constant, which was in the range of 10^{-6} – 10^{-7} s^{-1} , depending upon the sample. The rates were found to be insensitive to pH and the presence of competing cations, including Ca^{2+} (10^{-4} M), Al^{3+} (10^{-6} M) and Fe^{3+} (10^{-6} M).

Geckeis *et al.*⁹ also studied the dissociation of metal ions from humic substances. Two sets of experiments were performed. In the first, Eu^{3+} was added to humic acid in the laboratory, and its dissociation rate determined by resin exchange. In the second, dissociation rates for the metal ions that were naturally present in a humic-rich groundwater (including Eu) were determined using the same method. For the Eu added in the laboratory, the kinetic data were fitted with two humic non-exchangeable components: one relatively quickly dissociating and a slower one. With time, there was a movement of material from the faster to the slower component, which was accompanied by a shift of the bound Eu to larger humic species. For the Eu naturally present in the groundwater, the dissociation rates were slower, between 2.0×10^{-6} and $2.3 \times 10^{-7} \text{ s}^{-1}$, compared with 7.72×10^{-5} and $1.85 \times 10^{-6} \text{ s}^{-1}$ for the Eu added in the laboratory. More than this, there was a third fraction (*ca.* 28%) that showed no significant dissociation over the time of the experiment (100 days). Therefore, its dissociation rate could not be determined, but it must be significantly lower than the $2.3 \times 10^{-7} \text{ s}^{-1}$ determined for the second fraction. This fraction appears to be ‘pseudo-irreversibly’ bound.

In a similar study, Bryan *et al.*¹⁰ have studied the dissociation of anthropogenic actinides from a humic acid sample from West Cumbria, UK. The sample had been ‘naturally’ labelled with actinides in the discharges from the Sellafield nuclear reprocessing plant. Dissociation rate constants were determined for Am and Pu derived from the discharge. Because of the Sellafield discharge history, a large fraction of the Am and Pu would have been present at the site for approximately 25 years. For ^{241}Am , the dissociation rate

constant was $5.9 \times 10^{-8} \text{ s}^{-1}$, with 28% in the non-exchangeable fraction.

The importance of Am–humate interaction kinetics was shown during a series of batch and column experiments using sandy material from the Gorleben aquifer in Germany (equilibrated with humic substances for several months).¹¹ In the batch experiments, the removal of Am from the humic substances to the surface was slow, and more than 1000 h were required for equilibration. In the column experiments, the amount of metal–humate complex that broke through reduced with decreasing flow rate, as column residence time increased. Significantly, breakthrough increased with the length of time that the Am^{3+} and humic species were allowed to equilibrate prior to injection. Subsequent analysis² showed that this behaviour was associated with transfer of metal ion to the non-exchangeable fraction. Very similar behaviour was observed in pulsed uranium experiments.¹²

1.2 Mineral surface/humic substance interactions

Humic substance mobility is key to its impact upon metal ion transport. If the humic substance itself is not mobile in the environment, then regardless of its affinity for the metal ion, or the rate of dissociation, it will not promote migration. It has been known for some time that humic substances may sorb to inorganic surfaces,¹³ and that the adsorption and desorption processes may be slow. It is important to consider the effect of humic/metal complex sorption, because metal ‘trapped’ in the non-exchangeable fraction will behave with the characteristics of the humic material until it has had time to dissociate. However, there is some uncertainty about the effect upon metal ion transport, since some column experiments may be simulated using an equilibrium approach to humic sorption, whilst some require a kinetic description, and for others it is not necessary to consider humic sorption at all.^{1,5}

The uptake of humic substances by surfaces has been studied previously, mostly *via* batch experiments. A number of studies^{14–16} have found that the adsorption step may be simulated with Langmuir or modified Langmuir isotherms, although the derived parameters may be conditional, and the various humic fractions within the bulk population may have different interactions with the surface.¹⁷ Although the interaction mechanisms are uncertain, most recent authors agree that it is not possible to treat humic substances as single, or simple, ligands (*e.g.* Lenhart and Honeyman¹⁸). Even considering the sorption step on its own, the inherent humic heterogeneity must be addressed in some way to simulate the data. For example, Lenhart and Honeyman¹⁸ used a multi-ligand, equilibrium, approach with five distinct components, each with a distinct interaction, whilst Gu *et al.*¹⁹ have adopted a modified Langmuir model that does assume a single humic species, but where the affinity for that species varies with surface coverage. These systems show considerable hysteresis, or irreversibility, and a number of studies have found that some fractions desorb only very slowly,¹⁹ whilst others have found that for some fractions, even sorption can be slow.^{7,8} Some observed hysteresis effects may at least in part be due to the fact that fractionation accompanies sorption.^{20,21} McCarthy *et al.*^{22,23} have also conducted field tracer tests on

the mobility of natural organic matter in an iron-coated sandy aquifer. They found that there was retardation of material, but only of certain fractions. Although larger, more hydrophobic material did show evidence for retardation, the smaller, more hydrophilic fraction behaved like a conservative tracer.

Column experiments with Hg have demonstrated the impact of humic sorption upon metal ion mobility.²⁴ In the absence of humic substances, Hg was severely retarded, and no breakthrough was observed until 100 pore volumes, but in the presence of humic acid (HA), there was rapid breakthrough and Hg elution exactly followed the humic breakthrough, although it was still retarded with respect to a conservative tracer. The humic-bound Hg had assumed the properties of the humic material, and it was sorption of the humic/metal complex that was controlling the transport of the metal. Warwick *et al.*²⁵ have also demonstrated the retardation of humic/metal complexes, and Bryan *et al.*⁵ have observed the retardation of humic/metal complexes in column experiments, even when the column was pre-equilibrated with the humic substance concentration used during metal injection. However, others have observed the unretarded (conservative) transport of at least a fraction of humic/metal complexes in equilibrated column experiments.^{11,12}

1.3 Metal ion and humic transport models

There are two components to the interaction of metal ions and humic substances: the exchangeable and the non-exchangeable. Here, we concentrate upon the non-exchangeable; however, most work has concentrated upon the exchangeable, the initial strong uptake of metal ions by humic substances. For that component, it is found that there is significant heterogeneity, and for a single humic sample, there is a distribution of binding strengths. A number of advanced models that describe the exchangeable interaction have been developed, in particular the NICA model that uses a continuous distribution approach to simulate the heterogeneity²⁶ and Model V/VI that uses a number of discrete sites.²⁷ However, these models do not take account of the subsequent transfer to the non-exchangeable fraction.

In reality, there is a continuum of first-order dissociation rates between the instantaneous (*i.e.* the exchangeable) and the distinct, most long-lived (most slowly dissociating) fraction that accounts for a significant amount of the non-exchangeable metal (between 10 and 80%).⁶ Column modelling has shown that in order to simulate transport, it is necessary to include the non-exchangeable effect. Most approaches consider only two humic-bound components: the exchangeable and the slowest non-exchangeable fraction.^{1–3,5} Only one study⁴ has used an intermediate fraction. In most cases, the intermediate fractions effectively behave as if they were exchangeable. Many authors have found that even for the exchangeable fraction, there is a wide spectrum of binding strengths.²⁸ However, it seems that this too need not be included in order to simulate transport in laboratory column experiments.

Using the k1-D transport code, Bryan *et al.*⁵ modelled the effect of humic substances upon the transport of Co^{2+} through columns packed with sand and Eu^{3+} through intact

sandstone blocks. In both cases, two humic-bound metal fractions were required, exchangeable and non-exchangeable. For both Eu^{3+} and Co^{2+} , in the absence of humic substances, there was no significant elution, and in the case of Co^{2+} , sectioning revealed that all of the metal remained at the top of the column. The Co^{2+} behaviour in the absence of humic substances was equivalent to a (dimensionless) K_d of 1×10^6 . For the Co^{2+} experiments, the columns were not equilibrated with the humic substance prior to the injection of the metal. The humic/ Co^{2+} complex was retarded with respect to a conservative tracer, but the sorption appeared to be reversible and a single equilibrium constant was used to describe the behaviour. In the case of the Eu^{3+} experiments, the columns were pre-equilibrated with the humic substance but humic/ Eu^{3+} complex retardation was still observed. This time, the interaction appeared more complex, and required two kinetic equations and rate constants. However, Warwick *et al.*¹ were able to predict Eu^{3+} transport in humic-equilibrated columns using the k1-D code without considering the sorption of the humic/metal complex, although these experiments used sand rather than sandstone.

The KICAM chemical model has been used on several occasions to model the behaviour of radionuclides in column and batch experiments.^{2–4} Early versions had only two humic-bound components, one fast dissociating and another slower. Later, a third intermediate fraction was added. In common with the approach of Warwick *et al.*¹ and Bryan *et al.*,⁵ initial uptake is to the exchangeable or fastest fraction, and subsequent transfer between humic fractions is first order in both directions. The first-order dissociation rate for the most slowly dissociating fraction is $1 \times 10^{-6} \text{ s}^{-1}$.^{2–4}

Am-pulsed columns¹¹ were analysed by Schuessler *et al.*² using the KICAM model. The two-fraction version was used to model simultaneously column and batch data. Later, the two-site version of the KICAM model was incorporated within the k1-D transport code to predict the movement of Am in the columns.³ The majority of the Am–humic complex that did elute was unretarded. In fact, it eluted slightly ahead of one pore volume, probably due to size exclusion effects. However, there was a smaller amount of material that eluted more slowly, and appeared as a tail on the elution peak. These tails represent only a very minor fraction of the eluted metal, and are only visible on a log scale.¹¹ When the experiments were modelled by Schuessler *et al.*,³ these tails were not addressed, and it was assumed that all humic materials and complexes transported conservatively. However, van de Weerd and Leijnse²⁹ modelled the same data using two kinetic reactions, one to describe the interaction of Am with the humic substance (dissociation rate constant = $7.17 \times 10^{-6} \text{ s}^{-1}$) and another for the sorption of the humic–Am complex (desorption rate constant = $6.94 \times 10^{-6} \text{ s}^{-1}$). This approach was able to explain the tails on the main elution peaks, which they proposed were due to retardation of the humic–Am complex by sorption. In uranium-pulsed column experiments, also with Gorleben aquifer material, again there was rapid metal breakthrough associated with the humic acid just before one pore volume.¹² The amount of rapidly eluting material increased with pre-equilibration time, and decreased with column residence time. Tails on the main elution peaks were

also observed here, but were more significant than for Am. The origin of these tails is unclear. It is highly unlikely that this metal is not humic colloid associated since a much more significant retardation would be expected in the absence of humic material. This is either material that has been stripped from the humic substance, sorbed on the surface and then remobilised by fresh humic material, or more likely it is a humic–metal complex that has been sorbed on the surface and then displaced. Later Am column experiments required the three-fraction version of KICAM to explain the results.⁴ An extra fraction was required because of the larger range of pre-equilibration and contact times, which were in the range of 1 h to 3.5 years. Again, humic–metal complex sorption was not included in the model. In addition to the three ‘normal’ humic-bound fractions, evidence was also found for a fourth, inert, fraction of metal, which accounted for only a few percent of the Am, but whose concentration seemed to be independent of pre-equilibration time. Importantly, this fraction eluted through the columns regardless of the column residence time, *i.e.* this fraction appears to be instantaneously (pseudo-) irreversibly bound.

Most transport modelling has naturally focussed upon simulating the behaviour of the metal rather than the humic substance itself. However, there have been a few attempts to predict humic transport. McCarthy *et al.*^{22,30} modelled humic sorption with a two-site approach, whilst Gu *et al.*¹⁹ adapted their modified Langmuir model of sorption with an extra hysteresis parameter. Bryan *et al.*⁵ have modelled the transport of humic substances in pulsed and continuous flow column experiments. For un-equilibrated pulsed columns, humic sorption could be modelled with a single equilibrium constant. In continuous flow equilibrated experiments, the humic substance was still retarded, and two kinetic reactions were required to simulate the behaviour. In both cases, the same constants were used to model the transport of the humic–metal complex.

In the literature, the approach of van de Weerd *et al.*^{7,8} to humic sorption stands out, and it has been applied successfully to batch, column and field tracer data. The model assumes that the heterogeneity of the surface is small compared with that of the humic material, and so a single surface site is defined. The different humic fractions, categorised in terms of size and hydrophobicity, compete for the same humic binding site. Differences in size between the fractions mean that molecules of each fraction occupy a different surface area when sorbed. Hence, the surface capacity (defined either in number of molecules or mass per unit area) varies with fraction number. Each fraction has a chemical equation and

an associated kinetic Langmuir isotherm. For each fraction, *i*, a fractional surface coverage, θ_i , is defined,

$$\theta_i = \frac{Q_i}{Q_{i,\max}} \quad (1)$$

where Q_i is the amount of fraction *i* actually sorbed at the surface, and $Q_{i,\max}$ is the amount of material that would be sorbed if the surface were saturated only with material of fraction *i*. If θ_T is the total fractional surface coverage due to all *N* fractions, then,

$$\theta_T = \sum_{i=1}^N \theta_i \quad (2)$$

For each fraction, the amount of material as a fraction of the total in the bulk is represented by *f*. If $[HA_i]$ is the solution concentration of fraction *i* in solution (expressed in mg of carbon per $\text{dm}^3 = \text{mg C dm}^{-3}$), then the rate of change of Q_i is given by,

$$\frac{dQ_i}{dt} = k_{a,HA_i}[HA_i](Q_{i,\max}(1 - \theta_T)) - k_{d,HA_i}Q_i \quad (3)$$

where k_{a,HA_i} is the rate constant for the sorption reaction ($\text{dm}^3 \text{ mg}^{-1} \text{ s}^{-1}$) and k_{d,HA_i} is the first-order desorption rate constant (s^{-1}). The ratio of $k_{a,HA_i}/k_{d,HA_i}$ gives the equilibrium constant for the sorption of fraction *i* at the surface, K_{HA_i} . This ‘NOMADS’ model has successfully modelled the sorption of humic substances by iron oxide.⁷ By incorporating it within a 1-D transport code, it was also able to simulate laboratory column experiments and field-scale tracer studies.⁸ Van de Weerd *et al.*^{7,8} use either six or three fractions when modelling humic sorption. Excellent fits were found in all cases, and the NOMADS model is the best available description of the transport of humic material. Table 1 shows parameters for the six-fraction approach.⁸ As humic material size increases, so does sorption affinity. However, both the forward and backward rates decrease with size. Therefore, when the fractions compete for fresh surface sites, the model predicts that the smaller species might initially coat the surface, because of their faster kinetics. However, with time, at least some of this material could be displaced by larger species, depending upon humic concentration. At higher concentrations, equilibrium might not be attained, even after 700 h.⁸

1.4 Evidence from the environment

Direct evidence for the rapid transport of radionuclides in the environment by natural organic matter has been provided by McCarthy *et al.*²³ Am and Cm have been mobilised from

Table 1 Model parameters used by van de Weerd *et al.*⁸ to model humic substance sorption

Fraction name	Abundance of fraction as a function of total humic concentration, <i>f</i>	Humic sorption forward rate constant, $k_{a,HA_i}/\text{dm}^3$	Humic sorption backward rate constant, $k_{d,HA_i}/\text{s}^{-1}$	Humic sorption equilibrium constant, $K_{HA_i}/\text{dm}^3 \text{ mg C}^{-1}$	Sorption capacity of solid phase, $Q_{i,\max}/\text{mg C kg}^{-1}$
Hl: $M_w < 3 \times 10^3$	0.19	1.05×10^{-5}	1×10^{-4}	0.105	106.86
Hb: $M_w < 3 \times 10^3$	0.30	1.49×10^{-5}	7.08×10^{-5}	0.210	151.73
Hl: $3 \times 10^3 < M_w < 10^5$	0.08	1.82×10^{-6}	5.19×10^{-7}	3.50	170.99
Hb: $3 \times 10^3 < M_w < 10^5$	0.36	2.57×10^{-6}	3.67×10^{-7}	7.02	242.78
Hl: $M_w > 10^5$	0.04	5.75×10^{-7}	1.64×10^{-8}	35.0	172.46
Hb: $M_w > 10^5$	0.03	8.14×10^{-7}	1.16×10^{-8}	70.1	244.86

unlined disposal trenches at the Oak Ridge site in the United States, particularly during periods of high rainfall (and high flow rate). The radionuclides are observed to travel rapidly, despite the fact that both have high affinities for the mineral surfaces present at the site (K_d in the range 1×10^5 to 1×10^7 $\text{dm}^3 \text{kg}^{-1}$). Analysis of the mobile Am and Cm shows that they are associated with natural organic matter. Activity is able to migrate a distance of 15 m in a time range between a few days and a few weeks, which corresponds to a linear velocity in the range of $8.7\text{--}1.2 \times 10^{-5} \text{ms}^{-1}$. To investigate the mechanisms responsible for the high mobility of Cm and Am, a field-scale lanthanide injection experiment was conducted at the same site.³¹ Over a distance of 10 m, Nd^{3+} and Br^- tracer arrived together after only 2–4 days (linear velocity in the range $5.8\text{--}2.9 \times 10^{-5} \text{ms}^{-1}$). Eu^{3+} and Br^- appeared together at two sampling points, which were 50 and 73 m from the injection point after only 18 days (linear velocities of 3.2×10^{-5} and $4.7 \times 10^{-5} \text{ms}^{-1}$, respectively). The Eu^{3+} K_d with sediment from the site in the absence of humic substances is $19\,600 \pm 1280 \text{dm}^3 \text{kg}^{-1}$, which should give a retardation factor of the order of 50 000. Clearly, the metal ions are much more mobile than this.

1.5 Potential effects of humic kinetics in the environment

The ternary system of metal ion, humic substance and mineral surface is very complex. There are multiple bound metal fractions, and these will be present in humic substances both in solution and sorbed to surfaces. The reaction between the humic substance and mineral surface is no less complex than the metal humic system, and is less well understood.

In the case of the metal–humate interaction, there is general agreement that transport in laboratory column experiments can only be explained by the non-exchangeable binding of metal ions. For the humic–metal complex surface interaction, the literature provides no clear consensus. Sometimes humic sorption is neglected completely (*e.g.* Warwick *et al.*,¹ Schuessler *et al.*³), at other times equilibrium approaches seem to work,⁵ whilst in others a kinetic approach is necessary.^{5,29} Clearly, metal–humate complexes are capable of travelling as conservative tracers, and without retardation. This has been observed repeatedly in both laboratory column and field-scale injection experiments. More than this, column experiments have shown that the metal fraction that transports is the non-exchangeable. However, this does not mean that we can assume that in all cases non-exchangeably-bound metal will always transport conservatively. For example, at the Oak Ridge site, some part of Cm–, Am–, Eu– and Nd–humate have all been observed to travel conservatively,^{23,31} but that does not mean that some other fraction of the metal–humate complex has not been retarded. Further, in the column

experiments where a fraction of the metal elutes as a conservative tracer,^{11,12} there is no direct proof that other fractions were not retarded. The nature of the surface will obviously have an effect, as will the state of equilibration. Those experiments where the surfaces are equilibrated with the humic material prior to injection of the metal–humate complex tend to be those where metal transport may be explained without including retardation of the metal–humate complex,^{2,4} although this is not always the case.⁵ Systems that are not pre-equilibrated, or those where the injection of the metal ion is accompanied by an increased concentration of humic substances are those that do require humic/humic–metal complex sorption to be treated explicitly.⁵

The importance of non-exchangeable binding has been studied in laboratory column experiments, and there it is clear that it promotes metal ion mobility. However, the likely effects upon metal ion migration in the environment have not yet been determined. Therefore, the aim of this work is to determine the likely effects of humic non-exchangeable binding in field-scale transport calculations. Also, given that kinetic processes are inconvenient in transport calculations, the relationship between chemical rate constants and groundwater column residence time will be investigated, and rules developed that predict when and in what manner the chemical kinetics should be considered in field-scale studies, and when approximations may be used.

2. Experimental, results and discussion

All calculations were performed using the k1-D coupled chemical transport code, which has been used to predict metal transport in column experiments;^{1,3,5} its development, testing and application have been described elsewhere.³

2.1 Calculations excluding humic acid sorption

To make a calculation the hydrological and chemical parameters must be selected. Table 2 shows the parameters that were used for the initial calculations. Molecular diffusion was assumed to be insignificant compared with advection and dispersion. Porosity was set to 0.3, because this is typical of both the column experiments used to calibrate the model and also the conditions at the field site modelled by van de Weerd *et al.*⁸ A hypothetical column length of 100 m was chosen with a linear flow rate of $1 \times 10^{-6} \text{m s}^{-1}$, which is reasonable for a shallow porous site.⁸ A total simulation time of $5 \times 10^7 \text{s}$ was selected, since even a conservative tracer would not have saturated the column in that time.

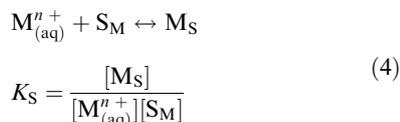
There does seem to be some uncertainty about the importance of the sorption of humic–metal complexes in transport. Some authors have found it necessary to include sorption

Table 2 Conditions and parameters used in transport calculations

Column length, L/m	100	Total mineral surface metal ion binding site concentration, $[\text{S}_T]/\text{mol dm}^{-3}$	5.70×10^2
Dispersivity ($L/10 \text{m}$)	10	Humic exchangeable binding site concentration, $[\text{HA}_{\text{exch},T}]/\text{mol dm}^{-3}$	1.98×10^{-5}
Porosity	0.3	Humic exchangeable equilibrium constant, $K_{\text{exch}}/\text{dm}^3 \text{mol}^{-1}$	8.33×10^5
Linear flow rate, $V/\text{m s}^{-1}$	1×10^{-6}	Metal ion/mineral surface equilibrium constant, $K_S/\text{dm}^3 \text{mol}^{-1}$	1.50×10^6
Simulation time/s	5×10^7	Humic non-exchangeable association rate constant, k_f/s^{-1}	2.29×10^{-8}
		Humic non-exchangeable dissociation rate constant, k_b/s^{-1}	5.9×10^{-8}

processes, whilst others have been able to model transport without. Therefore, the first set of calculations have assumed that the sorption of humic–metal complex does not occur, *i.e.* the only process that will retard the transport of the metal is the direct interaction of the metal ion with the mineral surface. We will return to the possible effects of humic sorption later.

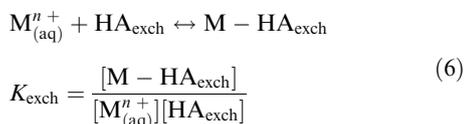
A simple chemical model was used to simulate the interaction of the contaminant metal ion with both the surface and the humic colloid. The approach is essentially that used by Bryan *et al.*^{1,3,5} to model a large number of column experiments. The interaction of the metal ion, M^{n+} , with the mineral surface is assumed to be rapid, and is described with an equilibrium reaction and constant, K_S ,



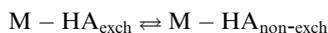
where S_M is the mineral surface metal binding site and M_S represents metal ion sorbed to the surface, and the total surface site binding concentration, $[S_T]$, is given by

$$[S_T] = [S_M] + [M_S] \quad (5)$$

Initial uptake to the humic exchangeable site is also treated as an equilibrium process,



whilst the transfer between the exchangeable and non-exchangeable fractions is described with a rate equation and constants, k_f and k_b ,



$$\frac{d[M - HA_{\text{non-exch}}]}{dt} = k_f[M - HA_{\text{exch}}] - k_b[M - HA_{\text{non-exch}}] \quad (7)$$

where HA_{exch} is the humic exchangeable site, $M - HA_{\text{exch}}$ and $M - HA_{\text{non-exch}}$ are metal ions bound to the humic material in the exchangeable and non-exchangeable fractions, respectively, K_{exch} is an equilibrium constant, and k_f and k_b are first-order rate constants. The charge of the humic substance and humic–metal complex, which will vary from molecule to molecule, is not shown. The total humic exchangeable binding site concentration, $[HA_{\text{exch},T}]$, is given by

$$[HA_{\text{exch},T}] = [HA_{\text{exch}}] + [M - HA_{\text{exch}}] \quad (8)$$

Note, the term ‘exchangeable’ does not imply that the metal ion is bound *via* an ion exchange mechanism. The metal ion is bound as an inner sphere coordination complex with multiple bonds between the metal ion and the humic acid functional group atoms. The exchangeable label indicates that the metal is instantaneously available for removal by a stronger competing ligand or surface binding site, whilst release from the ‘non-exchangeable’ mode is slow. Also, depending upon pH, the complexation of metal ions by the humic substance could be accompanied by the release of protons. These are not shown in

eqn (6). As a result, the magnitude of the equilibrium constant K_{exch} as defined in eqn (6) will be a function of pH. The effect of this variability is explored below.

The values of the chemical parameters are given in Table 2. The humic substance concentration (1.8 mg dm^{-3}) is that measured at the site studied by McCarthy *et al.*²³ and van de Weerd *et al.*,⁸ whilst the total injected metal ion concentration, $[M_T]_{\text{inj}}$, was $1 \times 10^{-10} \text{ mol dm}^{-3}$. K_{exch} , K_S , $[HA_{\text{exch},T}]$ and $[S_T]$ have been taken from Schuessler *et al.*³ The values of k_f and k_b were taken from Bryan *et al.*,¹⁰ since these were the rate constants determined for a humic acid ‘naturally’ labelled with Am. The sensitivity of the calculations to all of these parameters is discussed later.

All of the calculations have assumed that the humic acid concentration is constant at all points along the column. Hence, the initial column pore water has the same humic acid concentration as the injected solution. However, the column is free of metal ion at the start ($t = 0$). In column experiments, it is common to inject a short pulse of metal-containing solution followed by an electrolyte. However, in the environment the continuous injection of a contaminant metal ion seems a more likely scenario. Therefore, in all of these calculations, there is continuous injection of metal at a constant concentration. The partition between $M - HA_{\text{exch}}$ and $M - HA_{\text{non-exch}}$ in the injected solution was calculated assuming that the two fractions were in equilibrium, *i.e.*

$$[M - HA_{\text{non-exch}}]_{\text{inj}} = (k_f/k_b)[M - HA_{\text{exch}}]_{\text{inj}} \quad (9)$$

where the subscript ‘inj’ indicates that this is the concentration of that species in the solution entering the column.

Fig. 1 shows the results of a calculation using the system of processes given in eqn (4)–(9) and the parameters in Table 2 (◆). The results are plotted as a distribution plot, which shows the total metal concentration, $[M_T]$ ($= [M_{(aq)}^{n+}] + [M - HA_{\text{exch}}] + [M - HA_{\text{non-exch}}] + [M_S]$) present at a given distance from the injection end of the column. For comparison, the results of a calculation excluding non-exchangeable binding altogether are shown (□): in this calculation, eqn (7) was removed and all the metal placed in the exchangeable fraction (*i.e.* $[M - HA_{\text{exch}}]_{\text{inj}} = [M_T]_{\text{inj}}$). The results in the absence of humic acid are also shown (△). Comparing the three plots, the presence of the non-exchangeable fraction results in significant transport. There is very little difference between the ‘exchangeable only’ and ‘no humic acid’ plots. Under these conditions, in the absence of non-exchangeable binding, the humic acid is predicted to have little effect. In the plot that includes non-exchangeable binding the two distinct types of metal ion behaviour are discernible. The metal held in the exchangeable fraction is very easily removed by the mineral surface, and this is responsible for the sharp fall in concentration at short distances. In fact, the majority of the metal has not moved past the top of the column. Although the humic acid exchangeable interaction shows a high affinity for metal ions, the strong affinity and vast excess of surface sites means that the exchangeable fraction does not travel very far before being sorbed onto the surface. Beyond the sharp initial fall, there is a long, shallow curve stretching to the end of the column. This is metal from the non-exchangeable fraction that

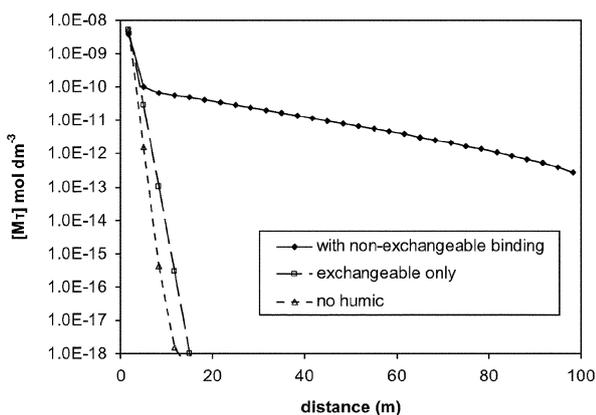


Fig. 1 Distribution of metal with distance, calculated using eqn (4)–(9) and the parameters in Table 2. Result including non-exchangeable binding shown as \blacklozenge , excluding non-exchangeable binding as \square , and excluding humic acid effects altogether as \triangle .

has been transported much further down the column. Experiments have shown that the non-exchangeable fraction is not more strongly bound than the exchangeable fraction, and that there is a small free energy difference between the two fractions.⁶ However, the dissociation of the metal from the non-exchangeable fraction is kinetically controlled, and the number or affinity of surface sites is no longer sufficient to prevent the movement of the radionuclide. The critical factor becomes the time that is available for transfer from the non-exchangeable to the exchangeable fractions to take place. If there is time for the metal to transfer, then it will not migrate, but, for example, if the flow rate is sufficiently fast, then it will. Clearly, the two fractions are behaving very differently, and for the purposes of their migration it is possible to treat them as essentially independent, once they are exposed to a mineral surface.

Using the parameters selected for this calculation, kinetics are having an effect. However, there is uncertainty over the values of the rate constants (k_f and k_b) that are applicable in the field, and a range of values have been reported from the various batch and column experiments. Also, in reality, each humic sample shows a range of non-exchangeable behaviour from instantaneously reversible (exchangeable) to the most long-lived non-exchangeable. In this calculation only the slowest fraction has been treated explicitly. The intermediate fractions will have dissociation rates that are faster. Further, it has been found that some metal ions that are ‘naturally incorporated’ into humic substances show slower dissociation than those added to humic substances in the laboratory, and some part of the metal loading dissociates so slowly that a rate constant cannot be defined (pseudo-irreversible behaviour).⁹ Therefore, it is important to study the effect of the choice of values for the rate constants k_f and k_b . Hence, a series of calculations was performed using different values of k_b and k_f . The two were varied together, such that the ratio of k_f/k_b remained constant (all other parameters were unaffected). The results of these calculations are shown in Fig. 2.

As the dissociation rate constant, k_b , increases, the extent of metal migration decreases. As k_b falls, mobility increases and the behaviour tends to some limit, for example, a calculation

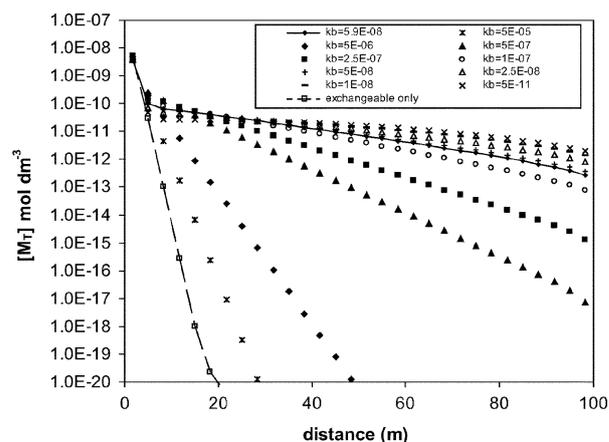


Fig. 2 Effect of rate constant, k_b , upon the distribution of metal down the column.

with $k_b = 1 \times 10^{-8} \text{ s}^{-1}$ produces virtually identical behaviour to one with $k_b = 5 \times 10^{-11} \text{ s}^{-1}$. The behaviour of the exchangeable fraction is unaffected by changes in k_b . To understand better the behaviour of the non-exchangeable fraction, it is helpful to separate out its contribution from that of the exchangeable fraction. Fig. 3 shows ratio plots for the same values of k_b as in Fig. 2: here the distribution of the non-exchangeable fraction down the column is expressed as a ratio of its concentration at the top of the column. The advantage of this type of plot is that it allows direct comparison with other species, regardless of the absolute concentration. In addition to the non-exchangeable fraction, the behaviours of a conservative tracer and the exchangeable fraction are also shown in Fig. 3. As k_b increases, the non-exchangeable fraction migrates less effectively (lower ratio at any given distance), because it transfers from the non-exchangeable to the exchangeable fraction increasingly quickly, and as soon as it does, it is rapidly removed to the mineral surface. As k_b increases, the non-exchangeable fraction

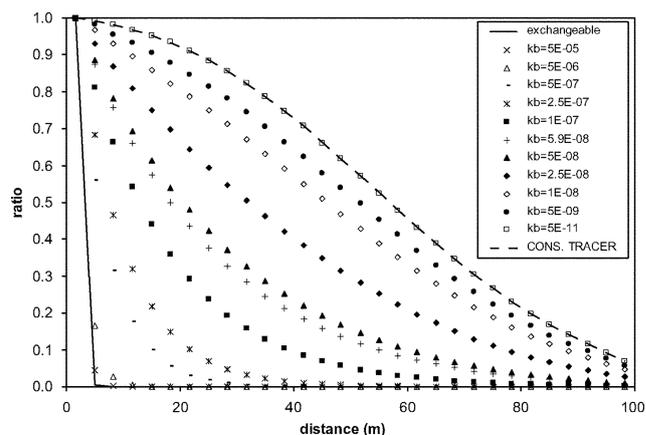


Fig. 3 Ratio plot – variation in concentration of non-exchangeably-bound metal with dissociation rate constant, k_b . Behaviour of exchangeably-bound metal and a conservative tracer are also shown. Data expressed as $[i]_x/[i]_{x=0}$ where $[i]_x$ and $[i]_{x=0}$ are concentrations of species i at distance x and $x = 0$, respectively.

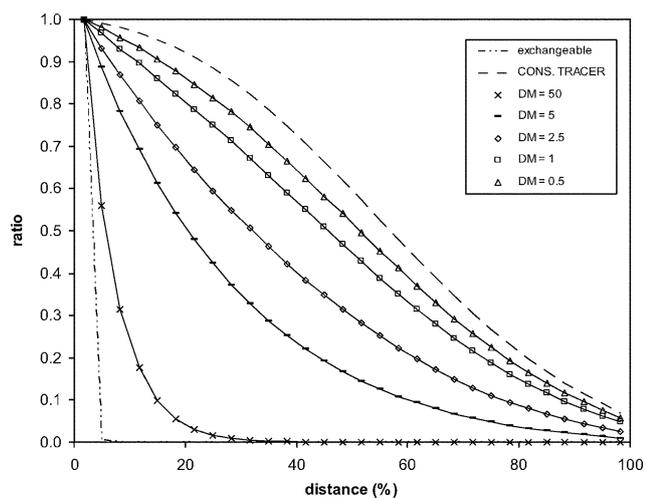


Fig. 4 Ratio plot (see Fig. 3 caption for definition) for two linear flow rates: (i) $1 \times 10^{-6} \text{ s}^{-1}$ (lines); (ii) $1 \times 10^{-5} \text{ s}^{-1}$ (symbols). In both cases, $T = 0.5$. Data are plotted against percentage distance [= $100(x/L)$].

behaves increasingly like the exchangeable fraction, and for $k_b > 5 \times 10^{-6} \text{ s}^{-1}$, the non-exchangeable plot appears identical to that of the exchangeable fraction. Conversely, as k_b decreases, its behaviour tends towards that of a conservative tracer, and for $k_b < 5 \times 10^{-9} \text{ s}^{-1}$, the behaviour is virtually identical.

The behaviour of a species controlled by kinetics may be rationalised using Damkohler numbers. Jennings and Kirkner³² applied Damkohler numbers to slow sorption onto surfaces during transport. The situation here is different, because the slow reactions involve species in the mobile phase (humic substances) rather than the stationary. The dimensionless Damkohler number for the non-exchangeable fraction, D_M , is defined by

$$D_M = \frac{L}{V} k_b \quad (10)$$

where L is the length of the column, and V is the linear flow rate. In this work a second dimensionless number, T , is defined as

$$T = \frac{tV}{L} \quad (11)$$

where t is the total elapsed time of the calculation.

Fig. 4 shows non-exchangeable ratio plots for different values of k_b , where some of the calculations shown in Fig. 3 are reproduced again (shown as lines), along with a second series of calculations performed with exactly the same chemical parameters but with a flow rate ten times higher and a simulation time ten times lower (results shown as symbols). All of the results in Fig. 4 have the same T ($= 0.5$). The plots for the higher flow rate (symbols) match exactly with plots at the lower flow rate (lines) that have the same D_M . At a flow rate a factor of ten higher, a rate constant a factor of ten higher is required to produce the same results. The x -scale in Fig. 4 is expressed in terms of percentage of the hypothetical column length, L , rather than absolute distance, since systems with the same D_M and T always give the same plots, regardless of the

actual column length (provided that the dispersivity, relative to L , is constant).

It is clear that the dissociation rate constant, k_b , is controlling transport. However, there are a number of other chemical parameters in these calculations, and the sensitivity of the results to these parameters must also be tested. To test sensitivity, calculations were performed based upon the standard parameter set (Table 2). However, each time, one parameter was varied whilst the remainder were kept constant. The specific tests were:

A: increasing humic acid concentration by a factor of ten (new $[\text{HA}_{\text{exch},T}] = 1.98 \times 10^{-4} \text{ mol dm}^{-3}$);

B: increasing the humic-metal exchangeable binding strength (K_{exch}) by a factor of ten (new $K_{\text{exch}} = 8.33 \times 10^6$);

C: decreasing the humic-metal exchangeable binding strength (K_{exch}) by a factor of ten (new $K_{\text{exch}} = 8.33 \times 10^4$);

D: increasing the mineral surface metal binding strength (K_S) by a factor of ten (new $K_S = 1.50 \times 10^7$);

E: decreasing the mineral surface metal binding strength (K_S) by a factor of ten (new $K_S = 1.50 \times 10^5$);

F: increasing the total metal concentration by a factor of ten (new $[\text{M}_T] = 1 \times 10^{-9} \text{ mol dm}^{-3}$), whilst keeping the distribution between exchangeable and non-exchangeable fractions constant (72%/28%);

G: decreasing the total metal concentration by a factor of ten (new $[\text{M}_T] = 1 \times 10^{-11} \text{ mol dm}^{-3}$), whilst keeping the distribution between exchangeable and non-exchangeable fractions constant (72%/28%);

H: increasing the forward rate constant, k_f , by a factor of ten (new $k_f = 2.29 \times 10^{-7}$), whilst keeping the distribution between exchangeable and non-exchangeable fractions constant ($[\text{M-HA}_{\text{non-exch},\text{inj}}] = 0.28 \times 10^{-10} \text{ mol dm}^{-3}$);

I: decreasing the forward rate constant, k_f , by a factor of ten (new $k_f = 2.29 \times 10^{-9}$), whilst keeping the distribution between exchangeable and non-exchangeable fractions constant ($[\text{M-HA}_{\text{non-exch},\text{inj}}] = 0.28 \times 10^{-10} \text{ mol dm}^{-3}$);

J: changing the distribution between exchangeable and non-exchangeable fractions, moving all the metal into the exchangeable fraction, leaving the non-exchangeable fraction empty at the point of injection, whilst keeping both k_f and k_b constant ($[\text{M-HA}_{\text{non-exch},\text{inj}}] = 0$, $[\text{M-HA}_{\text{exch},\text{inj}}] = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$).

The results of these sensitivity tests are shown in Fig. 5, along with the original result from Fig. 1 (line). The data are presented as total metal concentration vs. distance, normalised to the total injected metal concentration (necessary because of tests **F** and **G**). As a guide, the result of the calculation from Fig. 1 where the non-exchangeable fraction was removed completely is also shown in Fig. 5 (\blacktriangle).

Relatively large changes to humic exchangeable binding strength (K_{exch}), mineral surface binding strength (K_S) or humic acid concentration have little effect upon the predictions. The mineral surface with its high affinity and large site concentration is a much stronger effective sink than the humic acid itself, and the mismatch is so great that even large changes in $[\text{HA}_{\text{exch},T}]$, K_S or K_{exch} do not allow exchangeably-bound metal to transport significantly. Total metal concentration, $[\text{M}_T]$, also has no real effect, largely because it does not affect the relative partition between the exchangeable and

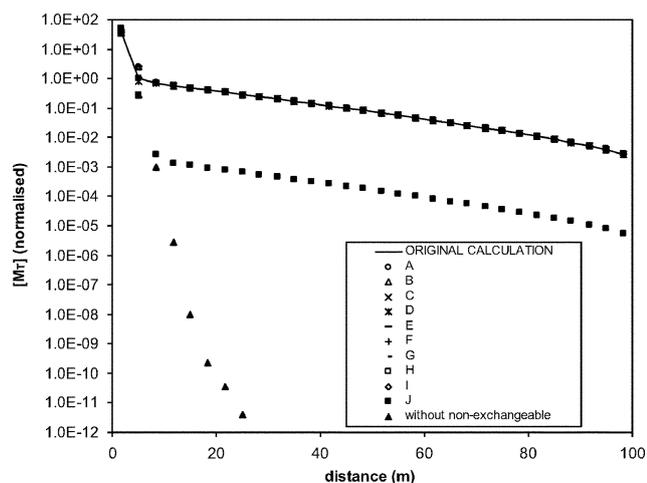


Fig. 5 Results of sensitivity tests A–J: tests defined in the text. Data plotted as the distribution of metal $[M_T]$ vs. distance, normalised to the injection concentration.

non-exchangeable fractions. Hence, moderate perturbations in $[M_T]$ have no effect, although there clearly must be some limit to this behaviour, since the humic acid only has a finite binding capacity. Provided that the bound metal represents less than *ca.* 10% of the humic acid binding site capacity, there is no significant effect. It might be more surprising that the value of the forward rate constant, k_f , has no effect, given that k_b is so significant. However, the exchangeable fraction is unable to compete with the mineral surface, and virtually all metal is stripped out of that fraction as soon as the humic–metal complex enters the column. As non-exchangeable metal slowly dissociates, it is also removed to the mineral surface instantaneously. As there is virtually no available metal in the exchangeable fraction to transfer into the non-exchangeable fraction, the value of k_f is not important. In calculations **H** and **I**, the partition of metal between exchangeable and non-exchangeable fractions was kept constant as k_f varied. However, in reality, changing the value of k_f relative to k_b would change the equilibrium distribution between the two fractions, and hence the amount of non-exchangeably-bound metal entering the column. This was investigated in the final sensitivity test (**J**). Here, all the metal was assigned to the exchangeable fraction before injection. This could be due either to a very short pre-equilibration time or an unusually small value of k_f . This is the only one of the sensitivity tests that has produced a significant difference. As expected, there is much less transport, since the non-exchangeable metal fraction is responsible for mobility. This result mirrors observed behaviour. For example, Artinger *et al.*¹¹ found that with pulsed Am columns, when the pre-equilibration time tended to zero, *i.e.* as the amount of metal non-exchangeably-bound tended to zero, breakthrough decreased. In test **J**, the non-exchangeable fraction is still present and k_f and k_b with their associated reactions are still present: only the concentration in the injection solution has been set to zero. Even though the non-exchangeable fraction is empty at injection, the presence of the reaction still has an effect. There is enhanced transport compared with the case with no non-exchangeable fraction at

all (**▲**). It is still promoting transport, but the amount of metal transporting is far smaller (an approx. factor of 400). Although the amount of metal ion that remains in the exchangeable fraction in the presence of the mineral surface is very small, it is not zero, and as metal accumulates at the top of the column the absolute amount in the exchangeable fraction will increase with time. Some of this small concentration of exchangeably-bound metal will transfer to the non-exchangeable fraction, which will then transport as before. It is significant that beyond the top of the column, the plot for test **J** runs virtually parallel to the others. Hence, although this metal has entered the non-exchangeable fraction after injection, it still behaves in an identical manner to that which is present in the fraction prior to injection. This is due to the large reduction in metal concentration beyond the top of the column – the metal entering the non-exchangeable fraction there swamps any transferring in further down the column. Therefore, these calculations predict that the only significant parameters will be the dissociation rate constant, k_b , and the amount of metal in the non-exchangeable fraction in the injection solution. More than this, for a given pair of k_b and $[M_{\text{non-exch}}]_{\text{inj}}$, the final distribution of metal with distance will depend only upon D_M and T .

Returning to the ratio plot (Fig. 3), it is clear that as k_b varies, there are two limiting behaviours: that of the exchangeable fraction at high k_b , and that of the conservative tracer at low k_b . The distinction between equilibrium and kinetic reactions is always artificial, since it depends upon the time scale of the observation. A reaction which may be treated as an ‘equilibrium’ over periods of hours, may well be ‘slow’ on a time scale of seconds. Given the conditions of the transport calculation, flow rate and column length, it is possible to reduce any series of reactions, regardless of origin or chemistry, to just three classes:

- (1) those reactions that are sufficiently fast to be treated as equilibria, *e.g.* high k_b ;
- (2) those that are sufficiently slow that they effectively do not take place (low k_b);
- (3) those reactions that can only accurately be described by the use of rate equations (intermediate k_b).

Therefore, we have the possibility of using the limiting behaviours if k_b is sufficiently large or small. Approximations are common in complex systems, but in the case of calculations for RPA there is a special requirement that any approximations should be conservative, *i.e.* they should not produce an underestimate of radionuclide transport. Hence, the viability of approximations will depend upon the application, and in the case of RPA whether or not they are conservative.

Approximations. Given that all systems with the same D_M number behave in exactly the same way, we may use D_M to judge the impact of chemical kinetics, and hence to judge when it is necessary to include chemical kinetics explicitly in transport calculations. As the value of D_M decreases, the non-exchangeably-bound metal tends towards the behaviour of a conservative tracer. This gives us our first alternative to including chemical kinetics in the transport calculations, the ‘decoupled’ approximation.

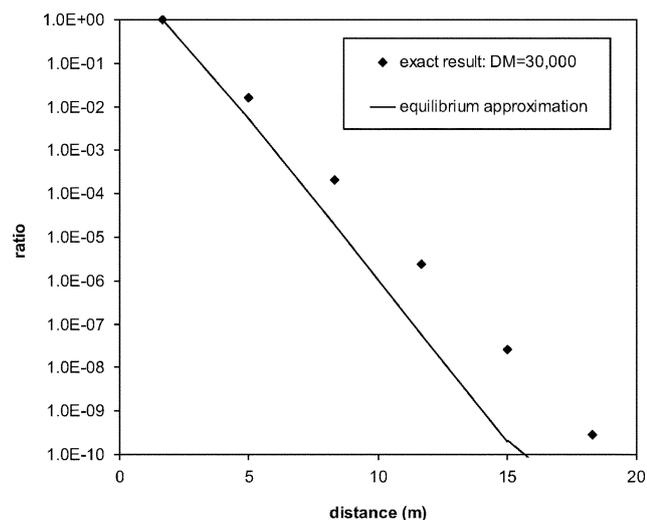


Fig. 6 Exact solution (◆) and equilibrium approximation (—) for a system with $D_M = 30\,000$.

Decoupled approximation. For systems with low D_M , virtually no metal ion can leave the non-exchangeable fraction in the time it takes to traverse the column. Therefore, once the partition between $M-HA_{\text{exch}}$ and $M-HA_{\text{non-exch}}$ in the injection solution has been calculated, the reaction that connects the exchangeable and non-exchangeable fractions is removed from the calculation and the two fractions are treated as independent species. Beyond the fact that it reduces the mathematical complexity of the model system (and hence computing time), the great advantage of this technique is that it is inherently conservative. The non-exchangeable fraction only tends towards the behaviour of a conservative tracer. Therefore, if we assume that it moves as a conservative tracer, then we will always overestimate its migration.

Equilibrium approximation. At the other extreme of high D_M values, the behaviour of the non-exchangeable fraction tends towards that of the exchangeable. Therefore, the alternative approximation – the equilibrium approximation – assumes that the non-exchangeable fraction may be treated in exactly the same way as the exchangeable fraction. The equilibrium assumption is simple to apply since most field-scale transport models assume equilibrium. One simply replaces the rate constants and rate equations with equilibria, *i.e.* assuming that all dissociation from the humic acid occurs instantaneously. Again, this will remove the kinetics from the calculation. However, although the behaviour of the non-exchangeable fraction does tend towards that of the exchangeable, it always moves slightly further than the exchangeable, *i.e.* this approximation is not conservative. The size of the error will decrease as D_M increases, but it will always be there. The main influence of humic kinetics is to increase migration. Therefore, any approximation that assumes that kinetics do not exist must be non-conservative. Fig. 6 shows an example ratio plot (see above) for $D_M = 30\,000$, which is well into the region where one would expect an assumption of equilibrium to be reasonable. However, even in this case, the equilibrium assumption has underestimated the

extent of migration, and as D_M decreased, the effect would become progressively more pronounced. It is possible that the difference between the exact and approximate results might not be significant. That would depend upon the magnitude of the upper boundary concentration of the radionuclide. In terms of the total distribution, the difference between the two plots is certainly small, representing less than a 1% error. How much of a problem this would be in the case of a real RPA exercise would depend upon the individual circumstances. It is clear that care must be taken when using an equilibrium approximation.

At intermediate values of D_M , neither the decoupled nor the equilibrium approximations will provide reliable results. At present, to include the kinetic reaction is the only way to produce reliable predictions in this region, although this will be computationally expensive. Indeed, many field-scale models such as those used in RPA do not include kinetics. However, the fact that behaviour depends only upon k_b and D_M means that an estimate of transport could be provided by ratio plots of the type shown in Fig. 3, although a library of these would be required, both to account for differences in T (Fig. 3 is only valid for $T = 0.5$) and also for systems with different transport properties, for example, the dispersivity of the system or variations in diffusion, *etc.*

Ranges of validity for approximations. Ideally, we would like a set of rules that would allow us to decide when to use a given approximation. However, that will depend upon the acceptable error. The equilibrium approximation is particularly problematic, since its estimates are not conservative. Since the decoupled approach is always conservative, it might be tempting to adopt it in all cases. The problem is that assuming that the radionuclide moves as a conservative tracer would lead to a gross overestimation of transport in many cases. Fig. 7 shows the variation in the fit for the decoupled and equilibrium approximations for the calculations in Fig. 3, expressed as χ^2 ,

$$\chi^2 = \sum_{i=1}^N \frac{(\text{approx}_i - \text{exact}_i)^2}{\text{approx}_i} \quad (N = 30) \quad (12)$$

where exact_i and approx_i are the exact value of the non-exchangeable ratio and the value for the approximation for column subdivision i , respectively. The point at which the error becomes unacceptable will depend upon the application. Beyond this, there is also uncertainty about the magnitude of the rate constant k_b , and so for a system with known V and L there could be a range of possible D_M values. To eliminate this uncertainty, experiments would be required using the site-specific humic substance to determine the most appropriate value of k_b . Once k_b has been properly defined, then it would be possible to define conditions where the two approximations or ‘full kinetics’ could be used. Fig. 8 (linear flow rate vs. distance) shows an example: the area is divided into a series of regions. In region ‘A’, the decoupled approximation is appropriate, and this will be still be true moving into the slice labelled ‘a’, but as we move down and right, the error introduced with the decoupled approximation will get larger and larger, although the prediction will always be conservative. In the bottom right hand corner (region ‘B’),

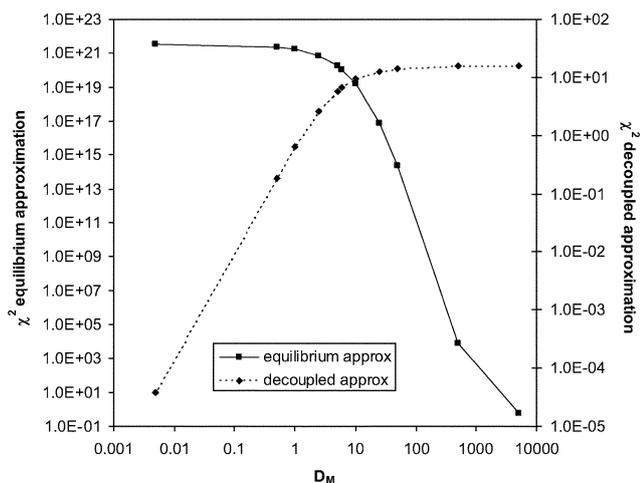


Fig. 7 Variation in χ^2 [eqn (12)] with D_M for equilibrium and decoupled approximations.

the equilibrium approximation will be more appropriate, although as we move up and to the left, towards slice 'b', the error incurred will become larger, and this time it will not be conservative. In region 'C', a full treatment of kinetics is best. The arbitrary limits in the figure are based on $k_b = 5.9 \times 10^{-8} \text{ s}^{-1}$ and D_M boundaries of 0.1/0.005 for the decoupled and 100/1000 for equilibrium. Of course, one does not have to use an approximation, a full calculation including the kinetic equation will always give the correct answer, but it may be computationally expensive.

2.2 Calculations including the sorption of humic–metal complexes

Thus far, all the calculations have assumed that the humic–metal complex does not sorb to the mineral surface as it transports, and a number of studies have been able to simulate the results of column experiments with that assumption.^{1,3} However, other cases have required the inclusion of sorption,⁵ and humic substances themselves are known to sorb to mineral surfaces.⁸

Therefore, a second series of calculations was performed, which included the effects of humic sorption. The first calculation in this series is essentially the same as the very first calculation (Fig. 1), but with extra equations and terms to account for the effects of humic sorption. Hence, eqn (4)–(9)

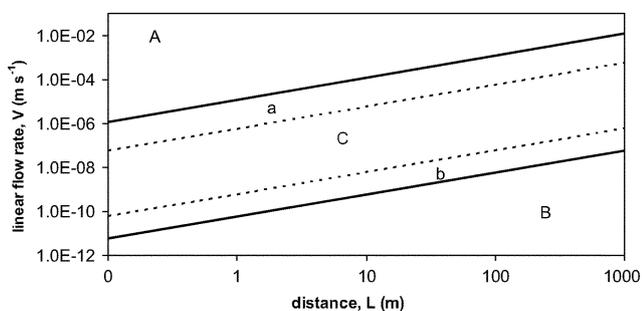


Fig. 8 Plot of linear flow rate vs. distance showing the regions where the decoupled and equilibrium approximations might be used. Labels are explained in the text.

with the parameters in Table 2 were included again. In addition, it was assumed that both humic substances and humic–metal complexes were able to sorb. To account for these effects, the approach of van de Weerd *et al.*^{7,8} was adopted. Hence, the calculations assume that there is a single humic binding site on the mineral surface, and that different fractions in solution compete for the binding sites, but that the binding capacity varies from fraction to fraction. The mathematical equations used to define sorption have already been given above [eqn (1)–(3)]. The binding site capacities, rate and equilibrium constants have been taken from van de Weerd *et al.*⁸ (Table 1). Where the sorption of humic–metal complexes has been required to model column experiments, it has been found that the interaction of the complex with the surface does not affect the interaction between the metal ion and the humic substance,⁵ and that assumption has been used here, *i.e.* the same values of k_b , k_f and K_{exch} are used to describe the interactions of metal ion with humic acid, regardless of whether the humic acid is free or sorbed. The aim of these calculations is to investigate the movement of contaminant species under realistic conditions. Hence, all of the calculations in this series assume that the mineral surface is in equilibrium with the ambient humic concentration, and that the introduction of the contaminant is not associated with a change in that concentration. The total metal concentration used here is very small compared with the humic concentration, and so the bulk humic substance, and its interaction with the surface is unaffected as the metal breakthrough proceeds.

Van de Weerd *et al.*⁸ have used up to six fractions to model humic sorption, which range from weakly to strongly sorbing. In the next calculations, the behaviours of metal bound to two humic fractions have been addressed: The first fraction (A) represents the fairly weakly interacting and abundant low mass material described by van de Weerd *et al.*⁸ ($Q_{i,\text{max}} = 106.86 \text{ mg C kg}^{-1}$, $k_{a,\text{HA}_i} = 1.05 \times 10^{-5} \text{ dm}^3 \text{ mg C}^{-1} \text{ s}^{-1}$, $k_{d,\text{HA}_i} = 1 \times 10^{-4} \text{ s}^{-1}$), and the second fraction (B) the larger, more strongly interacting material ($Q_{i,\text{max}} = 244.86 \text{ mg C kg}^{-1}$, $k_{a,\text{HA}_i} = 8.14 \times 10^{-7} \text{ dm}^3 \text{ mg C}^{-1} \text{ s}^{-1}$, $k_{d,\text{HA}_i} = 1.16 \times 10^{-8} \text{ s}^{-1}$). In these calculations it is assumed that the humic–metal complexes of both fractions transport identically to their host humic substance.

Fig. 9 shows the behaviour of metal associated with fractions A and B. On the same plot the behaviour in the absence of humic sorption is also shown, *i.e.* the original calculation from Fig. 1, along with the result in the complete absence of humic substance (—). Comparing the predictions, it is clear that humic sorption is having an effect upon the progress of the metal, and there is significantly less transport with sorption included. There is much less transport for fraction B, due to its much stronger interaction with the mineral surface.

We must now investigate the effects of varying the non-exchangeable fraction dissociation rate constant, k_b , in the presence of humic sorption. Therefore, calculations were performed for fraction A, including humic sorption, while varying the non-exchangeable forward and backward rate constants, k_f and k_b , and keeping the ratio between them constant. An 'exchangeable only' calculation with humic sorption was also performed. Fig. 10 shows the resulting distribution of metal. The result in the absence of humic

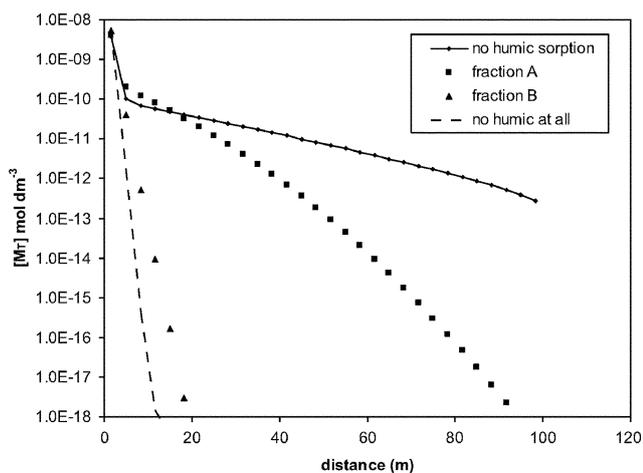


Fig. 9 Distribution of metal with distance for fractions A (■: $Q_{i,max} = 106.86 \text{ mg C kg}^{-1}$, $k_{a,HA_i} = 1.05 \times 10^{-5} \text{ dm}^3 \text{ mg C}^{-1} \text{ s}^{-1}$, $k_{d,HA_i} = 1 \times 10^{-4} \text{ s}^{-1}$) and B (▲: $Q_{i,max} = 244.86 \text{ mg C kg}^{-1}$, $k_{a,HA_i} = 8.14 \times 10^{-7} \text{ dm}^3 \text{ mg C}^{-1} \text{ s}^{-1}$, $k_{d,HA_i} = 1.16 \times 10^{-8} \text{ s}^{-1}$). Distribution of metal that results from no humic sorption (—○—) and in absence of humic acid (---) also shown.

sorption is also shown (—). As the dissociation rate constant increases, the extent of transport falls, and tends towards the ‘exchangeable only’ case. As k_b falls, the behaviour also tends to a limit, but with lower mobility than the case with no humic sorption. Fig. 11 shows non-exchangeable fraction ratio plots for the calculations in Fig. 10: the behaviours of the exchangeable fraction and the humic substance itself are also shown. As k_b falls, the behaviour tends towards that of the humic substance itself, rather than a conservative tracer: the non-exchangeably-bound metal cannot travel faster than its host humic material.

The model of van de Weerd *et al.*^{7,8} is the most successful approach to the sorption of humic material at mineral surfaces. Thus far, we have used the values of the forward and backward rate constants given by them. However, it is conceivable that some mineral surfaces might have different

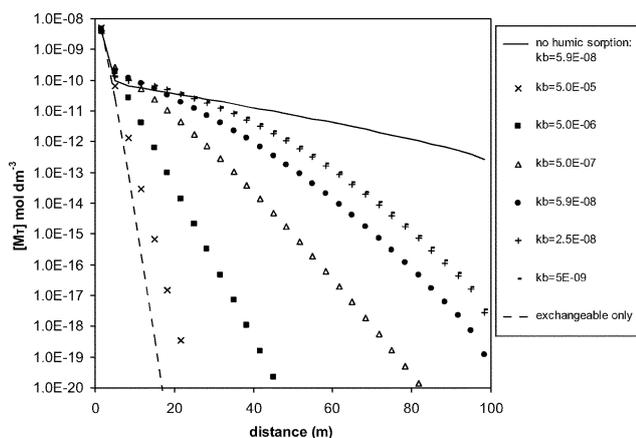


Fig. 10 Distribution of metal with distance for fraction A – effect of non-exchangeable dissociation constant (k_b). Behaviour in the absence of non-exchangeable binding (---) and in the absence of humic sorption (—) are also shown.

affinities or reaction rates for the various humic fractions. Also, the binding of a metal ion to a humic material might affect the sorption reaction. Hence, a series of calculations was performed to examine the effect of changing the sorption reaction rates upon metal transport. Taking the calculation for fraction B shown in Fig. 9 as a starting point, Fig. 12 shows the effect of varying the rate of the humic sorption reaction. For all these calculations, the non-exchangeable dissociation rate constant was fixed, $k_b = 5.9 \times 10^{-8} \text{ s}^{-1}$. The humic sorption rate constants (k_{a,HA_i} and k_{d,HA_i}) were varied, keeping the ratio, and hence the binding strength, constant. To complete the set of calculations, a calculation was performed that treated the humic sorption reaction as an equilibrium, *i.e.* both adsorption and desorption were instantaneous and k_{a,HA_i} and k_{d,HA_i} were replaced with an equilibrium constant (—). As a guide, the result of the calculation that is obtained in the absence of humic–metal complex sorption is shown again (—). As the rate constants decrease, the extent of metal transport increases, and for $k_{d,HA_i} < 1 \times 10^{-12} \text{ s}^{-1}$, $k_{a,HA_i} < 8.14 \times 10^{-11} \text{ dm}^3 \text{ mg C}^{-1} \text{ s}^{-1}$, there is no significant effect of humic sorption, not because the affinity of the humic acid for the surface has decreased, but because the adsorption rate is so low, compared with the residence time in the column, and there is insufficient time for sorption.

In the case of the non-exchangeable fraction, it was only the dissociation rate constant k_b that made a significant difference. However, for humic sorption both the forward, k_{a,HA_i} , and backward, k_{d,HA_i} , rate constants make a difference. It is the forward rate k_{a,HA_i} that controls access to the mineral surface sorption sites, and this is responsible for the increase in migration with decreasing rate in Fig. 12. However, fraction B has a lower forward rate constant than fraction A, but yet it produces higher retardation. This is because fraction B has a higher affinity, determined by the equilibrium constant

$$K_{HA_i} = k_{a,HA_i}/k_{d,HA_i}$$

Therefore, both rate constants are important in controlling behaviour.

It is clear that the humic fraction to which the metal complex belongs makes a significant difference to mobility. Given that van de Weerd *et al.*^{7,8} have claimed that six fractions with different humic–surface interactions may be present, a series of calculations has investigated the transport behaviour of the non-exchangeable fraction in a system with six different humic fractions. The parameters and relative abundances are taken directly from van de Weerd *et al.*⁸ and are given in Table 1. Calculations are shown for two total humic substance concentrations, 1.8 and 18 mg C dm^{-3} (Fig. 13). The results are shown as ratio plots for the non-exchangeable fraction: the plots with filled symbols and no connecting lines represent the lower humic concentration, whilst the open symbols connected by lines represent the higher concentration. In the absence of humic sorption, the calculation results were independent of humic substance concentration (test A, Fig. 5). However, here it has a significant effect.

Metal ion behaviour in a system with both humic sorption and non-exchangeable kinetics is harder to rationalise than systems without sorption or with independent kinetic

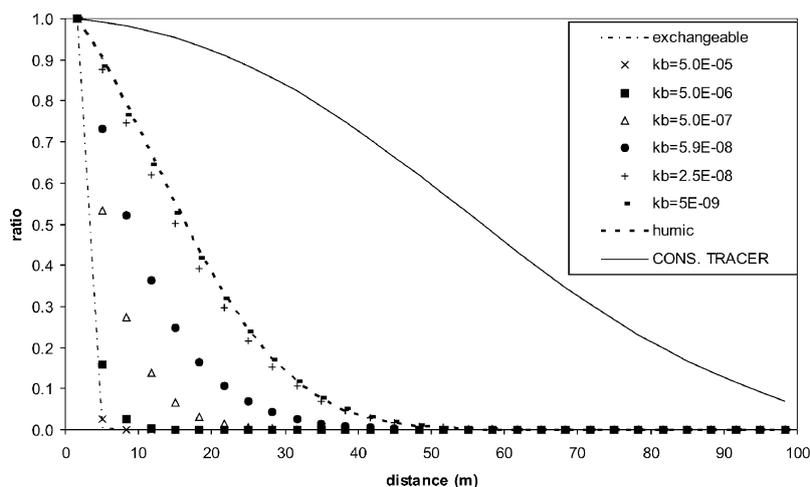


Fig. 11 Ratio plot for non-exchangeably-bound metal associated with fraction A for calculations in Fig. 10 (effect of non-exchangeable dissociation rate constant, k_b).

processes because here they interact. The rate of the humic sorption process affects the residence time of the humic material in the water column, and hence the relative effect of the non-exchangeable dissociation rate. However, the sorption behaviour of the humic-metal complexes may be examined simply, even in the case of a six (or more) fraction humic sample. In the environment, we expect all mineral surfaces to be in equilibrium with the ambient concentration of humic substance. Further, for the study of contaminant (trace) metal transport, we expect the metal loading of the humic substance to be relatively low. Therefore, we may assume that the presence of the contaminant metal does not significantly affect the interaction between the bulk of the humic substance and the mineral surface, even if it might affect the particular humic molecule to which it is attached. For each fraction, i , the change in the concentration of sorbed humic-metal complex,

$[M-HA_{s,i}]$, with time will be given by

$$\frac{d[M-HA_{s,i}]}{dt} = k_{a,HA_i}[M-HA_i][S_{HA_i}] - k_{d,HA_i}[M-HA_{s,i}] \quad (13)$$

where $[M-HA_i]$ is the concentration of metal in solution bound to humic fraction i , and $[S_{HA_i}]$ is the unoccupied surface binding site concentration for fraction i .

To predict the movement of a metal-humic complex behaving as any fraction, it is not necessary to include the transport of the bulk humic material with all its fractions explicitly in the transport calculations. We may use eqn (1)–(3) to calculate the vacant site concentrations for each fraction ($[S_{HA_i}]$). Then, for each fraction, any occupied site is effectively blocked and the available site concentration is constant ($= [S_{HA_i}]$). Hence, we may combine k_{a,HA_i} and $[S_{HA_i}]$ to give a pseudo-first-order forward rate constant, k'_{a,HA_i} (s^{-1}),

$$k'_{a,HA_i} = k_{a,HA_i}[S_{HA_i}], \quad (14)$$

and define a Damkohler number for the humic sorption reaction, D_{HUM} ,

$$D_{HUM} = \frac{k'_{a,HA_i} L}{V}, \quad (15)$$

which may be used to characterize the humic sorption reaction. As D_{HUM} approaches zero, the behaviour of the metal-humic complex will tend towards that of a conservative tracer; whilst as D_{HUM} tends to ∞ , the extent of sorption will increase and tend towards equilibrium behaviour, in which case the concentration of the sorbed humic-metal complex at any point and time is given by

$$[M-HA_{s,i}] = K'_{HA_i}[M-HA_i], \quad (16)$$

where

$$K'_{HA_i} = \frac{k'_{a,HA_i}}{k_{d,HA_i}} \quad (17)$$

At the upper and lower limits, a kinetic calculation may be avoided by assuming that the humic-metal complex: either

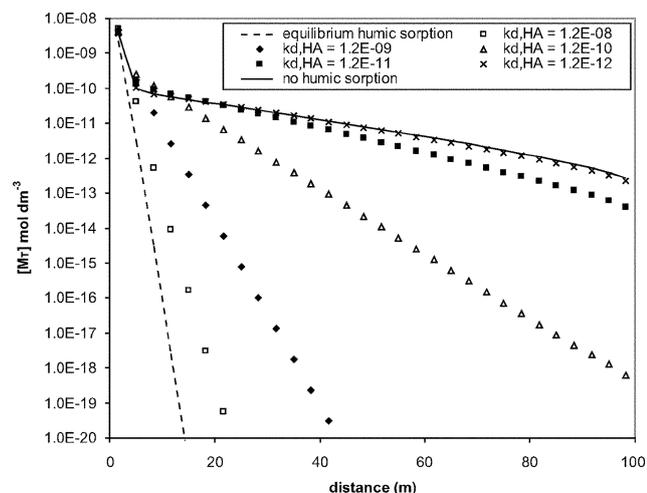


Fig. 12 Effect of humic sorption rate constant on transport of metal. Data plotted as total metal concentration vs. distance. For all plots, $k_b = 5.9 \times 10^{-8} s^{-1}$. Calculations made using equilibrium to describe humic sorption are shown as the dashed line, and results in the absence of humic sorption are shown as the solid line.

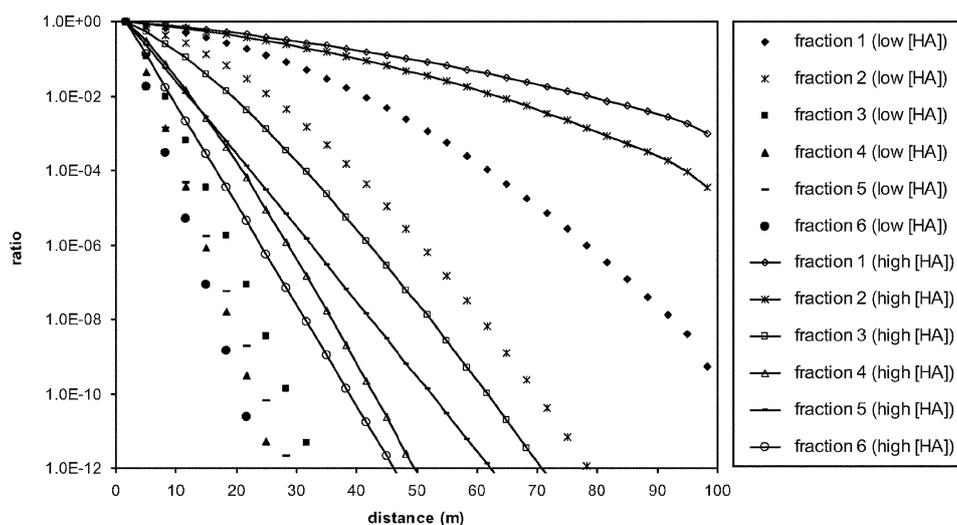


Fig. 13 Ratio plots for non-exchangeably-bound metal ion for humic fractions 1–6 (Table 1) at 1.8 mg C dm⁻³ ('low [HA]') and 18 mg C dm⁻³ ('high [HA]').

does not sorb at all, and so transports with the velocity of the groundwater (low D_{HUM}); or that it does sorb, and that the interaction may be described with an equilibrium constant K'_{HA_i} (high D_{HUM}). Assuming that the humic material does not sorb will give a conservative prediction, whilst the equilibrium approach will not, since the equilibrium assumption produces the maximum possible retardation, and the real behaviour only tends to this as D_{HUM} increases.

If a humic–metal complex sorbs, then that in itself will cause some retardation. However, sorption will also increase the residence time of the complex in the water column, allowing more time for removal of metal from the non-exchangeable fraction to the mineral surface. The extent of this effect will depend upon the affinity of the complex for the surface and the humic Damkohler number (D_{HUM}). If D_{HUM} is small, then the residence time is too short for sorption to the mineral surface to be significant, the complex transports with the velocity of the groundwater, and there is no effect upon the metal–humic kinetics, *i.e.* the behaviour of the metal is still controlled solely by k_b , and D_M may still be used to define the behaviour of the contaminant:

$$D_M = \frac{k_b}{V} L \Big|_{D_{\text{HUM}} \rightarrow 0} \quad (18)$$

However, in the case of significant sorption of the humic–metal complex, the Damkohler number for the non-exchange-

able fraction must be adapted to take account of the increased residence time. If D_{HUM} is large ($D_{\text{HUM}} \rightarrow \infty$) and the humic sorption process may be described with an equilibrium constant, K'_{HA_i} , then the effective metal ion Damkohler number, $D_M^{\text{effective}}$, will be given by

$$D_M^{\text{effective}} = \frac{k_b}{V} L (1 + K'_{\text{HA}_i}) \Big|_{D_{\text{HUM}} \rightarrow \infty} \quad (19)$$

For systems with intermediate values of D_{HUM} , eqn (18) and (19) may be used to provide a range of Damkohler numbers, the most representative value lying somewhere in between.

Table 3 shows the values of D_{HUM} , D_M and $D_M^{\text{effective}}$ for the six humic fractions in the calculations shown in Fig. 13 at a humic concentration of 18 mg C dm⁻³ (open symbols and lines). The values of D_{HUM} are all relatively large, the smallest being 370. Hence, the humic sorption process is sufficiently rapid, compared with the residence time, such that an equilibrium constant should give a reasonable approximation. At lower humic concentrations, the higher free site concentration, and hence higher k'_{a,HA_i} , will give even larger D_{HUM} values. Increasing the humic concentration would reduce the numbers, but in order for the weighted average of the D_{HUM} values across the fractions to fall below 100, the humic concentration would have to be in excess of 800 mg C dm⁻³, far higher than one would normally expect in the environment. Therefore, with these values of flow rate and distance, assuming that

Table 3 Variation of D_{HUM} , D_M and $D_M^{\text{effective}}$ with humic fraction for the calculations in Fig. 13 at a humic concentration of 18 mg C dm⁻³. Note: K'_{HA_i} in this table is not the same as K_{HA_i} in Table 1

Humic substance fraction	Humic sorption Damkohler number, D_{HUM}	Humic–metal complex sorption equilibrium distribution coefficient, K'_{HA_i}	Non-exchangeable Damkohler number (excl. sorption effects), D_M	Non-exchangeable Damkohler number (incl. sorption effects), $D_M^{\text{effective}}$
1	4.2×10^3	0.421	5.90	8.38
2	8.5×10^3	2.20	5.90	13.0
3	1.2×10^3	22.5	5.90	138
4	2.3×10^3	63.7	5.90	382
5	3.7×10^2	226	5.90	1340
6	7.5×10^2	643	5.90	3800

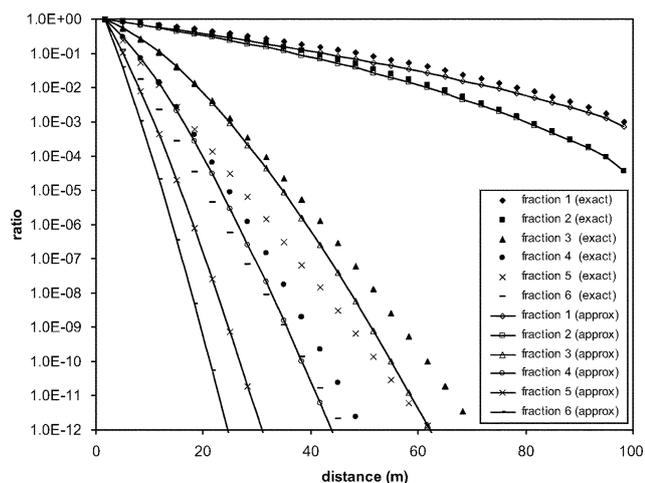


Fig. 14 Non-exchangeable fraction ratio plots for humic fractions 1–6 and a humic concentration of 18 mg C dm^{-3} : exact solutions (filled symbols) and approximations (open symbols and lines) using an equilibrium constant to describe humic sorption.

humic sorption may be described as an equilibrium, should always be a reasonable estimate. For normal, ambient humic concentrations, only under conditions of very high flow rate or very short column length should this assumption be invalid. There is a significant increase in $D_M^{\text{effective}}$ between fractions 1 and 6 (Table 3). The $D_M^{\text{effective}}$ for fraction 1 (8.4) means that the non-exchangeable interaction would be expected to have a significant effect upon transport, and the plot (Fig. 13) shows that there is significant migration. However, the $D_M^{\text{effective}}$ for fraction 6 (3800) indicates that the metal will have sufficient time to dissociate from the humic material before it transports, and indeed there is very little migration beyond the start of the column.

Just as approximations can be used to describe the non-exchangeable interaction, a similar approach may be applied to humic sorption. For low D_{HUM} values, sorption could be ignored and the reaction removed, whilst at high D_{HUM} an equilibrium approach would be most appropriate. At intermediate values only a full kinetic description will provide a reliable prediction.

Fig. 14 shows the exact solutions for the systems in Table 3 as ratio plots (filled symbols) with approximations (open symbols and lines) calculated by describing sorption with the equilibrium constant K'_{HA_i} . Making this simplification, and including only the metal ion non-exchangeable kinetics, reduces the calculation time significantly. The approximations are fairly close to the exact calculations, but, as expected, slightly underestimate transport, particularly for higher values of K'_{HA_i} since the assumption of equilibrium is not conservative.

To assess the importance of non-exchangeable kinetics in a system that includes humic sorption processes and to determine the most appropriate approximations, first one should calculate D_{HUM} . If it is small, then D_M may be used to determine if non-exchangeable kinetics are significant, whilst if it is large, $D_M^{\text{effective}}$ should be used. If D_{HUM} has an intermediate value, then D_M will provide an indication of the maximum possible effect of non-exchangeable kinetics, and $D_M^{\text{effective}}$ the minimum. Fig. 15 shows the procedure that

should be used for selecting the most appropriate approximations, if any, to describe the non-exchangeable interaction and humic–metal complex sorption. Depending upon D_{HUM} and D_M or $D_M^{\text{effective}}$, there are nine possible options, five of which are conservative and four non-conservative. Four of the options avoid all kinetic equations, another four include one kinetic process, and only one option requires a kinetic description of both humic sorption and the non-exchangeable interaction. Of course, the exact solution with a kinetic description of both processes will always give the correct solution, but that will require the longest calculation times.

2.3 Application of methodology to previous work

The Damkohler methodology outlined above may be used to rationalise the behaviour of metal–humic complexes at the Oak Ridge site described by McCarthy *et al.*^{23,31} For the Eu^{3+} and Nd^{3+} tracer studies, we have an estimate of the linear flow rate, V , because a bromide tracer was also injected, which appeared at the same time as the lanthanides. Of course, there is no conservative tracer for the Am and Cm mobilised from the trenches, but since their apparent linear velocities are the same as for Eu^{3+} and Nd^{3+} , we may assume that they are behaving in the same way. Therefore, using $k_b = 5.9 \times 10^{-8} \text{ s}^{-1}$, the D_M values would lie in the ranges: 0.01–0.07 for Am/Cm; 0.01–0.02 for Nd^{3+} ; and 0.01–0.06 for Eu^{3+} . All of these are in the range where we would expect any metal ion bound non-exchangeably to behave as a conservative tracer in the absence of sorption processes. Van de Weerd *et al.*⁸ have applied their model of humic sorption to this site. The relevant parameters are given in Table 1. The pseudo-first-order sorption rates ($k'_{\text{a,HA}_i}$) for a humic concentration of 1.8 mg C dm^{-3} are in the range from 3.45×10^{-5} to $7.84 \times 10^{-4} \text{ s}^{-1}$, depending upon the fraction, which corresponds to D_{HUM} in the range 100–1000 for the more weakly sorbing (smaller) fractions, and 5–50 for the larger, more strongly sorbing, species. Combined with the effective sorption equilibrium constants (K'_{HA_i}) which lie in the range 4–6000, this gives an estimate of $D_M^{\text{effective}}$ in the range 0.05–441. The lower end of the range corresponds to the most weakly sorbing fractions, and the higher end to the strongest sorbing fractions. For the more weakly sorbing fractions, we expect sorption to be in equilibrium, but not for the stronger fractions, where sorption will take place, but less than would be implied by the values of K'_{HA_i} and $D_M^{\text{effective}} = 441$. Therefore, even taking sorption into account, we predict that some part of the humic-bound metal should transport rapidly, since part of the population does have low $D_M^{\text{effective}}$. Further, the fractions with the very low values of $D_M^{\text{effective}}$ account for *ca.* 50% of the total humic acid population. Hence, the non-exchangeable effect can explain the rapid transport of Am and Cm from the disposal trenches. In the absence of non-exchangeable binding, the observations of rapid transport at the site are anomalous, given the high affinity of metal ions for the available mineral surfaces. However, with non-exchangeable binding, it is the residence time that determines the amount of metal that will be immobilised and not the mineral surface affinity.

We may also interpret the results of metal–humate column experiments using Damkohler numbers. The flow rates in the

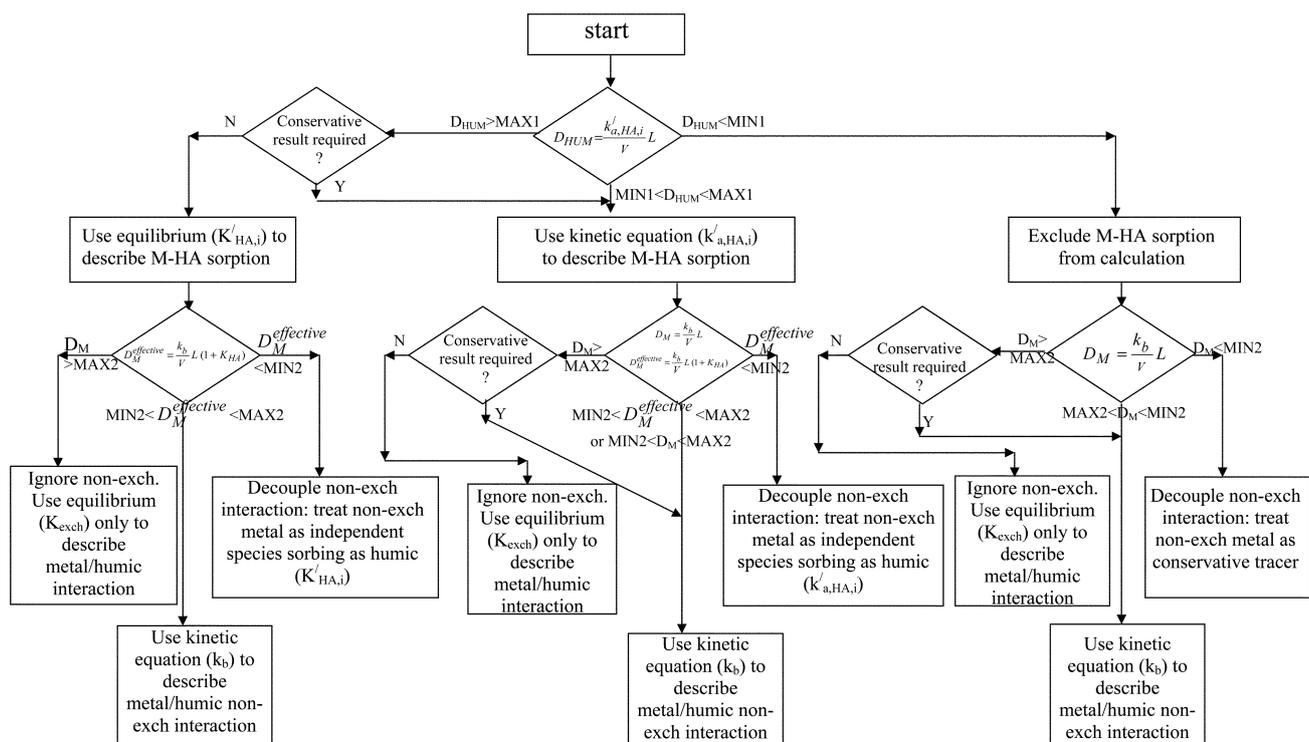


Fig. 15 Flow sheet to provide the most appropriate approximations (if any) for systems including humic sorption and the non-exchangeable interaction. MAX1 and MIN1 are the arbitrary Damkohler number limits for the humic sorption reaction, and MAX2 and MIN2 are the limits for the non-exchangeable interaction. These values would depend upon the requirements of the calculation and the acceptable errors.

experiments tend to be high and the path lengths short, giving short residence times. Considering the Am-pulsed column experiments of Artinger *et al.*,¹¹ a typical residence time is 14 h. Combining this with the Am k_b of $5.9 \times 10^{-8} \text{ s}^{-1}$ gives a typical D_M of 3×10^{-3} . Even allowing for a large difference in k_b for the humic material from that work would still give a very small D_M . The humic sorption model of van de Weerd *et al.*^{7,8} has not been applied to the surfaces and humic samples used in the metal–humate column experiments. However, the humic concentrations tend to be high and vary from column to column, but 20 mg C dm^{-3} is representative of the range. Using the parameters for the six humic fractions in Table 1 would give D_{HUM} values in the range 0.1–4.0 for the strongly and weakly sorbing fractions, respectively, and $K'_{HA,i}$ values of the order of those in Table 3. Now the exact values for these systems may be slightly different, but these numbers do help to rationalise the results. In the absence of humic sorption effects, the very low values of D_M suggest that the non-exchangeably-bound metal will transport conservatively. Even if we consider humic sorption, then we expect the transport of humic–metal complex to be relatively effective, because the high humic concentration will result in low effective affinities and sorption rates ($k'_{a,HA,i}$). The fractions with the higher affinities have low D_{HUM} numbers (0.1), and so the extent of sorption during transit of the column will be significantly less than expected at equilibrium, *i.e.* from the values of $K'_{HA,i}$ in Table 3. For the weakly sorbing fractions, D_{HUM} is higher (4.0), but still does not represent equilibrium, and anyway the effective affinities ($K'_{HA,i}$) will be very low, perhaps < 1 (Table 3). Under these conditions, it is not surprising that at least some part of the

non-exchangeable metal elutes as a conservative tracer. The Damkohler numbers also allow us to explain the tails that follow the main elution peaks in the Am- and U-pulsed columns of Artinger *et al.*^{11,12} These tails follow directly after the main metal peak just before one pore volume, and persist for a few pore volumes. This must be humic–metal complex that has been retarded by sorption. It seems unlikely that this is metal bound to a strongly sorbing humic fraction, since once such a species had sorbed, we would expect much more significant retardation. However, the behaviour is consistent with the more weakly sorbing fractions. Hence, although the material in the main elution peak could be associated with any fraction, the tails almost certainly represent the weakly sorbing fractions. Although there is rapid breakthrough and conservative tracer behaviour in the experiments, the Damkohler analysis suggests that the extent of this rapid transport might be reduced at the slower flow rates and larger distances that might be encountered in a field-scale system. Indeed, batch experiments with the same systems took 1000 h to reach equilibrium: clearly there are processes there that will not be evident in a column experiment with a residence time of 14 h.

The humic sorption model of van de Weerd *et al.*^{7,8} also allows us to explain the inconsistency in the approach of Bryan *et al.*⁵ to fitting humic sorption: for a series of pulsed column experiments that were not pre-equilibrated with humic material, the data could be fitted with an equilibrium constant, whilst Eu columns that had been pre-equilibrated required a kinetic description. For the unequilibrated columns, the free sorption site concentration ($[S_{HA,i}]$) would be high, giving high $k'_{a,HA,i}$ and large D_{HUM} values which allow an equilibrium

approximation to work, whilst pre-equilibration of the Eu columns would block many of the sorption sites, reducing $[S_{\text{HA}_i}]$, $k'_{\text{a,HA}_i}$ and D_{HUM} to the point where an equilibrium approximation would not suffice.

Fig. 15 allows us to decide whether to include kinetics in transport calculations, or if approximations may be used. We may use the metal ion injection experiments at the Oak Ridge site as an example. To use the diagram, we must first define the cut-off values for the approximations, which will depend upon the acceptable error. However, for the sake of our example, suppose that we decide that we may use a decoupled approximation for Damkohler numbers less than 0.1 ($\text{MIN1} = \text{MIN2} = 0.1$), and an equilibrium approximation for values greater than 100 ($\text{MAX1} = \text{MAX2} = 100$). We must first appreciate that the heterogeneous nature of the system means that we will not necessarily get a single answer for a given site. The values of D_{HUM} for the six humic fractions range from 5 (strongly sorbing) to 1000 (weakly sorbing): we will use the diagram twice, for the two extremes. Taking the most strongly sorbing fraction first, a D_{HUM} of 5 is in the region where neither approximation is valid for simulating the humic sorption reaction, and so we must use the kinetic equation and $k'_{\text{a,HA}_i}$ to describe the sorption of the metal–humic complexes. For this humic fraction, we have D_{M} of the order of 0.01–0.07, and $D_{\text{M}}^{\text{effective}}$ of 60–420. The large value of $D_{\text{M}}^{\text{effective}}$ means that we cannot be sure that the decoupled approximation would work ($D_{\text{M}}^{\text{effective}} > \text{MIN2}$), whilst the low D_{M} value of 0.01 rules out an equilibrium approximation; therefore, in this case, we must use the kinetic equation (k_{b}) to describe the metal ion–humic interaction ($\text{MIN2} < D_{\text{M}}^{\text{effective}} < \text{MAX2}$; or $\text{MIN2} < D_{\text{M}} < \text{MAX2}$). For the more weakly sorbing fraction, the higher value of D_{HUM} (1000) means that we may use an equilibrium approximation (with $K'_{\text{HA}_i} = 4$) to simulate humic sorption ($D_{\text{HUM}} > \text{MAX1}$), provided that a conservative result is not essential. For this fraction, D_{M} will be the same (0.01–0.07), and $D_{\text{M}}^{\text{effective}}$ in the range 0.04–0.28. The equilibrium approximation is still ruled out by the value of D_{M} . For the decoupled approximation, we have a choice since the range of possible $D_{\text{M}}^{\text{effective}}$ values straddles the limiting value (0.1). If ease of calculation were critical, we might opt for the decoupled approximation for the metal ion–humic interaction, especially given that the result will be conservative; whereas if accuracy is more important, we would use the kinetic equation, with k_{b} .

As a second example, we may apply Fig. 15 to the Eu^{3+} sandstone columns of Bryan *et al.*⁵ In the original work, kinetic equations were used to simulate both humic sorption and metal ion–humic interaction. Two humic fractions were defined ($k'_{\text{a,HA}_1} = 1.7 \times 10^{-5} \text{ s}^{-1}$, $K'_{\text{HA}_1} = 1.1$, and $k'_{\text{a,HA}_2} = 6.0 \times 10^{-6} \text{ s}^{-1}$, $K'_{\text{HA}_2} = 60$) that have D_{HUM} values of 0.6 and 0.2 for the weaker and stronger sorbing fractions, respectively. This time, for both fractions, D_{HUM} dictates that a kinetic equation is used to simulate humic sorption. The value of D_{M} is of the order of 0.02, which gives $D_{\text{M}}^{\text{effective}}$ values of 0.04 (weakly sorbing fraction) and 1.2 (strongly sorbing fraction). Hence, although the transport of non-exchangeably-bound metal bound to the weakly sorbing fraction could be simulated with a decoupled approximation ($D_{\text{M}}^{\text{effective}} < \text{MIN2}$), that bound to the strongly sorbing fraction would require the full

kinetic equation. This explains why a kinetic description of both processes was necessary to simulate the behaviour in the column experiments.

3. Conclusions

The phenomenon of the non-exchangeable binding of metal ions by humic substances has helped us to understand the rapid breakthrough of metal ions in tracer tests at the Oak Ridge site and the apparent rapid transport of radionuclides from the shallow waste repository. Coupled with slow humic sorption processes, it has also explained the results of metal–humate column experiments.

Probably the most important result here is that in predictions using realistic system conditions and chemical parameters, the humic non-exchangeable interaction is predicted to produce rapid transport of contaminant metal ions, and although certain fractions of a metal–humic non-exchangeable complex might be prevented from migrating by sorption interactions, the evidence from the Oak Ridge site and column experiments is that this will not prevent 100% of the metal loading from migrating. One might think that, because of the long calculation times involved in RPA calculations, which can be of the order of thousands of years and longer, chemical kinetics cannot be important. However, it is not the total simulation time that matters but the residence time in the groundwater column, which could be considerably shorter. Hence, humic non-exchangeable binding could be important, even for long-term calculations.

Given that the extent of transport is so sensitive to the non-exchangeable dissociation rate, the observation of significantly slower rates for metals that have been complexed by humics in the environment rather than in the laboratory is important.^{9,10} Even more important is the observation of the pseudo-irreversible binding of metal ions by Geckeis *et al.*⁹ for naturally complexed Eu in groundwater, and by Artinger *et al.*⁴ for Am added to humic materials in the laboratory. If these observations are generally true, then such metal fractions would migrate very effectively, particularly if they are associated with weakly sorbing humic fractions, or in systems with high flow rates or high humic concentrations. For RPA calculations, the only defensible approach is to assume that these fractions migrate conservatively.

At humic concentrations that might be expected in the environment, the sorption of humic–metal complexes could well cause significant retardation of contaminant metals by direct sorption. However, that same sorption will increase the amount of time that it takes humic material to traverse a given distance. Therefore, any metal ion non-exchangeably-bound to that humic substance will require a longer time to travel that distance than in the absence of humic sorption, which will give longer for the metal to dissociate from the humic substance and become immobilised on the mineral surface. Hence, humic sorption can cause retardation by two mechanisms. The various fractions of humic substance have different sorption properties. For example, in Fig. 13 for metal bound to fraction 1, humic sorption has very little effect, whereas for fraction 6 there is a major effect, and residence time has been increased

by a factor of over 600 at a humic concentration of 18 mg C dm⁻³, producing very little transport.

If the binding of a metal ion affects the sorption properties of the host humic molecule/particle (sorption rate constant), then that would affect mobility. In particular, if the presence of the metal ion enhanced sorption of the humic-metal complex, then that might prevent the non-exchangeably-bound metal transporting. It is possible that some part of the non-exchangeably-bound metal is prevented from transporting by sorption processes. However, the observation of rapid humic-mediated transport at the Oak Ridge site^{23,31} and in column experiments¹¹ means that metal binding cannot always produce greatly enhanced sorption of humic-metal complexes on surfaces. Clearly, it would be very useful to be able to quantify the effect of metal ion binding upon humic sorption rate. Another problem is that the important data for the non-exchangeable interaction, k_b and the amount in the fraction, have only been measured for bulk humic samples. To assess the impact of humic-mediated transport accurately, the behaviour specific to each humic fraction should be studied.

The model that we have used here to account for metal ion/humic chemistry is very simple, and although it has successfully predicted the transport of metal ions in laboratory column experiments (e.g. Bryan *et al.*⁵), humic substances are extremely heterogeneous materials, and it is important to consider what effect this complexity might have on the general predictions made here. In particular, we have used a single equilibrium constant (K_{exch}) to simulate the exchangeable interaction, but there is actually a range of binding strengths for a given humic sample and metal ion, and models of exchangeable binding strength take this into account (e.g. Model V/VI, Tipping *et al.*²⁷; NICA, van Riemsdijk *et al.*²⁶). However, these calculations have demonstrated that transport calculations are insensitive to the value of exchangeable binding strength (tests **B** and **C**, Fig. 5). Therefore, including a distribution of exchangeable binding constants, rather than a single value, would make little difference to the results, and so we have been able to disregard the distribution of exchangeable binding strengths. Also, the exchangeable binding strength is a function of solution conditions, such as pH.^{26,27} Therefore, K_{exch} will vary with solution conditions. However, the magnitude of the exchangeable binding strength makes little difference to the result. In fact, the calculations have shown that only the magnitude of the dissociation rate constant, k_b , controls the extent of transport. Although the exchangeable binding strength varies significantly with solution conditions, the rate constant is extremely insensitive to conditions, such as pH and the concentrations of other ions.⁶ Hence, natural variations in these conditions should not greatly affect the conclusions.

This is not to imply that the distribution of binding strengths and the variation with pH and ionic strength are unimportant. The non-exchangeable fraction accounts for a minority of bound metal, because in free energy terms it does not represent a more strongly bound fraction. Hence, in a static system at equilibrium it will not greatly affect the partition between solid and solution, or the amount of humic-bound metal ion. These will be determined by the exchangeable binding strength. Hence, during the special

conditions during transport, it is the kinetics that determine the behaviour, and which must be included in a model, but once transport has taken place, to determine speciation it is the exchangeable interaction that must be taken into account, and the advanced models of the exchangeable interaction should be used.

We have a set of rules based on Damkohler numbers that allow us to determine the importance of kinetics, and to determine the validity of the various approximations. Unfortunately, the most attractive approximation, the assumption that these chemical processes may be treated as equilibria, will not give a conservative prediction. Currently, the only way to make a conservative prediction is to either make the calculation with the kinetics included, or to assume that the non-exchangeably-bound metal transports as a conservative tracer. However, on a more positive note, these calculations have shown that in a system where non-exchangeably-bound metal transport is significant, then the number of important parameters is fairly small. For the reactions of the metal ion itself, the behaviour is dominated by the value of k_b , and then by the amount of metal ion in the non-exchangeable fraction at the upper boundary. The other important parameters are the humic concentration and the sorption and desorption rate constants for the humic fraction to which the metal is bound.

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