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A PROCEDURE TO ASSESS THE IMPORTANCE OF CHEMICAL KINETICS IN THE HUMIC MEDIATED TRANSPORT OF RADIONUCLIDES IN RADIOLOGICAL PERFORMANCE ASSESSMENT CALCULATIONS

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[Abstract]

Previous work has shown that humic substances can bind metal ions in two fractions: the exchangeable, where it is available instantaneously for reaction with other sinks (such as mineral surfaces); and the non-exchangeable, from which it may only dissociate slowly. In the absence of metal ion/humic/mineral surface ternary complexes, if the dissociation rate is slow compared to the solution residence time in the groundwater column, then metal in the non-exchangeable will have a significantly higher mobility than that in the exchangeable. 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.

Sorption of humic/metal complexes at mineral surfaces may reduce 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 magnitude of the effect depends upon the concentrations of the mineral surface humic binding sites and the humic in solution, along with the magnitudes of the equilibrium constant and the forward and backward rate constants.

The non-exchangeable dissociation reaction and the sorption reaction may be classified in terms of two Damkohler numbers, which can be used to determine the importance of chemical kinetics during transport calculations. These numbers could be used to 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.
[Ivanov et al.]

[Introduction]

Over the last decade, a transport model has been developed that can predict the humate mediated transport of metal ions in laboratory column experiments (e.g. Bryan et al 2005). Previous studies have shown that humic substances bind metal ions in two different modes (King et al 2001). 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, metal transfers to the ‘non-exchangeable’ fraction, where it is not more strongly bound, but it may not dissociate instantaneously, rather its release is kinetically controlled. While it is effectively 'trapped' within the non-exchangeable fraction, the metal ion takes on the characteristics of its host humic.

A simple model of metal ion interactions has been used by Bryan et al (2005) to model column experiments: initial uptake to the humic exchangeable site is described as an equilibrium process,

$$M^{n+}_{aq} + HA_{exch} \rightleftharpoons M_{exch} \quad K_{exch} = \frac{[M_{exch}]}{[M_{aq}]^{n}[HA_{exch}]} \quad (1)$$

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

$$M_{exch} \rightarrow M - HA_{non-exch} \quad \frac{d[M_{non-exch}]}{dt} = k_f[M_{exch}] - k_b[M_{non-exch}] \quad (2)$$

where $HA_{exch}$ is the humic exchangeable site, $M_{exch}$ and $M_{non-exch}$ are metal ions bound to the humic 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 interaction of humics with mineral surfaces is complex, and again kinetic effects are important. There is multi-component behaviour, although the best description is surface dependent. For iron oxides, Van de Weerd et al (1999) found that the surface heterogeneity is small compared to the humic. Others have also found that this approach works for hematite, but that quartz and magnetite sorption are better described with a model that has multiple surface binding sites and a single humic species, and that goethite sorption shows intermediate behaviour (Abrahamsen et al 2006; Farrelly et al 2006). Further work is required to clarify the nature of the interaction. However, although different surface models have different numbers of humic fractions and binding sites, they do all use the same chemical equation to describe the interaction of a particular humic molecule or humic/metal complex, $M-HAi$, with a given surface binding site, $S_{HA,i,j}$, to give a ternary complex, $M-HAS_{S,i,j}$.

$$M - HA_{free,i} + S_{HA,i,j} \rightarrow M - HA_{S,i,j} \quad \frac{d[M - HA_{S,i,j}]}{dt} = k_{HAS,i,j}[M - HA_{free,i}] [S_{HA,i,j}] - k_{HASH,i,j} [M - HA_{S,i,j}] \quad (3)$$

where $k_{HAS,i,j}$ and $k_{HASH,i,j}$ are the sorption and desorption rate constants.
Humic interactions could affect the transport behaviour of radionuclides, and there are implications for the post-closure radiological performance assessment (RPA) of nuclear waste repositories. However, calculations that include kinetics are computationally expensive. Therefore, it is important to identify exactly when it is necessary to include them explicitly in transport calculations.

[Objectives]

The aim of this work is to develop rules that predict when, and in what manner, humic chemical kinetics should be considered in field scale transport calculations in support of R.P.A.

[Modelling: No Humic Sorption]

We must first examine the effect of the metal/humic kinetic reaction (2), and in our initial treatment, we assume that the metal/humic complex does not sorb as it transports, i.e. the only processes that retards the migration of radionuclides is removal to the mineral surface. Such behaviour may be rationalised using Damkohler numbers (Jennings and Kirkner 1984). The Damkohler number for the non-exchangeable fraction, $D_M$, is defined by:

$$D_M = \frac{L}{V} k_b$$  \hspace{1cm} (4)

where, $L$ is the length of the column, and $V$ is the linear flow rate. Systems with the same $D_M$ always give the same the final distribution, regardless of $L$, provided that the relative dispersivity is constant (Bryan et al 2006). Only the desorption rate constant need be considered, because during transport the rate of transfer to the non-exchangeable is negligible (Bryan et al 2006). It is possible to reduce any series of kinetic reactions, regardless of origin or chemistry, to just three classes:

1. Those reactions that are sufficiently fast to be treated as equilibria (high $k$);
2. Those that are sufficiently slow that they effectively do not take place (low $k$);
3. Those that are only accurately described with rate equations (intermediate $k$).

Therefore, we have the possibility of using the limiting behaviours if $k$ is sufficiently large or small. We may use $D_M$ to judge when it is necessary to consider chemical kinetics explicitly. As $D_M$ decreases, the non-exchangeably bound metal tends towards the behaviour of the host humic, and for low $D_M$, virtually no metal ion can leave the non-exchangeable fraction in the time it takes to traverse the column. Therefore, the reaction that connects the exchangeable and non-exchangeable is removed from the calculation, and the two fractions are treated as independent species: the great advantage of this approach is that it is inherently conservative. At high $D_M$, the kinetic equation (2) could be replaced with an equilibrium. However, this approximation is not conservative, the size of the error decreasing as $D_M$ increases. The consequences for a real R.P.A. exercise would depend upon the circumstances. At intermediate $D_M$, the kinetic equation must be used, although this will be computationally expensive. Ideally, we would like a set of rules to determine when to use the approximations, but, that depends upon the acceptable error, which is a function of $D_M$ and distance from the source term. The equilibrium approximation is particularly problematic, since it is not conservative. Fortunately, systems with the same $D_M$ behave in the same way, and the likely error
at any distance may be determined as a function of $D_M$. Therefore, in each case, acceptable upper and lower limits for $D_M$ (MAX2 and MIN2, respectively; Figure 1) could be calculated to act as thresholds.

**[Modelling: With Humic Sorption]**

The sorption behaviour of humic/metal complexes may be examined simply, even for multiple fractions. In the environment, mineral surfaces will be in equilibrium with the ambient concentration of humic substance. For contaminant (trace) metal transport, the metal loading of the humic will be low. Therefore, the contaminant metal does not significantly affect the interaction between the bulk of the humic and the mineral surface, even if it affects its particular host humic molecule. It is not necessary to include the transport of the bulk humic with all its fractions explicitly in the transport calculations. We may use equations of type (3) for each fraction and site to calculate the vacant site concentrations ($[SHA_{ij}]$), and we may combine $k_{HAS_{ij}}$ and $[SHA_{ij}]$ to give a pseudo first order forward rate constant, $k'/HAS_{ij}$, and hence define a Damkohler number for the humic sorption reaction, $D_{HUM}$, to characterize humic sorption,

$$k'/HAS_{ij} = k_{HAS_{ij}} [SHA_{ij}], \quad (5)$$

$$D_{HUM} = \frac{k'/HAS_{ij}}{L} \quad (6)$$

As $D_{HUM}$ approaches zero, the metal/humic complex behaviour tends towards a conservative tracer, whilst as $D_{HUM}$ tends to $\infty$, the extent of sorption will tend towards equilibrium behaviour, in which case the concentration of sorbed humic/metal complex at any point and time is given by,

$$[M-HAS_{ij}] = K'/HAS_{ij} [M-HA]; \quad \{K'/HAS_{ij} = k'/HAS_{ij}/k_{HAS_{ij}} \} \quad (7)$$

A kinetic calculation may be avoided by assuming that the humic/metal complex either: does not sorb at all, and so transports with the velocity of the groundwater (low $D_{HUM}$), which will be conservative; or that the interaction may be described with an equilibrium constant, $K'/HAS_{ij}$ (high $D_{HUM}$), which will not be conservative. At intermediate $D_{HUM}$, only a full kinetic description will provide a reliable prediction. Thresholds may be defined to determine when the approximations could be used (MAX1 and MIN1; Figure 1).

Sorption of humic/metal complex will cause direct 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. If $D_{HUM}$ is small, the residence time is too short for sorption to the mineral surface to be significant, i.e. the metal behaviour is largely controlled by $k_b$, and $D_M$ may still be used,

$$D_M = \frac{k_b}{V} \bigg|_{D_{HUM} \rightarrow 0} \quad (8)$$

In the case of significant sorption (large $D_{HUM}$), this must be adapted to take account of the increased residence time, and the effective metal ion Damkohler number, $D_M^{effective}$, is given by,
For intermediate $D_{\text{HUM}}$, equations 8 and 9 provide a range of Damkohler numbers, the most representative value lying somewhere in between.

To assess the importance of humic kinetics one should first calculate $D_{\text{HUM}}$. If it is small, then $D_{\text{M}}$ may be used to determine whether non-exchangeable kinetics are significant, whilst if it is large, $D_{\text{M}}^{\text{effective}}$ should be used. If $D_{\text{HUM}}$ has an intermediate value, then $D_{\text{M}}$ will provide an indication of the maximum possible effect of non-exchangeable kinetics, and $D_{\text{M}}^{\text{effective}}$ the minimum. Figure 1 illustrates the procedure: there are 9 possible options, 5 conservative and 4 non-conservative. 4 avoid all kinetics, 4 include 1 kinetic process, and only 1 requires a kinetic description of both interactions. The exact calculation with a kinetic description of both processes always gives the correct solution, but requires longer calculation times.

**[Conclusions]**

Damkohler numbers allow the importance of kinetics, and the validity of approximations to be determined. Unfortunately, the most convenient approximation, equilibrium, is not conservative. Currently, the only way to make a conservative prediction is either to make the calculation including kinetics, or to assume that the non-exchangeably bound metal transports as a conservative tracer. More experimental work is required to improve the understanding of ternary complex formation. When that understanding has improved, there are a set of rules to determine the implications for R.P.A.

**[References]**

Figure 1: Procedure for assessing the importance of kinetics in R.P.A. calculations