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Uranium (VI) Binding to Humic Substances: Speciation, Estimation of

Competition, and Application to Independent Data.

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Abstract. In groundwaters containing natural organic matter (NOM), mostly humic substances (HS), it is expected that it plays a role on the behaviour of uranium in the environment. Another point is the actual effect of the competition with major cations and carbonate ions for U(VI)-NOM complexation. Our aim is to acquire experimental data for the U(VI)-HS complexation with two new different methodologies. The NICA-Donnan model is then used to predict uranium speciation in different groundwaters.

Introduction

The human contributions to the uranium geochemical cycle can lead to an increase of uranium concentration in some environments. The information of its speciation in the field and in trace concentration is not an easy task, and the use of model can help in providing reasonable estimates. Under oxidizing conditions, uranium is essentially under the form of U(VI) complexes; under reducing conditions U(OH)₄(aq) is the dominant form in solution (Guillaumont et al. 2003). U(VI) sorption onto minerals (Sylwester et al. 2000) can be well described by surface complexation and/or ion exchange model. In contrast, sorption of U(VI) to soils and sediments is more complicated because of the difficulty to fully characterize the species present and/or the properties and contribution of the solid-phase sorbents, including natural organic matter (NOM). NOM exits in natural waters, soils and sediments – mostly humic substances (HS) (MacCarthy 2001) –, and can play an important role on uranium speciation. A robust experimental data basis is needed to derive parameters to predict the behavior of trace elements in field systems. The NICA-Donnan model describes metal-NOM binding (Kinniburgh et al. 1999): it accounts for the NOM chemical

heterogeneity, competition between metals, and ionic strength effects. It is based on the electrostatic interaction of metal within a Donnan gel,

$$C_{i,D} = C_i \exp\left(-\frac{z_i F}{RT} \Psi_D\right)$$

where C_i and $C_{i,D}$ are the concentration in bulk and Donnan phase, respectively. The specific bonding is described by the Non-Ideal Competition Adsorption model,

$$Q_{i,T} = \sum_{i} Q_{\max,j} \times \frac{\left(\widetilde{K}_{i,j} C_{D,i}\right)^{n_{i,j}}}{\sum_{i} \left(\widetilde{K}_{i,j} C_{D,i}\right)^{n_{i,j}}} \times \frac{\left[\sum_{i} \left(\widetilde{K}_{i,j} C_{D,i}\right)^{n_{i,j}}\right]^{p_{j}}}{1 + \left[\sum_{i} \left(\widetilde{K}_{i,j} C_{D,i}\right)^{n_{i,j}}\right]^{p_{j}}}$$

where logK; $\tilde{i}_{i,j}$ and $n_{i,j}$ are the median affinity constant and heterogeneity parameter of metal i for the jth distribution of sites, and p_j the heterogeneity parameter of the jth distribution of sites. Only a few datasets cover a sufficiently wide range of [U]_{free}, ionic strength, and *p*H to provide NICA-Donnan generic parameters (Milne et al. 2003). Our aim is to implement this experimental data basis using two different methodologies i.) the Flux Donnan Membrane technique (FDM), and ii.) an insolubilized humic acid (IHA). Independent data sets from the literature can be analyzed and compared to blind predictions.

Materials and methods

 $Mg(NO_3)_2$, KNO_3 (Panreac), EDTA (Sigma-Alrich), H_3PO_4 (Normapur, Prolabo), $UO_2(NO_3)_2$ (SPEX certiprep 5% HNO_3) and water (Milli Q, Millipore) were used. The Gorleben humic acid (GHA) was extracted from one of the deep groundwaters in the Gorleben area (Wolf et al. 2004).

FDM is a dynamic modification of the standard Donnan Membrane Technique (DMT, Temminghoff et al. 2000) with both improved detection limits and faster response. A strong ligand is added on the acceptor side to increase the amount of free metal ion transported to the acceptor, and on the analysis of the metal flux. The theoretical basis for the FDM has been described in details elsewhere (Marang et al. 2006), and will not be recalled here. The cation exchange membrane (BDH, Laboratory Supplies) consists of a matrix of polystyrene and divinyl-benzene: ion exchange capacity and thickness are given by the supplier as 0.8 mM/g and $0.16 \pm 0.1 \text{ mm}$, respectively. The area of the membrane is 7 cm². The membranes were preconditioned by first soaking in 0.1 M HNO₃ to remove trace metal impurities. Then, they were washed with a 1 M Mg(NO₃)₂ solution. Finally, the membranes were equilibrated in the final background electrolyte: 2 mM Mg(NO₃)₂. Both donor and acceptor solutions were circulated at a constant rate of 2.5 mL/min. The acceptor and donor volumes were 25 mL and 200 mL, respectively. The FDM was calibrated vs. equilibration time when transport on the donor side was dominated either by uranium diffusion in solution (case 1) or by uranium diffusion in the membrane (case 2). Calibration conditions are summarised in Table 1. In case 1, the calibration was performed with a high concentration of phosphoric acid (H₃PO₄) on the acceptor side. In case 2, EDTA (ethylenediamine tetraacetic acid) and H₃PO₄ were present in the donor and acceptor side, respectively. The concentration of EDTA and H₃PO₄ needed for the two calibration conditions were estimated with the help of ECOSAT code (Keizer and van Riemsdijk 1994), which includes NICA-Donnan, using known thermodynamic binding constants (Guillaumont et al. 2003; Hummel et al. 2005), and Mg-NOM complexation (Marang 2007). For the U(VI)-HS study, the donor solution contains 10 mg/L of GHA with 8 $10^{-8} \leq [U(VI)]_{total}$ (M) $\leq 10^{-5}$. The acceptor solution consisted of 10⁻² M H₃PO₄. The *p*H was fixed at 4. The acceptor and donor sides were sampled after 24 hours, and calibration 1 was used for high metal to ligand ratio or they were sampled after 48 hours and calibration 2 used for low metal to ligand ratio.

Table 1. Experimental conditions of the FDM for the U(VI) calibrations for solution controlled diffusion (case 1) and for membrane-controlled diffusion (case 2), and comparison between experimental and theoretical calibrations curves slopes for uranium when the transport is solution-controlled (case 1) and membrane-controlled (case 2)

	Case 1	Case 2
[EDTA] in Donor	0	0.5 mM
[H ₃ PO ₄] in Acceptor	100 mM	100 mM
Background Electrolyte	2 mM	2 mM
[U] _{Total} in donor	5 μΜ	20 μΜ
рН	4	4
	$A_1 = \frac{A_e D_i}{V_{acc} \delta} (s^{-1})$	$A_{2} = \frac{A_{e} D_{i} B^{Z_{i}}}{V_{acc} \delta_{m} \lambda} (s^{-1})$
	2.3 10-6	1.47 10 ⁻⁵

The synthesis and characterization of IHA are detailed elsewhere (Weber et al. 2006). A mixture of 50 mg/L of IHA was reacted with solutions of known [U(VI)]_{total} in 2 mM Mg(NO₃)₂; *p*H ranged from 4 to 6.8. The solutions were then centrifuged during 20 min at 4000 rpm. The supernatant was removed to perform subsequent chemical analysis. Uranium concentrations were determined by time resolved laser induced spectrofluorimetry using the standard addition method in 5% H₃PO₄ (0.1 M, detection limit of 10⁻¹⁰ M) (Marang 2007). HA concentrations were analyzed by TOC (Schimadzu TOC-Vcsh).

Results and Discussion

Experimental slopes of the calibrations curves are given in Table 1. The U(VI) binding isotherm to GHA is given in Fig. 1a: data points corresponding to $[UO_2^{2+}]_{\text{free}} > 10^{-7}$, were obtained using the case 1 calibration; data point with $[UO_2^{2+}]_{\text{free}} < 10^{-7}$, were obtained with the case 2 calibration curve. The discrepancy between data points corresponding to $10^{-8} < [U]_{\text{free}} < 10^{-7}$, could be due to a mixed contribution of membrane and solution diffusion controlled flux (Marang et al. 2006). The data points corresponding to the experiments made with the IHA show a much smaller U(VI) binding under similar conditions (Fig. 1). Moreover, the slope of the binding is steeper (*i.e.* \approx 0.7).



Fig. 1. Uranium(VI) complexation isotherms (log $[U]_{bound}$ vs. log $[UO_2^{2+}]_{free}$) at pH 4 with Gorleben HA (10 mg/L). The background electrolyte was 2 mM Mg(NO₃)₂.

The data in Fig. 1 show that the binding increases as *p*H increases from *p*H 4 to 5 but remains constant thereafter. This difference is due to the difference of reactivity among both extracts; indeed HS are heterogeneous (Milne et al. 2001). Weber *et al.* (2006) have shown that the abundance of the high proton affinity sites (S2) of IHA is halved compared to the pristine HA due to condensation reactions during insolubilization. Using *p*H, [U(VI)]_{total}, [Mg²⁺], and C(GHA), [U(VI)-GHA] was simulated using the GHA parameters (Table 2) and the U(VI) parameters from the study of Saito *et al.* (2004). There is a good agreement between prediction and experimental data. Further fitting of the experimental data is only possible for the low-affinity sites (S1), keeping the S2 parameters values from Saito *et al.* (2004) constant. Median affinity constant, log \tilde{K}_1 , and heterogeneity parameter, n₁, are reported in Table 2. Fitting of log \tilde{K}_2 does not improve the results due to its low importance under these [U(VI)]_{total} and *p*H conditions.

The log \tilde{K}_1 and n_1 were adjusted to the IHA data. Site density (Q_{max}) and proton parameters were obtained from Weber *et al.* (2006), Mg²⁺ parameters are from Marang (2007). The four series were fitted altogether resulting in deviation for the *p*H 4 and 6.8 series (Fig. 1b). In the calculation of U(VI)-IHA binding, only free UO₂²⁺ was considered to bind specifically, and [UO₂²⁺]_{free} is calculated from [U]_{free} (Guillaumont et al. 2003). For the two fittings, the resulting log \tilde{K}_1 are in accordance and are reported together with n_1 in Table 2. For IHA, the lack of increase after *p*H 6 results from the formation of UO₂(OH)_n²⁻ⁿ and UO₂CO₃(aq), complexes for $10^{-8} \leq [U]_{total} M \leq 10^{-5}$ (Zeh et al. 1997). Only the S1 sites are adjusted; the S2 sites are fixed after Saito *et al.* (2004). These new parameters can now be used to predict uranium speciation in natural samples.

	S1	S2
	Low proton affinity	High proton affinity
	groups	sites (Saito et al. 2004)
Gorleben		
$\tilde{logK_{i,UO_2^{2+}}}$	4.59 ± 0.05	6.92ª
$n_{UO_{2^{2+}}}$	0.33 ± 0.13	0.39a
IHA		
$\tilde{logK_{i,UO_2^{2+}}}$	4.72 ± 0.08	6.92ª
$n_{UO_{2^{2^{+}}}}$	0.76 ± 0.08	0.39ª

Table 2. Nica-Donnan model parameters used in this study.

In mildly acid oxic media the data from Savannah River Site (SC, USA, Jackson et al. 2005), can be used. The concentrations of anions are not reported, and ions from the carbonate system are supposed to be in equilibrium with ambient CO₂(g) (0-5 and 5-10 cm depth); Eh is assumed to be oxic even if slightly reducing condition could occur. DOC values were considered as HA (50% C). UO₂-HA complexes account for more that 99.99% for the six cases in Jackson *et al.* (2005) (Fig. 2), which is in agreement with field data.

In more basic media, Ranville *et al.* (2007) quantified the association of U(VI) with NOM collected from a vertical porewater profile through a clay-rich aquitard (Hendry and Wassenaar 2000). The low measured binding of uranium by NOM implies that the competition of U(VI) carbonate complexes, which is also in agreement with the modeling. Major part of uranium should be present as ion-paired complexes (Ca,Mg)_nUO₂(CO₃)₃²ⁿ⁻⁴ (Dong and Brooks 2006), depending on depth (Fig. 2).



Fig. 2. Calculated speciation of uranium using ECOSAT and NICA-Donnan data from Saito et al. (2004) in the groundwaters from Jackson et al. (2005) (left), and from Ranville et al. (2007) (right).

In a more reductive case of an Underground Research Laboratory (Mol, Belgium), Bruggeman & Maes (2010) reported an influence of NOM (mostly HA) on the U(VI) fixation to pyrite. The authors compared a synthetic Boom Clay water (SBCW), with no NOM added, to a real Boom Clay water (RBCW) (de Craen et al. 2004). Excluding NOM, U(VI) in solution should be present under the form of CaUO₂(CO₃)₃²⁻ and UO₂(CO₃)₃⁴⁻. In this laboratory experiment, according to Bruggeman and Maes (2010), the solubility seems to be controlled by a UO_{2+x} phase, mostly U₃O₈. Fig. 3 presents the digitized data compared to the calculated speciation. NOM influence was anticipated for [U]_{total} < 1 μ M. The calculated speciation is in fair agreement with the observation as less than 9% of uranium is awaited to be fixed to NOM at 1 μ M. The proportion of U-NOM complexes, on S2 sites, is awaited to increase with decreasing [U]_{total}, and the proportion of fixed uranium to pyrite should decrease. It is difficult to propose any further interpretation as the FeS₂/HA system is complicated, but the general trend is rather satisfying.



Fig. 3. Solid phase uranium concentration vs. solution phase uranium concentration obtained by Bruggeman & Maes (2010) on pyrite (5 g/L) in Synthetic (SBCW) or Real (RBCW) Boom Clay water (left), compared to uranium-NOM speciation estimated in the same RBCW conditions (right).

Conclusions

This paper presents the results of the study of U(VI)-HA complexation. U(VI) is strongly bound to HA for pH < 6. For higher pH, elevated carbonate concentrations significantly limit the formation of U(VI)-HA complexes. The ECOSAT code was then used to predict the uranium speciation in different groundwaters. When pH is lower than 7, U(VI) is majorly controlled by NOM and will follow its fate in the different horizons of the soils and groundwaters. For higher pH values the situation is more complicated; for high total concentration of uranium, there is a minor amount of uranium associated to NOM. Conversely, when the total concentration of uranium is less than 10^{-7} M, the interaction of U(VI) with NOM becomes important even in reductive environments.

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