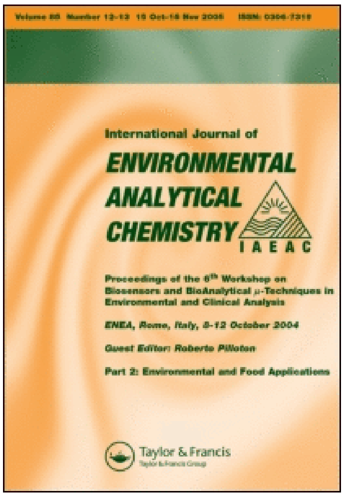
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Distribution coefficient and redox behaviour of uranium in Authie Bay (northern France)

Gabriel Billon[a]; Baghdad Ouddane[a]; Nicolas Proix[b]; Jacques Desormieres[c]; Yolande Abdelnour[c]; Abdel Boughriet[d]

[a] Laboratoire de Chimie Analytique et Marine, Université des Sciences et Technologies de Lille 1, 59655 Villeneuve d'Ascq Cedex, France [b] Laboratoire d'Analyses des Sols 273, Institut National de la Recherche Agronomique, 62000 Arras, France [c] VARIAN s.a., 91941 Les Ulis Cedex, France [d] I.U.T. de Béthune Département de Chimie, Rue de l'Université, Université d'Artois, 62408 Béthune Cedex, France

To cite this Article Billon, Gabriel , Ouddane, Baghdad , Proix, Nicolas , Desormieres, Jacques , Abdelnour, Yolande and Boughriet, Abdel(2005) 'Distribution coefficient and redox behaviour of uranium in Authie Bay (northern France)', International Journal of Environmental Analytical Chemistry, 85: 14, 1013 — 1024

To link to this Article: DOI: 10.1080/03067310500107112

URL: http://dx.doi.org/10.1080/03067310500107112

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem.
Vol. 85, No. 14, 10 December 2005, 1013–1024

Distribution coefficient and redox behaviour of uranium in Authie Bay (northern France)

GABRIEL BILLON†, BAGHDAD OUDDANE†, NICOLAS PROIX‡,
JACQUES DESORMIERES§, YOLANDE ABDELNOUR§
and ABDEL BOUGHRIET*¶

†Laboratoire de Chimie Analytique et Marine, Université des Sciences et Technologies de Lille 1,
Bât C8 (2ème étage), 59655 Villeneuve d'Ascq Cedex, France
‡Institut National de la Recherche Agronomique, Laboratoire d'Analyses des Sols 273,
rue de Cambrai, 62000 Arras, France
§VARIAN s.a., 7, avenue des Tropiques, Z.A. Courtaboeuf, BP 12, 91941 Les Ulis Cedex, France
¶Université d'Artois, I.U.T. de Béthune Département de Chimie, Rue de l'Université,
BP 819, 62408 Béthune Cedex, France

(*Received 28 September 2004; in final form 22 February 2005*)

Some mechanistic aspects associated with uranium release/immobilization and sedimentation in Authie Bay are presented in the present work. For this purpose, U contents in estuarine oxic waters, porewaters and sediment solids are determined. These analytical data allow us to appraise the partitioning of this metal between the liquid phase and the particulate matter/sedimentary material by calculating its distribution coefficient. Our findings further reveal that the distribution coefficient varies significantly with depth probably in response to the microbial activities in these sediments. This is confirmed by our studies on the geochemical behaviour of Fe and Mn in Authie Bay sediments. Finally, studies on the thermodynamic characteristics of sedimentary U in Authie Bay are undertaken in order to select possible U water–mineral equilibria that could involve in this environment, and to help define conditions of sedimentary U bioreduction.

Keywords: Uranium; Iron; Manganese; Early diagenesis; Redox potential; Partition coefficient; Thermodynamic calculation

1. Introduction

Sharp changes in thermodynamic equilibrium conditions occur in estuarine environments where freshwaters mix with saline waters, thus affecting the geochemistry of many elements. In particular, previous studies on the behaviour of U in estuaries showed that the geochemistry of this metal varies greatly [1–4]. Uranium(VI) is the most stable valence form under oxidizing geochemical conditions [5, 6]. Metal oxides

---

*Corresponding author. Fax: +33-3-20434822. Email: abdelatif.boughriet@univ-artois.fr

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310500107112

and colloids are partly responsible for particle uptakes of U(VI), e.g. as schoepite [1, 7]. Furthermore, in estuarine carbonate-containing waters, uranium(VI) is mostly complexed with carbonate, but also with hydroxide, phosphate, sulphate, etc. [5, 7], and these aqueous complexes contribute to enhance greatly U(VI) solubility in these waters [5].

On the other hand, several works on partition-coefficient (K_d) measurements for the sorption of uranium onto soils and sediments were previously reported [8]. These investigations show a large scatter of K_d values because of an important variability for sorption phenomena occurring between uranium and natural solid phases (calcium carbonate, iron oxides, organic matter and clays/aluminosilicates) [8] and relevant geochemical parameters characterizing the natural aqueous system under study (redox potential, pH, biomass activity, phosphate and carbonate contents...). These K_d values are generally designed to evaluate the importance of soil and sediment compositions on risks associated with migration/removal/or disposals of natural U or anthropogenic U in rivers, ponds, lakes or groundwaters in the vicinity of inhabited zones [8].

The U behaviour in these aquatic systems depends strongly upon the mineralogical composition and the anoxicity of sediments, as well as the extent of human activities (see [9–11]). Recently, we published preliminary results on uranium present at trace levels in anoxic sediments derived from Authie Bay [12]. This site has been chosen because industrial activities in its basin is weak [13] and thereby enables us the identification and examination of different diagenetic processes implicating natural uranium in a strictly unpolluted aquatic environment. Our preliminary results might be used as reference data for assessing in the future the impact of anthropogenic inputs on estuarine U in polluted zones. In order to gain complementary information about the electrochemistry of this metal in this site, we have undertaken in the present work detailed investigations on the geochemical and thermodynamic behaviour of U in Authie Bay and have assessed its partitioning between the liquid phase and the sedimentary material. Analytical data on oxic water U, porewater U, and sediment U are used to calculate K_d values and to obtain information about the extent of U immobilization/sedimentation. Studies on the thermodynamic properties of sedimentary U are also undertaken: (1) to help define conditions of formation of sedimentary U species; (2) to establish uranium water–mineral equilibria that could involve in this estuarine medium; and finally (3) to better understand thermodynamic/electrochemical phenomena implicating this metal in Authie Bay.

2. Experimental

2.1 *Location and sampling*

Authie Bay is located in northern France, as shown in figure 1. Water and sediment samplings were performed at different sites along Authie Bay (see figure 1) at low tide during the following periods: November 1998 and November 1999. Mainly, two cores were taken upstream and downstream (at two stations called Dns (downstream) and Ups (upstream) respectively, see figure 1) in Authie Bay with a 30-cm-long Perpex tube. These cores were immediately isolated from the atmosphere (so as to prevent any oxidation reactions in the sediment) inside a plastic bag previously purged

Figure 1. Location of the sampling sites (in northern France) where waters and sediments have been collected.

with nitrogen. They were then sliced under a nitrogen atmosphere inside a glove box; these sliced sediment samples were put separately inside plastic containers, which were previously purged with nitrogen atmosphere, and stored inside an ice box. In the laboratory, a part of each sediment sample was centrifuged at room temperature using an X340 Prolabo centrifuge (4000 rpm). Anoxic porewaters were recovered afterwards under a nitrogen atmosphere in a glove box, and filtered with 0.45 µm Alltech filters (cellulose acetate membrane), and immediately acidified with ultra-pure nitric acid (100 µL in 10 mL of porewater) before elemental analysis. The remaining parts of crude sediment samples were frozen under nitrogen at −20°C, so as to prevent any major modifications of the materials before further chemical treatments.

3. Analytical procedures

3.1 *Porewater and oxic estuarine water analyses*

The pH and natural redox potential (denoted as E_h in the text) are determined at various depths and at every centimetre in the field just after the sampling. For this purpose, we used either a glass electrode (Ingold) or a platinum electrode, which was directly introduced into the sediment core. These indicator electrodes were both combined with an Ag/AgCl reference electrode with a potential equal to +0.22 V *versus* a hydrogen normal electrode (HNE). It should be noted that in what follows, all redox potentials are referred to the absolute reference electrode noted HNE in the text.

Inorganic carbon (i.e. H_2CO_3, HCO_3^- and CO_3^{2-}) in porewaters was analysed using an automatic pH titrator (Metrohm; model Titrino 736 GP); pH analyses of interstitial fluids were carried out on several samples in triplicate with a titrated solution of HCl: $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. The standard deviations measured reflect the error in the pH metric measurements, and the relative error percentages were found to be lower than 5%.

Fluoride in interstitial waters was determined with relative standard deviations lower than 10%, using a specific electrode composed of a LaF_3 monocristal. For that, standard additions were carried out on each sample, as described in the literature [14].

Sulphate in interstitial waters and oxic estuarine waters was detected with relative standard deviations lower than 10% by a UV-visible spectrophotometer (Kontron Instruments: model UVIKON 860) at a wavelength of 650 nm, as described previously [15].

Concentrations of Ca^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Na^+ and Sr^{2+} in porewaters, and all solutions recovered from sediment solids were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian, Liberty Serie II, axial view). Concentrations of uranium in all these waters as well as sediment solids were determined using ICP-MS: either a Perkin-Elmer model (Elan 6000, Sciex, USA; analyses were carried out in the INRA laboratory, Arras (France)), or a Varian model (Ultra Mass 700, Australia); ICP-MS analyses were carried out in the VARIAN laboratory, in Les Ulis (France). Errors in the ICP-AES and ICP-MS measurements were found to be lower than 5%.

The equilibrium speciation of numerous dissolved components in porewaters extracted from sediments (which were sampled in Authie Bay) was investigated by using the MINEQL$^+$ computer program for calculating equilibrium state in these aqueous systems [16]. For this purpose, we have considered the following aqueous species: (1) the cations Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, Mn^{2+}, U(VI) and (2) the anions Cl^-, HCO_3^-, F^-, SO_4^{2-}, PO_4^{3-}, and we have undertaken a compilation of stability constants for equilibria involving these different ionic species.

3.2 *Sedimentary solid-phase analyses*

Metals present in sediments were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian, Liberty Serie II, axial view) and inductively coupled plasma mass spectroscopy (ICP-MS; Ultra Mass 700, Varian, Australia) after the following mineralization: briefly, the dried sediment was sieved at 63 µm, and 0.5 g of the fine fraction was attacked first by 10 mL of a concentrated HF solution at ebullition during 12 h; and second, after evaporation of this acid 10 mL of a freshly prepared HNO_3/HCl mixture (1/2 v:v) were added to eliminate at ebullition the remaining solid grains. Extraction procedures of metals from sedimentary phases were validated using the Canadian international Standards MESS-1, PACS-1 and BCSS-1. In all cases, the recovery percentages of element concentrations were found to be higher than 90%.

4. Results

4.1 *Partition coefficient for uranium*

The partition coefficient, K_d, for uranium is defined as [17]:

$$K_d(U) = [U]_{sed}/[U]_{diss}, \tag{1}$$

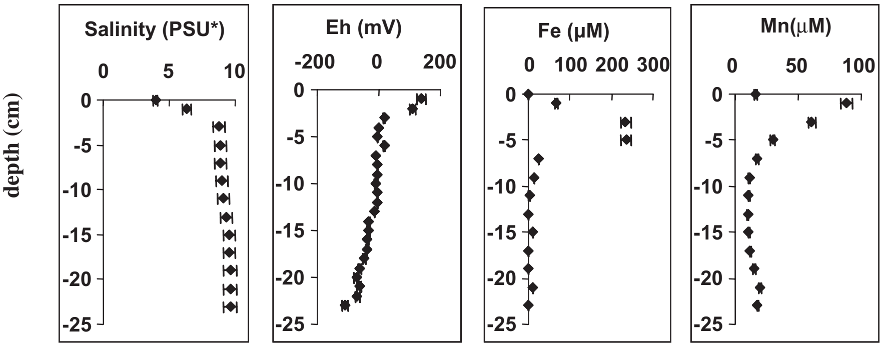
where $[U]_{sed}$ represents the total content of uranium in the particulate or sedimentary material after attacking it according to the chemical treatment described in the experimental section, and $[U]_{diss}$ is the total concentration of dissolved U in oxic surface waters or porewaters.

Equality (1) cannot be considered as a thermodynamic definition; however, it is often used by geochemists, geologists and oceanologists for estimating the extent of release, transport and/or deposition of an element as a result of its adsorption, desorption, complexation and/or the involvement of redox reactions in natural systems [8]. In this context, K_d measurements were carried out on several water and sediment samples (see table 1) taken at different stations along Authie Bay (see figure 1). For comparison, K_d measurements were also undertaken on seawaters collected from several sites along the English Channel as well as on river waters in northern France.

Table 1. Uranium concentrations found in the solid phase (with a relative standard deviation of 10%) and liquid phase (with a relative standard deviation of 5%) of sediments sampled in the Authie Bay and in coastal waters in northern France, and estimation of the partition coefficient, K_d.

Sample	U (solid) $\mu g\,g^{-1}$	[U] (dissolved) $\mu g\,dm^{-3}$	K_d (U) $mL\,g^{-1}$
Table 1A:Oxic conditions			
Authie estuary (upstream)	1.27	0.87	1460
Authie estuary (downstream)	2.04	3.10	638
Boulogne harbour	2.09	3.35	624
Graveline	1.06	3.36	315
Wimereux	2.15	3.25	661
Aa estuary	1.09	0.83	1313
Table 1B:Reducing conditions			
Authie estuary (upstream); sediment core			
Depth: 0–2 cm	1.60	1.60	1000
Depth: 6–8 cm	1.67	0.16	10,437
Depth: 8–10 cm	1.64	0.16	10,250
Depth: 10–12 cm	1.55	0.16	9688
Depth: 12–14 cm	1.45	0.15	9667
Depth: 14–16 cm	1.58	0.15	10,533
Depth: 18–20 cm	1.67	0.21	7952
Depth: 22–24 cm	1.58	0.44	3591
Authie estuary (downstream); sediment core			
Depth: 0–2 cm	1.29	3.05	423
Depth: 4–6 cm	1.40	1.42	986
Depth: 8–10 cm	1.47	1.76	835
Depth: 10–12 cm	1.35	2.10	643
Depth: 14–16 cm	1.31	4.05	323
Depth: 16–18 cm	1.36	4.28	318
Depth: 18–20 cm	1.37	4.52	303

Upstream sediment core



Downstream sediment core

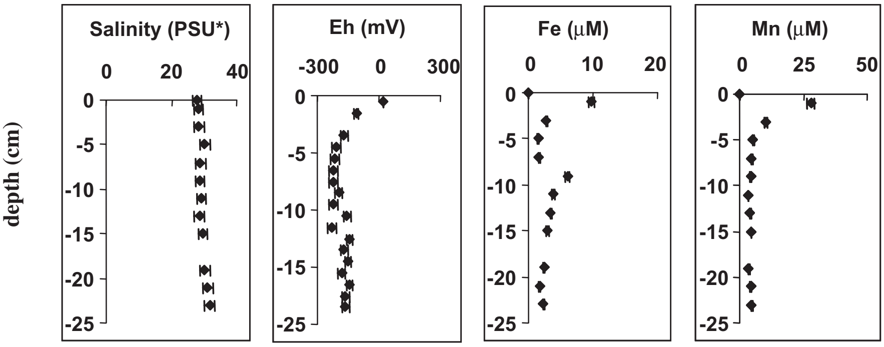


Figure 2. Concentration profiles of salinity, manganese(II) and iron(II) in interstitial waters and redox potentials (*vs*. HNE) measured along the sediment cores sampled in upstream and downstream Authie Bay (see figure 1). PSU: practical salinity unit.

In addition, two sediment cores were taken downstream and upstream in Authie Bay (see figure 1), where they were immediately sliced under strictly anoxic conditions. ICP-MS analyses of U both in recovered porewaters and sediment solids allow us to reach the K_d values at different depths (see table 1). It should be noted that under oxic conditions, contents of dissolved uranium have been found to be roughly three to four times higher in coastal seawaters than in fluvial waters located along extreme northern French coasts (table 1A). This explains why the K_d values obtained for seawaters are weak compared with those found in riverine waters (table 1A). Accordingly, the enrichment of marine U in estuarine waters is intimately related to a salinity increase in the analysed samples.

In sediments, redox potentials (E_h) decrease significantly with depth in both cores (see figure 2), indicating the involvement of early diagenesis processes (see, for instance, [18, 19]). These E_h depletions seem to indicate the involvement of significantly reductive processes. In the case of iron and manganese, we observe in both upstream and downstream sediments relevant concentration changes (i.e. we initially detect a strong increase in iron(II) and manganese(II) followed rapidly by a concentration drop; see figure 2) which finally leads to a dramatic consumption of dissolved Fe and Mn when E_h becomes very low: $<+20\,\mathrm{mV}$ *versus* HNE (figure 2). All these phenomena are intimately related to diagenesis processes well known in the literature [20–22].

In the case of U, its chemical behaviour in these cores differs from those of Fe and Mn, as pointed out above. Indeed, the evolution of dissolved U indicates a rapid decrease followed by a slow increase that is especially observed for downstream sediments (see table 1B). Note that salinity cannot be considered as a main factor influencing the variation of contents of dissolved sedimentary U, since salinity values are found to be relatively constant except near the surface of the upstream sediment core (see figure 2).

The Fe(III) and Mn(III, IV) electron acceptors compete with U(VI) in sediments. The preference of an electron acceptor depends upon kinetic factors and enzymatic reactions which are limited by the bacterium–metal oxide interface involving surface complexation and attachment [23–25]. Note that electron transfer resulting from complex bacterial mechanisms differs from that predicted from thermodynamic calculations [26–30]. Indeed, it is now understood that bacteria have an important role in the biogeochemical cycling of uranium by reducing soluble species and solid minerals of U(VI) into U(IV) oxides [11]. Low reductive 'biopotentials' as low as -400 mV develop on the bacterium surface [26–30]. Hence, any electron acceptor can potentially be reduced on the microbe membrane if its redox potential is higher than the redox potential of this organism [7, 29]. Our investigations show that natural potentials detected in buried sediments from Authie Bay reach values lower than -200 mV *versus* HNE (and even up to -280 mV *vs.* HNE), suggesting the involvement of intense bacterial activities [7, 26–30]. These ranges of natural potentials measured are close enough to those mentioned by Fredrickson *et al.* [7] during bacterial reduction experiments which were performed to assess the ability of metal-reducing bacteria such as *Shewanella putrefaciens strain CN32* to reduce U(VI). In this context, the decrease in dissolved uranium in the first few centimetres of the two cores studied (ca 10 times at 6–8 cm depths in upstream sediments and ca twice at 4–6 cm depths in downstream sediments; see table 1B) seems to be intimately related to a possible bio-reduction of dissolved U(VI) into precipitated U(IV). Conversely, contents of solid U found in the two cores do not change significantly with depths (see table 1B). This explains why K_d values increase dramatically for upstream sediments (up to 10,533) and, to a lesser extent, for downstream sediments (up to 986). It is worth noting that at very low natural potential (i.e. lower than -100 mV, and even -200 mV *vs.* HNE in some deep layers), a release of dissolved U is observed, thereby contributing to a decrease in K_d values (see table 1B). Note further that at these potentials, only uranium (IV) can exist in porewaters in agreement with our thermodynamic data, which will be reported below.

In this section, we have shown that the reductions of Fe(III), Mn(III, IV) and U(VI) in our sediments do occur immediately in the first few centimetres of the sediment core during early diagenesis. In addition, these diagenetic processes lead to sedimentary sulphurations with the production of iron sulphides, i.e. acid volatile sulphides (AVS) and chromium reducible sulphur (CRS). These investigations were recently published by us [12]. In what follows, we have attempted to identify specific thermodynamic characteristics of uranium in Authie Bay sediments.

4.2 *Electrochemical interpretation of the sedimentary behaviour of U*

There are two types of potential electron acceptors which are presumed to exist in sedimentary environments: (i) aqueous species (e.g. U(VI), which is mostly as uranyl phosphate, hydroxide and carbonate complexes); and (ii) solid compounds (e.g. Fe(III), Mn(III, IV) and U(VI) which are mostly as oxides and/or hydroxides). The standard potentials of several Fe, Mn and U redox couples are determined from Gibbs free energies reported in the literature [5, 31]. Furthermore, the MINEQL$^+$ computer program [16] is applied to calculate presumed equilibrium state in aquatic systems by computing the concentrations of main cations (Ca^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Na^+ and Sr^{2+}) and anions (Cl^-, HCO_3^-, F^-, PO_4^{3-}, SO_4^{2-} and S^{2-}) found in porewaters extracted from sliced sediment samples at different depths. In particular, this program enables us to estimate the equilibrium concentrations of all the aqueous Fe, Mn and U species in this sedimentary medium taking into account the total contents of dissolved metals and their complexing agents, their various equilibrium constants and the data on the pH and $p\mathrm{CO}_2$ of the porewaters. The iterative computation further allows us to reach the free concentrations for major ionic and neutral components/complexes in porewaters. Overall, our computational data indicate that the uranium in porewaters derived from Authie Bay is complexed (1) under oxic or weakly anoxic conditions (i.e. at $E_h > -30$ mV *vs.* HNE) with carbonate ions to give $UO_2(CO_3)_3^{4-}$ (80% upstream and 20% downstream) and $UO_2(CO_3)_2^{2-}$ (20% upstream and 30% downstream) and with phosphate ions to give $UO_2(HPO_4)_2^{2-}$ (50% in downstream); and (2) under strong anoxic conditions (i.e. at $E_h < -100$ mV *vs.* HNE) with hydroxide ions to give $U(OH)_5^-$ (~100% in upstream), and with phosphate ions to give $U(HPO_4)_4^{4-}$ (~100% in downstream) because phosphate concentrations in this interstitial medium are particularly high ($[PO_4]_{total} = 950\ \mu mol\ dm^{-3}$).

Owing to the chemical speciation of the various aqueous components and complexes – which are presumed to exist in these interstitial waters – the free ion concentrations of U, Fe and Mn species are determined. This allows us to reach the reduction potentials of some interesting electrochemical systems which proceed from the basic couples: U(VI)/U(IV), Fe(III)/Fe(II), Mn(III)/Mn(II), and Mn(IV)/Mn(II) (see table 2 and figure 3).

Based on single arguments of thermodynamic feasibility and with due consideration to the computed contents of reactive entities in porewaters, our findings reveal that the strongest calculated potential values correspond as a whole to the systems: $U(VI)_{dissolved} \rightarrow U(IV)_{solid}$ [mostly, the electrochemical couples involving the carbonate U(VI) complexes, i.e. $UO_2(CO_3)_3^{4-}/UO_{2(s)}$, $UO_2(CO_3)_2^{2-}/UO_{2(s)}$, and $UO_2CO_{3(dissolved)}/UO_{2(s)}$].

In reality, this situation is more complicated by microbial mechanisms implicating metal-reducing bacteria (which become electron donors as they metabolize lactate [7]) with constraints to electron transfer between the micro-organism or cell and Fe(III), Mn(III, IV) and/or U(VI) components. The competition between these different electron acceptors to reach the active site on the organisms as well as the exact reduction sequence that occurs in the sedimentary medium are beyond the scope of this research (for more details about microbial Fe, Mn and U reductions, for instance, see [7, 30, 32]). However, we can contend that the reactions involving only solid U (i.e. the electrochemical couples: $U(VI)_{solid} + 2e^- \rightarrow U(IV)_{solid}$, see table 2) cannot thoroughly explain the increase in dissolved U in buried sediments. In addition, the reductions of 'carbonate–U(VI)' complexes into U(IV) oxides cannot predominate kinetically in these porewaters as well because such reactions lead to a depletion of dissolved U in the medium. Consequently, only the reactions $U(VI)_{solid} + 2e^- \rightarrow U(IV)_{dissolved}$ which are reported in table 2 can interpret the generation of dissolved U in the interstitial

Table 2. Standard potentials (E°) and redox potentials (E_{redox}) of some electrochemical couples presumed to be potentially active in the sedimentary environment.[a]

Redox couples	E° (V)	E_{redox}(V)
$FeOOH_{(s)} + 3H^+ + e^- \Longleftrightarrow Fe^{2+} + 2H_2O$	+1.080	+0.227
$Fe(OH)_{3(s)} + 3H^+ + e^- \Longleftrightarrow Fe^{2+} + 3H_2O$	+1.015	+0.162
α-$FeOOH_{(goethite)} + 3H^+ + e^- \Longleftrightarrow Fe^{2+} + 2H_2O$	+0.804	−0.049
α-$Fe_2O_{3(hematite)} + 6H^+ + 2e^- \Longleftrightarrow 2Fe^{2+} + 3H_2O$	+0.790	−0.063
$Fe_3O_{4(magnetite)} + 8H^+ + 2e^- \Longleftrightarrow 3Fe^{2+} + 4H_2O$	+1.097	+0.025
$MnOOH_{(manganite)} + 3H^+ + e^- \Longleftrightarrow Mn^{2+} + 4H_2O$	+1.050	+0.183
$Mn_3O_{4(hansmannite)} + 8H^+ + 2e^- \Longleftrightarrow 3Mn^{2+} + 4H_2O$	+1.823	+0.731
$MnO_{2(manganate)} + 4H^+ + 2e^- \Longleftrightarrow Mn^{2+} + 2H_2O$	+1.292	+0.651
$MnO_{2(pyrolusite)} + 4H^+ + 2e^- \Longleftrightarrow Mn^{2+} + 2H_2O$	+1.229	+0.796
α-$UO_{3(s)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(am.)} + H_2O$	+0.525 ($UO_{2\,am.}$); 0.671 ($UO_{2\,uran.}$)	+0.110 ($UO_{2\,am.}$); 0.256 ($UO_{2\,uran.}$)
β-$UO_{3(s)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(am.)} + H_2O$	+0.515 ($UO_{2\,am.}$); 0.661 ($UO_{2\,uran.}$)	+0.100 ($UO_{2\,am.}$); 0.246 ($UO_{2\,uran.}$)
γ-$UO_{3(s)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + H_2O$	+0.497 ($UO_{2\,am.}$); 0.644 ($UO_{2\,uran.}$)	+0.082 ($UO_{2\,am.}$); 0.229 ($UO_{2\,uran.}$)
$UO_3 \cdot 2H_2O_{(s)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 3H_2O$	+0.412 ($UO_{2\,am.}$); 0.559 ($UO_{2\,uran.}$)	−0.003 ($UO_{2\,am.}$); 0.144 ($UO_{2\,uran.}$)
$UO_3 \cdot 9H_2O_{(s)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 10H_2O$	+0.418 ($UO_{2\,am.}$); 0.564 ($UO_{2\,uran.}$)	0.003 ($UO_{2\,am.}$); 0.149 ($UO_{2\,uran.}$)
$UO_2(CO_3)_3^{4-} + 3H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 3HCO_3^-$	+0.551 ($UO_{2\,am.}$); 0.691 ($UO_{2\,uran.}$)	−0.288 ($UO_{2\,am.}$); −0.148 ($UO_{2\,uran.}$)
$UO_2(OH)_2 \cdot H_2O_{(schoepite)} + 2H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 3H_2O$	+0.405 ($UO_{2\,am.}$); 0.545 ($UO_{2\,uran.}$)	−0.010 ($UO_{2\,am.}$); 0.130 ($UO_{2\,uran.}$)
β-$UO_2(OH)_2 + 2H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 2H_2O$	+0.433 ($UO_{2\,am.}$); 0.574 ($UO_{2\,uran.}$)	0.018 ($UO_{2\,am.}$); 0.159 ($UO_{2\,uran.}$)
$UO_2(CO_3)_2^{2-} + 3H^+ + 2e^- \Longleftrightarrow UO_{2(s)} + 2HCO_3^-$	+0.377 ($UO_{2\,am.}$); 0.517 ($UO_{2\,uran.}$)	−0.499 ($UO_{2\,am.}$); −0.359 ($UO_{2\,uran.}$)
$UO_2(CO_3)^0 + 2e^- \Longleftrightarrow UO_{2(s)} + CO_3^{2-}$	−0.029 ($UO_{2\,am.}$); 0.112 ($UO_{2\,uran.}$)	−0.275 ($UO_{2\,am.}$); −0.134 ($UO_{2\,uran.}$)
$UO_2(HPO_4)_2^{2-} + 2e^- \Longleftrightarrow UO_{2\ (s)} + 2HPO_4^{2-}$	−0.283 ($UO_{2\,am.}$); −0.143 ($UO_{2\,uran.}$)	−0.269 ($UO_{2\,am.}$); −0.129 ($UO_{2\,uran.}$)
$UO_2(HPO_4)^0 + 2e^- \Longleftrightarrow UO_{2(s)} + HPO_4^{2-}$	+1.104 ($UO_{2\,am.}$); 1.244 ($UO_{2\,uran.}$)	0.807 ($UO_{2\,am.}$); 0.947 ($UO_{2\,uran.}$)
$UO_2(OH)_2 \cdot H_2O_{(schoepite)} + H^+ + 2e \Longleftrightarrow U(OH)_5^-$	+0.043	0.207
$UO_2(OH)_2 \cdot H_2O_{(schoepite)} + 2H^+ + 2e \Longleftrightarrow U(OH)_4^0 + H_2O$	+0.180	0.208
$UO_2(OH)_2 \cdot H_2O_{(schoepite)} + 4HPO_4^{2-} + 6H^+ + 2e^- \Longleftrightarrow U(HPO_4)_4^{4-} + 5H_2O$	1.584	0.156

[a] Values have been obtained from the activities of the different elements present in the porewaters of downstream sediments derived from the Authie Bay at depths of 22–24 cm. am.: amorphous; uran.: uranyl.

waters where the natural potential is significantly very low (< -100 mV *vs.* HNE). Hence, only the electrochemical couples involving the mineral schoepite, i.e $UO_2(OH)_2 \cdot H_2O/U(OH)_5^-$ and $UO_2(OH)_2 \cdot H_2O/U(HPO_4)_4^{4-}$ predominate in strongly anoxic sediments from Authie Bay [7, 30, 32].

On the other hand, we have tried to identify predominant solid phases in the sedimentary process according to the solubility products. Our calculations indicate that porewaters are (over)saturated with respect to both crystallized UO_2 and $CaU(PO_4)_2 \cdot 2H_2O$ as uranium(IV) solids precipitated in buried sediments. Conversely, surface porewaters are undersaturated with uranium(VI) oxides and phosphates, suggesting that U(VI) precipitated in the water column tends to be dissolved in the upper sediments. However, the amounts of dissolved U(VI) found in these upper layers remain relatively weak (see table 1), probably because of complex kinetic considerations which are not addressed in this article.

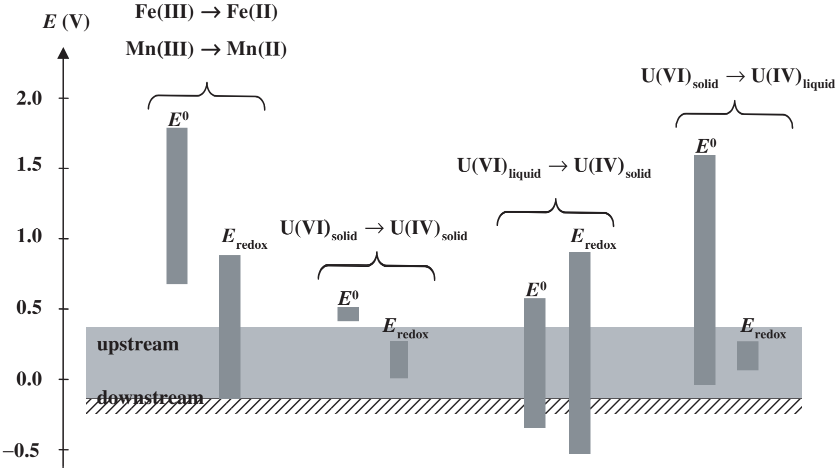


Figure 3. Comparison between the natural redox potentials measured in the sediment samples with a platinum electrode and the potentials corresponding to couples involving iron, manganese and uranium species which are presumed to be present in our environmental system.

5. Conclusion

The results of K_d measurements for the sorption of uranium under oxic and anoxic conditions onto particles/sediments in Authie Bay are reported in the present work. These studies are conducted to support U migration/removal/deposition investigations and mechanistic aspects associated with the presumed bioreduction of uranium. Thus, the K_d values obtained for oxic/bottom waters collected upstream are higher than those found downstream. This phenomenon results from low contents of natural dissolved U(VI) detected in Authie river. Detailed chemical analyses on a sediment core – which was sampled upstream in Authie Bay and directly sliced in the field under a nitrogen atmosphere in order to avoid any oxidation reactions – reveal variable bacterial activities with depths (by examining both the concentration profiles of ferrous and manganeous ions in porewaters and increases of Fe and Mn sulphides in sediment solids). The microbial mechanisms help to increase strongly the partition coefficient of U with depth as a result of bioreduction of dissolved U(VI) and U bio-immobilization to give UO_2(solid). Higher bacterial activities are detected in another sediment core sampled downstream of Authie Bay presumably due to strong sulphate concentrations and an input of 'young' marine organic matter which is degradated easier during early diagenesis. The bioreduction of both dissolved U(VI) and solid U(VI) (e.g. schoepite) does compete in this sedimentary medium, and generates the $U(OH)_5^-$ and $(HPO_4)_4^{4-}$ complexes (in which U is at oxidation state IV) under strongly anoxic conditions. This subsequent release of uranium in porewaters leads instead to a decrease in K_d values at lower depths (as observed mostly for buried sediments collected downstream in Authie Bay; see table 1B). Thermodynamic considerations are then addressed for calculating specific redox potentials of different Fe, Mn and U couples presumed to exist in the sedimentary medium studied. Based only on potential free energy change $\Delta E = E_{redox} - E_h$ (where E_{redox} is the redox potential of metallic electron acceptors (Fe, Mn or U), and E_h represents the natural redox potential which was correctly measured in the sedimentary medium with a platinum electrode) and by assuming that no kinetic constraints implicating enzymes occur in this natural system, the oxidizing species of Fe(III), Mn(III, IV) and U(VI) are expected to be reduced simultaneously in the first few centimetres of the sediment. The predominant aqueous oxidizing species of U(VI) (i.e. $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$ and $UO_2(HPO_4)_2^{2-}$) are totally consumed at depths lower than 5 cm; and at lower depths, the solid species $UO_2(OH)_2 \cdot H_2O$, schoepite (rather than UO_3, or $UO_3{,}\alpha H_2O$ as the initial product of U(VI) reduction in the range of the sediment pH) becomes the strongest oxidizing species of U(VI), and thereby its bioreduction seems to predominate kinetically in the medium. Indeed, schoepite is reduced to give $U(OH)_5^-$ ions and $U(HPO_4)_4^{4-}$ ions as the anoxicity of the buried sediment rises, thus explaining the increase in dissolved U at lower depths where redox potentials are very low (< -100 mV *vs.* HNE).

Overall, this work shows unambiguously the involvement of U reduction (accompanied with Fe and Mn reductions) occurring in both the liquid and solid sedimentary phases in which several electrochemical processes take place. However, more kinetic considerations must be taken into account for improving the pathway of U(VI) reduction in Authie Bay sediments.

In our opinion, this study should be of great interest for geochemists working on early diagenetic processes in estuarine environments. Like Mn and Fe, which are mostly studied in the literature, U seems to be dependent upon the anoxicity of the medium as well. The scientific procedure described in this article for uranium should be developed and applied to other sites which are more polluted and have not yet been examined, in order to assess eventual ecosystem perturbations bound to anthropogenic activities. We do believe that the experimental procedure described here might be improved further by a better knowledge of reactions implicating sedimentary organic matter.

Acknowledgements

This work was supported by the Region Nord Pas-de-Calais (CPER Authie) and the PNETOX program. Many thanks to Jean-François Barthe (LCAM, ELICO) for the core samplings.

References

[1] P.S. Andersson, D. Porcelli, Ö. Gustafsson, J. Ingri, G.J. Wasserburg. *Geochim. Cosmochim. Acta*, **65**, 13 (2001).

[2] W.S. Moore. In *U-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences*, M. Ivanovich and R.S. Harmon (Eds), pp. 396–422, Clarendon Press, Oxford (1992).

[3] D. Porcelli, P.S. Andersson, G.J. Wasserburg, J. Ingri, M. Baskaran. *Geochim. Cosmochim. Acta*, **61**, 4095 (1997).

[4] P.S. Andersson, D. Porcelli, G.J. Wasserburg, J. Ingri. *Geochim. Cosmochim. Acta*, **62**, 385 (1998).

[5] D. Langmuir. *Geochim. Cosmochim. Acta*, **42**, 547 (1978).

[6] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C.N.-T. Cregu, H. Wanner. *Chemical Thermodynamics Uranium*, Elsevier Science, Amsterdam (1992).

[7] J.K. Fredrickson, J.M. Zachara, D.W. Kennedy, M.C. Duff, Y.A. Gorby, S.M. Li, K.M. Krupka. *Geochim. Cosmochim. Acta*, **64**, 3085 (2000).

[8] United States Environmental Protection Agency. Available online at: http://epa.gov/radiation/cleanup/partition.htm (accessed 2005).
[9] R.F. Anderson, M.Q. Fleisher, A.P. LeHuray. *Geochim. Cosmochim. Acta*, **53**, 2215 (1989).
[10] P.W. Swarzenski, B.A. McLee, J.M. Skei, J.F. Todd. *Mar. Chem.*, **67**, 181 (1999).
[11] J.K. Fredrickson, J.M. Zachara, D.W. Kennedy, H. Dong, T.C. Onstott, T.C. Hinman, S.M. Li. *Geochim. Cosmochim. Acta*, **62**, 3239 (1998).
[12] G. Billon, B. Ouddane, N. Proix, J. Desormières, Y. Abdelanour, A. Boughriet. *Int. J. Environ. Anal. Chem.*, **84**, 775 (2004).
[13] G. Billon. Géochimie des métaux et du soufre dans les sédiments des estuaires de la Seine et de l'Authie. Thesis, University of Lille (2001).
[14] AFNOR. In *Eaux Méthodes d'Essais*, Groupe-AFNOR-Editions (Ed.), pp. 15–21, Paris (1990).
[15] AFNOR. In *Eaux Méthodes d'Essais*, Groupe-AFNOR-Editions (Ed.), pp. 191–194, Paris (1990).
[16] W.D. Schecher, D.C. McAvoy. *MINEQL+: A Chemical Equilibrium Modeling System; version 4 for Windows*. Environmental Research Software, Hallowell, Maine (1998).
[17] J.W. Morse, F.T. Mackenzie. *Geochemistry of Sedimentary Carbonates*, Elsevier, Amsterdam (1990).
[18] Y. Song, G. Müller. *Sediment–Water Interactions in Anoxic Freshwater Sediments*, Springer, Heidelberg (Lecture Notes in Earth Sciences, 1999).
[19] A.C.M. Bourg, J.P.G. Loch. In *Biogeodynamics of Pollutants in Soils and Sediments*, W. Salomons and W.M. Stigliani (Eds), pp. 87–100, Springer, Berlin (1995).
[20] J.G. Farmer, M.A. Lovell. *Environ. Technol. Lett.*, **5**, 257 (1984).
[21] J.G. Farmer. *Environ. Geochem. Health*, **13**, 76 (1991).
[22] D.E. Buckley, J.N. Smith, G.V. Winter. *Appl. Geochem.*, **10**, 175 (1995).
[23] R.G. Arnold, T.J. DeChristina, M.R. Hoffman. *Biotechnol. Bioeng.*, **32**, 1081 (1988).
[24] D.R. Lovley, E.J.P. Phillips. *Appl. Environ. Microbiol.*, **54**, 1472 (1988).
[25] C. Myers, K.H. Nealson. *Science*, **240**, 1319 (1988).
[26] A.S. Beliaev, D.A. Saffarini. *J. Bacteriol.*, **180**, 6292 (1998).
[27] C. Myers, J. Myers. *Biochim. Biophys. Acta*, **1326**, 307 (1997).
[28] J. Myers, C. Myers. *Biochim. Biophys. Acta*, **1373**, 237 (1998).
[29] P. Bianco, J. Haladjian. *Biochimica*, **76**, 605 (1994).
[30] A.I. Tsapin, K.H. Nealson, T. Myers, M.A. Cusanovich, J. van-Beuumen, L.D. Crosby, B.A. Feinberg, C. Zhang. *J. Bacteriol.*, **178**, 6386 (1996).
[31] G. Michard. *Equilibres chimiques dans les eaux naturelles*, Publisud, Paris (1989).
[32] J.M. Zachara, J.K. Fredickson, S.M. Li, D.W. Kennedy, S.C. Smith, P.L. Gassman. *Am. Mineral*, **83**, 1426 (1998).