Remobilisation of uranium from contaminated freshwater sediments by bioturbation

Sandra Lagauzère, Mikael Motelica-Heino, Eric Viollier, G. Stora, J.M. Bonzom

Biogeosciences
Open Access
Discussions

Remobilisation of uranium from contaminated freshwater sediments by bioturbation

S. Lagauzère[1], M. Motelica-Heino[2], E. Viollier[3], G. Stora[4], and J. M. Bonzom[1]

[1]Laboratoire d'Ecotoxicologie des Radionucléides, Institut de Radioprotection et de Sûreté Nucléaire (IRSN)/PRP-ENV/SERIS, Cadarache, Bât. 186 – BP 3, 13 115 Saint-Paul-Lez-Durance, France
[2]Université d'Orléans, ISTO, UMR7327 CNRS/INSU 1A, rue de la Férollerie, 41071 Orléans Cedex 02, France
[3]Laboratoire de Géochimie des Eaux, Université Paris Diderot, Sorbonne Paris Cité, Institut de Physique du Globe de Paris, UMR7154 CNRS, 75013 Paris, France
[4]Université Aix-Marseille, CNRS/INSU, IRD, Mediterranean Institute of Oceanography (MIO), UM 110, 13288 Marseille, France

Abstract

Previous studies have demonstrated that benthic macro-invertebrate bioturbation can influence the remobilization of uranium initially associated with freshwater sediments resulting in a high release of this pollutant through the overlying water column. Giving the potential negative effects on aquatic biocenosis and the global ecological risk, it appeared crucial to improve our current knowledge concerning the uranium biogeochemical behaviour in sediments. The present study aimed to assess the biogeochemical modifications induced by *Tubifex tubifex* (Annelida, Clitellata, Tubificidae) bioturbation within the sediment permitting to explain such a release of uranium. To reach this goal, uranium distribution between solid and solute phases of a reconstructed benthic system (i.e. in mesocosms) inhabited or not by *T. tubifex* worms was assessed in a 12 day laboratory experiment. Thanks notably to fine resolution (mm-scale) measurements (e.g. DET gels probes for porewater, bioaccumulation in worms) of uranium and main chemical species (iron, sulfate, nitrate, nitrite), this work permitted (i) to confirm that the removal of bottom sediment particles to the surface through the digestive tract of worms greatly favours the oxidative loss of uranium in the water column, and (ii) to demonstrate that both uranium contamination and bioturbation of *T. tubifex* substantially influence major microbial-driven biogeochemical reactions in sediments (e.g. stimulation of denitrification, sulfate-reduction and iron dissolutive reduction). This study provides the first demonstration of biogeochemical modifications induced by bioturbation in freshwater uranium-contaminated sediments.

1 Introduction

Trace metal pollution of rivers, lakes and estuaries is a preoccupant ecological problem in many industrialized areas worldwide. Despite recent efforts to improve water quality, notably in most of developed countries, many aquatic ecosystems are still threatened by pollution accumulated in sediments and groundwaters. In this context, the case

of uranium released by mining extraction is of particular interest due to its complex biogeochemical behavior and its potential high ecotoxic risk for aquatic biocenosis. Whereas the natural geochemical background level of uranium in freshwater sediments is considered lower than $10 \, \mu g \, U \, g^{-1}$ (dry weight) (Kurnaz et al., 2007), much higher

5 concentrations, up to a few thousands $\mu g \, U \, g^{-1}$, have been measured in rivers and lakes close to former or operating mining sites (Neame et al., 1982; Lottermoser and Ashley, 2006; Lozano et al., 2002; Hart et al., 1986). The long-term storage capacity of such contaminated sediments depends on numerous geochemical and biological parameters affecting the solubility and thus the mobility of uranium.

10 The biogeochemical behaviour of uranium in surface sediments is in fact directly related to its speciation, the chemistry of the solute and solid phases and to processes including precipitation, dissolution, adsorption, complexation, and to a large extent to numerous transformations occurring in early diagenesis processes. Uranium speciation is primarily related to pH and oxido-reduction potential values (Langmuir, 1978)

15 but also strongly depends on the CO_2 partial pressure, the ionic force of solute phases, the total concentration in uranium, the presence of organic and mineral ligands (Ragnarsdottir and Charlet, 2000; Davis et al., 2002, 2004, 2006; Denison, 2004; Curtis et al., 2006) and microbial activity (Renshaw et al., 2007). In most surface freshwaters (i.e. under oxic conditions, pH 5–9), uranium occurs under a free and soluble form, the

20 uranyl ion UO_2^{2+}, which is at the (+VI) oxidation state. Depending on the pH and the ionic composition of the water, the uranyl ion can form complexes with other ions, principally hydroxyles or carbonates, phosphates, fluorides, chlorides, but also with some organic compounds such as humic acids (Ragnarsdottir and Charlet, 2000; Marang, 2007). Adsorption on mineral (e.g. oxy/hydroxydes of iron or manganese and clays)

25 or organic particular phases also plays an important role by reducing the mobility of uranyl ions in water (Curtis et al., 2006). Thereby, uranium coming in contact with the sediment is either on a soluble form, free or complexed, and will diffuse towards the porewater, or sorbed to suspended matter and will be incorporated by sedimentation. In anoxic sediments, uranium is reduced to U(+IV) which is an insoluble form and tends

to be immobilised and thus to accumulate in the deeper sediment layers by formation of insoluble nanoparticulates or large aggregated oxides like uraninite or schoepite (Liger et al., 1999; Phrommavanh, 2008). Additionally, the reduction of uranium can also occur biotically through metal-reducing bacteria metabolism in sediment (Lovley et al., 1991). This process has notably been used in recent bioremediation programs of contaminated sites where immobilisation of uranium in sediments was favoured by organic amendment at the sediment surface (Renshaw et al., 2007; Wall and Krumholz, 2006; Wilkins et al., 2006; Barlett et al., 2012).

Inversely, mechanical disturbances of top sediment can hamper the incorporation of uranium in bottom anoxic layers and its immobilization. Among them, the modifications of sediment properties induced by benthic macro-invertebrate activities (i.e. bioturbation) are likely to be of first importance. As demonstrated for diverse trace metals, bioturbation can increase their remobilization from the sediment through the overlying water by favouring the oxidative loss of previously accumulated solid phases (Motelica-Heino et al., 2003; Naylor et al., 2004, 2006, 2012). Three major processes are involved: (i) oxygen penetration in bottom sediment due to active water pumping in burrows (i.e. bioirrigation), (ii) removal of particles from the bottom sediment to its surface, (iii) and indirect effects due to induced heterogeneity (e.g. redox conditions, organic matter availability, fluxes of solutes) and stimulation/inhibition of microbial communities. However, little work has been undertaken so far to evaluate these processes in sediments accumulating uranium in freshwater systems (Komlos et al., 2008; Phrommavanh, 2008) and the few previous studies on this topic concerned marine ecosystems (Zheng et al., 2002; Morford et al., 2009). In freshwaters, some organisms able to survive in contaminated environments, such as tubificid worms (Annelida, Clitellata), are known to induce a strong sediment reworking that could impact the remobilisation of metals (Zheng et al., 2002; Alfaro-De-la-Torre and Tessier, 2002; Ciutat and Boudou, 2003; Ciutat et al., 2007; De Haas et al., 2005; Petersen et al., 1995; Soster et al., 1992; Zoumis et al., 2001). Tubificid worms represent a dominant group of freshwater benthic macro-invertebrates. Their populations can reach very high densities notably

in organic-rich sediments. Despite no active bioirrigation of their gallery network, the effects induced by tubificid worms on the sediment matrix are crucial for the global biogeochemical functioning and the metal distribution at the benthic interface. Due to their particular mode of feeding which consist on ingestion of sediment particles in bottom layers and rejection at the sediment–water interface (i.e. upward-bioconveying, sensu Gérino et al., 2003), they create a removal of associated compounds including metals initially immobilized under reduced forms. This phenomenon has been recently observed in uranium-contaminated sediment inhabited by *Tubifex tubifex* worms (Lagauzère et al., 2009a–c). In these mesocosm experiments, it was demonstrated that despite important ecotoxic effects of uranium on the worms (e.g. malformations, autotomy, mortality), their bioturbation activity remained sufficiently important to stimulate diagenetic processes (e.g. increase of oxygen uptake) and to induce a 2- to 10-fold higher release of uranium through the overlying water. However, underlying biogeochemical processes occurring under these conditions still need to be assessed to explain the remobilization of uranium.

The main goal of this study was thus to assess the influence of the bioturbation of *T. tubifex* in a benthic ecosystem for which sediment was initially contaminated with uranium. We conducted a laboratory experiment using mesocosms with natural sediment artificially contaminated in uranium and inhabited or not by *T. tubifex*. The distribution of uranium between solid and solute phases, including bioaccumulation in *T. tubifex* worms, was estimated to calculate fluxes between the sediment and the water column, and a mass budget. In parallel, high-resolution profiles of dissolved uranium, iron, manganese, sulfates, nitrates and nitrites were measured to give an overview of the main biogeochemical reactions occurring in sediment and to propose hypothesis of their interactions with uranium in presence or absence of *T. tubifex* worms.

2 Material and methods

2.1 Preparation of the aquaria

Surface sediment and water were collected in a dead arm of the Esparron Lake, a reservoir-lake upstream from a man-made dam on the river Verdon (Alpes de Haute-Provence, Southern France). This site was chosen for the pristine quality of its surface water and the fine texture of the sediment (median grain size, $D_{50} = 33.8\,\mu m$). Sediments were treated to eliminate the grosser particulate phases (vegetal fragments, stones, wastes) and the maximum of organisms by sieving at 2 mm and freezing at $-20\,°C$ for 48 h. The sediments were then homogenised mechanically and stored at $4\,°C$ until the preparation of the aquaria. The water was filtered at 20 μm to eliminate macro- and meiofauna and also stored at $4\,°C$ before use. The principal physical and chemical parameters of the sediment and overlying water were reported in a previous work (Lagauzère et al., 2009c). Briefly, analyses revealed a highly calcareous medium (total calcite in sediments: 70 %, water hardness: $152\,Eq\,mg\,CaCO_3\,L^{-1}$), with a pH of 8.2–8.6 and a low organic matter content (2.4 %) for a lake sediment.

The sediment was artificially contaminated with a solution of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ in a large HDPE container (height $= 65$ cm, $\varnothing = 41$ cm, 68 L drum from CurTec[®], the Netherlands) in order to obtain a nominal uranium concentration of $600\,\mu g\,U\,g^{-1}$ (dry weight). The tank was then daily shaken during 2 weeks before the beginning of the experiment to allow adsorption of uranium on the sediment particles and a homogenous contamination. The effective measured concentration after 2 weeks was $539\,\mu g\,U\,g^{-1}$. This concentration level was chosen as a function of results obtained in previous works with similar experimental conditions. It corresponds to a bioturbation activity though diminished that generates an important remobilisation of uranium from the sediment to the water column (Lagauzère et al., 2009a, c). A non-contaminated sediment tank was similarly prepared for control aquaria. For each condition (contaminated and control), nine aquaria were prepared in cylindrical PVC boxes

(12 cm in diameter, 20 cm in height). The aquaria were filled with 10 cm of sediment and an overlying 10 cm water column. They were randomly placed in a large tank with controlled temperature (21 °C) and photoperiod (16 h light/8 h dark). Each aquarium received a constant air bubbling in the water column. This setting has been stabulating for 4 weeks before the introduction of the *T. tubifex* worms. Slight additions of distilled water were done on a daily basis to compensate the water losses due to evaporation. Volumes extracted for sampling were replaced by initial lake water.

2.2 Origin, acclimatization and introduction of benthic organisms

The *T. tubifex* worms were purchased from a commercial breeding (Grebyl and Fils, Arry, France). They were acclimated to the experimental conditions during several weeks and were fed twice a week with Tetramin[®] flakes (Tetra Werke, Melle, Germany) put into suspension ($3\,\mathrm{mg\,ind^{-1}}$ from a $10\,\mathrm{g\,L^{-1}}$ suspension). Before the beginning of the experiment, the worms were starved in artificial sand for 48 h. In each aquarium devoted for worm addition, 28 g of *T. tubifex* was added at the sediment surface. This mass corresponds to ca. 60 000 individuals per square meter, which is representative of an average natural density for freshwater ecosystems (Budd, 2005). The air bubbling was stopped for three hours to allow the worms to settle to the sediment–water interface.

2.3 Experimental procedure

On the 9 aquaria prepared for each condition (contaminated/control), 3 were retrieved on the first day of the experiment (day 0) i.e. after the 4 weeks of stabilization, 3 received *T. tubifex* worms on day 0 and were retrieved after twelve days (day 12), and the remaining 3 did not receive any organisms and were also retrieved on day 12. The coding of experimental treatments was the following: C- for control, U- for contaminated sediment, T- for presence of *T. tubifex*, followed by −0 or −12 for the time of sampling

(for instance, UT-12 corresponds to "contaminated sediment/presence of worms" after 12 days).

2.4 Physico-chemical measurements

2.4.1 Measurements in the water column: temporal monitoring

Temperature, pH and dissolved oxygen concentration of the water column were measured one day before the introduction of the *T. tubifex* worms and then every second day until the end of the experiment (day 12). The concentration in total uranium in the water column was monitored from non-filtered and acidified water samples (2 % HNO_3) analysed by ICP-AES (Optima 4300 DV, Perkin Elmer, USA). The apparent uranium exchange flux between the sediment and the water column was calculated from the uranium concentrations at day 0 and day 12 (based on the variation of uranium in the water column divided by the area of the water–sediment interface). The concentrations of dissolved chemical species, including uranium, were estimated from the average values measured from the water-exposed part of the DET probe (see below). The differences in concentrations between day 12 and day 0 were also expressed in terms of mean fluxes.

2.4.2 Pore-water concentration profiles of the dissolved chemical species

In each aquarium, the concentration profiles of the dissolved elements were determined by using two constrained DET probes (Diffusive Equilibrium in Thin-films) purchased from DGT Research Ltd (Lancaster, UK). One of the probes was devoted to the analysis of major cations and uranium by ICP-AES (Optima 4300 DV, Perkin Elmer, USA) whereas the second one was used for the analysis of major anions by ionic liquid chromatography (DX120, column AS11HC 4 mm, eluant KOH, Dionex, Sunnyvale, USA). These peeper-gel probes consisted of plastic holders (240 mm × 40 mm × 5 mm) with an open window (18 mm × 150 mm). From the aperture, a series of parallel

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

agarose-gel strips (1 mm × 1 mm × 18 mm) were exposed through a 0.2 µm Nylon membrane to the ambient medium for equilibration. Before use, the probes were de-oxygenised in a 0.01 M NaCl solution with nitrogen for 48 h. They were afterwards deployed in the sediment of each aquarium 48 h before the desired analysis time (i.e.

5 2 days before the introduction of the organisms for treatments C-0 and U-0 and at day-10 for treatments C-12, CT-12, U-12 and UT-12). After sampling, the probes were placed in a glove box under nitrogen atmosphere. The gels strips were gently retrieved and directly eluted in 1 mL HNO$_3$ 2 % for samples analysed by ICP-AES (major cations and uranium) and in 1 mL Milli-Q water for samples analysed by ionic chromatography

10 (major anions). All measurements were performed in the 6 days following the sampling. During their storage, the samples were kept at 4 °C and daily hand-shaked. Calculations were made based on the assumption of gel strips dimension homogeneity.

2.4.3 Determination of net accumulation rates in overlying waters

Accumulation rates were calculated from differences between start-end concentrations

15 of dissolved species divided by the duration of the experiment. Positive values indicate a net input to the overlying water. In contrast, negative values suggest a net elimination/output of dissolved species.

2.4.4 Determination of diffusive instantaneous fluxes at the sediment–water interface and sediment uranium consumption rates

20 Each vertical profile of dissolved chemical species was simulated using the PROFILE software (Berg et al., 1998) in order to estimate uranium consumption rates below the sediment-water interface and instantaneous diffusive fluxes of other solutes.

Briefly, the diffusive flux J at the sediment–water interface was estimated from the sediment porewater concentration profile obtained with DET probe using the Fick's first

law of diffusion (Li and Gregory, 1974; Berner, 1980):

$$J(z) = -\varphi \cdot D_\text{s} \cdot \frac{\partial C(z)}{\partial z}$$

where ϕ is the porosity, D_s is the diffusion coefficient in sediments ($\text{cm}^2 \text{s}^{-1}$), C is the concentration (mmol cm^{-3}), z is the depth (cm) and $\partial C(z)/\partial z$ is the concentration gradient across the sediment–water interface.

D_s was estimated from values of the diffusion coefficient in water D reported in the literature corrected for temperature and salinity (Li and Gregory, 1974; Boudreau, 1997; Schultz and Zabel, 2000) and the tortuosity θ of the sediment using the following equation:

$$D_\text{s} = \frac{D}{\theta^2}$$

where θ was calculated from the porosity using the empirical relation given by Boudreau (1997):

$$\theta^2 = 1 - \ln(\varphi^2)$$

In our experiments the subsurface porosity was estimated at 0.75 in absence of worms and 0.83 in presence of worms, independently of the uranium contamination. Thus the tortuosity values were $\theta^2 = 1.57$ without worms (treatments C-0, C-12, U-0, U-12) and $\theta^2 = 1.37$ with worms (treatments CT-0, CT-12, UT-0, UT-12).

Differential equations were then solved numerically at a steady state to reproduce $C(z)$ and provide the best "reasonable" estimation of $R(z)$ (Berg et al., 1998). The boundary conditions were the concentration in the overlying water at the top and an absence of flux in deeper sediment. All fluxes were integrated over overlying water height in order to be compared to net accumulation rates in overlying waters.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2.4.5 Determination of the uranium concentration in the solid phase of the sediment

After aforementioned analyses, at day 0 for U-0 and at day 12 for U-12 and UT-12, the water was retrieved with a syringe and the sediment column was gently sliced at
5 a resolution of 1 cm. Each slice was dried at 60 °C for 72 h and then homogenised by manual grinding with a mortar. Three sub-samples of 1 g of dry sediment were then mineralised by successive addition of HNO_3, HCl and H_2O_2. After two cycles of mineralization/evaporation (105 °C, 90 min) the solutions were filtered at 0.45 µm (Minisart acetate cellulose filters) and subsequently analysed by ICP-AES to determine
10 the concentration of total uranium in the sediment. These data were used to calculate the global mass budget of uranium over the duration of the experiment.

2.4.6 Determination of the uranium bioaccumulation in *T. tubifex* worms

Four hours before dismantling the contaminated aquaria containing *T. tubifex* worms (UT-12) the air bubbling was stopped to allow the worms to come out of the sediment.
15 A sample of worms was collected with a pipette to determine the bioaccumulation of uranium in them. After two hours of integument depuration in non-contaminated water at ambient temperature (22–25 °C), samples of worms were dried at 60 °C for 48 h and then mineralised with the following procedure. Each sample (ca. 630 mg) was mineralized by addition of 5 mL of HNO_3 at 65 % and 5 mL H_2O_2 at 30 % followed by two
20 cycles of heating at 95 °C for 90 min. After complete evaporation, the solid residues were put in suspension in 10 mL HNO_3 at 2 % at ambient temperature for 24 h. Samples were then filtered at 0.45 µm (Minisart acetate cellulose filters) and analysed by ICP-AES. The quality control sample was prepared by adding a known concentration of uranium to mineralized *T. tubifex* worms; this preparation was necessary because
25 no certified biological material was available for uranium measurement by ICP-AES in aquatic organisms. To estimate the amount of uranium in the total biomass the measured concentration was related to the mass of worms initially introduced in the aquaria

with a minoration of 10 % to take into account the mortality of the species at this concentration of uranium (Lagauzère et al., 2009c).

2.5 Statistical analysis

All statistical analyses were performed with the Statistica software (StatSoft, Inc., OK, USA). Before each statistical analysis, the normality of the data was tested with a Shapiro–Wilk's test and the homogeneity of the variances by a Levene's test. These tests were repeated after transformation of the data when these hypotheses were not fulfilled. A threshold of significance of 5 % was applied for all statistical analysis.

i. The temporal variation of physico-chemical parameters of the water column were analysed by repeated-measures ANOVAs (RM-ANOVAs) for each treatment.

ii. The variation of total uranium concentration in the water was analysed by a Student's t test. To separate the effects of bioturbation and the effects of uranium contamination, the variations of other parameters (iron, sulfates, nitrates and nitrites) were analysed by two-ways ANOVAs ("Tubifex"/"uranium") completed by post-hoc Fisher's LSD tests.

iii. The diffusive fluxes at the sediment–water interface in the different treatments were analysed by one-way ANOVAs and compared by post-hoc Fisher's LSD tests.

3 Results

3.1 Chemistry of the water column

For all the experimental treatments, the water temperature was maintained at 21.2 (±0.1) °C, the dissolved oxygen concentration at 8.1 (±0.3) mg L^{-1} and the pH at 8.4

Remobilisation of uranium from contaminated freshwater sediments

S. Lagauzère et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(±0.2) with no significant difference between the treatments and times of sampling (RM-ANOVAs: $P > 0.05$; two-ways ANOVAs: $P > 0.05$).

The concentration of total uranium in the water column of contaminated aquaria, with and without *T. tubifex* worms, according to time is presented in Fig. 1, with the apparent net accumulation rate of uranium in the water column as an inset. In both cases, the concentrations of uranium increased during the experiment but they reached clearly higher values in presence of worms in the sediment (117 ± 9.6 nmol U cm^{-3}, i.e. > 3 times the concentration at day 0). It resulted in a net accumulation rate of total uranium significantly higher (i.e. 5 times) in presence of worms (Student's test: $t = -14.7$, $P = 0.000$). The concentration of dissolved uranium measured with DET probes (see below) showed the same results (Fig. 2a–c).

Although several other compounds were effectively measured during the analyses, only total dissolved concentrations of iron, sulfate, nitrate and nitrite were retained here as certain compounds (e.g. manganese, potassium, phosphates) had concentrations below the detection limits of the measurement devices (ICP-AES: 1 µg L^{-1}, ionic chromatography: 10 µL m^{-1}), or simply provided no relevant information (e.g. chlorides, calcium).

The results were the following:

i. Iron was not detectable in the water column of any aquarium (detection limit $<$ 1 µL m^{-1}) (Fig. 3a and b).

ii. Independently of the uranium contamination, the concentrations in sulfate increased significantly in the water column in presence of worms (ANOVA "Tubifex": $F_{8,1} = 36.7$; $P = 0.000$; "uranium": $F_{8,1} = 0.98$; $P = 0.35$; "Tubifex·uranium": $F_{8,1} = 0.85$; $P = 0.38$; Fisher LSD: $P < 0.05$) (Fig. 4a–c).

iii. The concentrations of nitrate in the control aquaria decreased without worms but increased strongly in their presence (Fig. 5a). In the contaminated aquaria, the nitrate concentrations increased with time but it was greatly stronger in presence of worms (Fig. 5b). The highest fluxes observed under the effect of bioturbation

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

appeared similar between control and contaminated aquaria (ANOVA "Tubifex": $F_{8,1} = 482$; $P = 0.000$; "uranium": $F_{8,1} = 3.85$; $P = 0.04$; "Tubifex·uranium": $F_{8,1} = 32.8$; $P = 0.000$; Fisher LSD: $P < 0.05$) (Fig. 5c).

iv. For nitrite, despite low variations, slightly significant effects were noticed for bioturbation (ANOVA "Tubifex": $F_{8,1} = 14.22$; $P = 0.005$) and uranium contamination (ANOVA "uranium": $F_{8,1} = 223$; $P = 0.000$) but not for the interaction Tubifex·uranium (ANOVA "Tubifex·uranium": $F_{8,1} = 0.89$; $P = 0.37$). In the control aquaria, the nitrite concentrations diminished with time and this effect was amplified by bioturbation (Fig. 6a and c). In contrast, in the contaminated aquaria the nitrite concentrations slightly increased with time independently of the bioturbation (Fisher LSD: $P < 0.05$) (Fig. 6b and c).

3.2 DET- Porewater concentration profiles

3.2.1 Uranium

The water column and sediment porewater concentrations profiles of uranium for the three contaminated treatments (U-0, U-12 and UT-12) are presented in Fig. 2a–c. In all cases, the average concentrations of uranium determined in the water column by the DET probes was similar to those obtained from non-filtered water samples (above-mentioned results), indicating that almost all of uranium in the water column was under a dissolved form. These results confirm an increase of uranium concentrations in the water during the experiment with a much more pronounced effect in presence of worms.

Under the sediment–water interface, the shape of uranium profiles is similar in all treatments and shows decreasing concentrations with depth (Fig. 2a–c), probably due to its diffusion from the overlying water and its reduction within the anoxic sediment. Modelling estimations from PROFILE reveal significant differences. On one hand, in absence of worms, the diffusive instantaneous inward

flux more than doubled with time, from $-0.09 \pm 0.00 \times 10^{-3}\,\mathrm{nmol\,U\,cm^{-3}\,h^{-1}}$ (U-0) to $-2.21 \pm 0.01 \times 10^{-3}\,\mathrm{nmol\,U\,cm^{-3}\,h^{-1}}$ (U-12). In response to increasing concentrations in overlying water and subsequently increasing chemical gradient, uranium consumption rate increased, indicating a strong kinetic dependency to substrate (i.e.

5 uranyl) concentration. On the other hand, the diffusive flux was lower with bioturbation ($-0.07 \pm 0.01 \times 10^{-3}\,\mathrm{nmol\,U\,cm^{-3}\,h^{-1}}$). Indeed, uranyl production occurred in a fine layer directly under the interface and the reduction started 1 cm deeper than in undisturbed sediment. This production, accounting for $5.75 \times 10^{-5}\,\mathrm{nmol\,U\,cm^{-2}\,s^{-1}}$, may be relative to oxidation of upward-diffusing reduced uranium and then limited the total in-

10 ward flux.

Order of magnitudes of instantaneous fluxes (Fig. 2d) and time integrated fluxes (inset graph of Fig. 1) can be compared: they both indicate that the presence of worms clearly increased the uptake flux of uranium as a response to increased transfer to overlying water from dissolution/release of particle-bounded uranium. Biogeochemical

15 pathways responsible for uranium consumption at depth did not seem to be quantitatively modified by worm activities, at least at the experiment time scale.

3.2.2 Other dissolved species

Here again, for clarity and interest, only dissolved concentration profiles of total iron, sulfate, nitrate and nitrite are presented (Figs. 3–6).

20 *Total iron* – without bioturbation (C-0, C-12), the iron profiles show increasing concentrations from the sediment–water interface to a certain depth and then a decrease (Fig. 3a). They are characteristics of an upward diffusion of Fe^{2+} in top sediment, the remobilisation of iron through dissolutive reduction of iron oxi/hydroxides in deeper sediment, and a removal by precipitation onto mineral phases within the bottom sediment.

25 With bioturbation (CT-12), the concentrations of iron in the sediment were globally lower and decreased gradually with depth but no peak appeared on the profiles (Fig. 3b). The

same trends were observed in contaminated aquaria (U-0, U-12, UT-12) with an additional increase of concentrations in the deepest part of the profiles (Fig. 3b).

All profiles indicated an upward diffusive flux at the top of the sediment (Fig. 3c) though no dissolved iron was detected in the water column. This could be explained by a direct precipitation of released iron since the water was well oxygenated.

Sulfate – in the uncontaminated aquaria (C-0, C-12), the sulfate concentration profiles showed a net production under the sediment–water interface and consumption in depth (Fig. 4a), resulting in a net outward flux towards the water (Fig. 4c). With bioturbation (CT-12), the highest concentrations were detected in the water column and sulfates diffuse towards the sediment where they were directly consumed under the interface (Fig. 4d). The presence of uranium also modified these profiles (Fig. 4b): the production of sulfate under the sediment–water interface was not yet observed in undisturbed aquaria (U-0, U-12) but occurred in a fine layer in bioturbated ones (UT-12). Finally, the consumption of sulfate in bottom sediment probably due to bacterial sulfate-reduction resulted in an inward diffusive flux in all contaminated aquaria (Fig. 4c).

Nitrate – in control aquaria without worms (C-0, C-12), the concentrations of nitrate were low and the profiles were poorly marked (i.e. no significant flux at the sediment–water interface), only indicating a slight consumption within sediment (Fig. 5a and d). On the other hand, the concentrations were higher in presence of worms (CT-12) and the profile showed a slight outward diffusive flux (Fig. 5a and d). In contaminated aquaria, the profiles appeared clearly different. Without bioturbation (U-0, U-12), despite some irregularities in the shape of the profiles, the concentrations of nitrate gradually increased in the sediment, indicating a clear production of this compound (Fig. 5b). The resulting diffusive fluxes were directed towards the sediment (Fig. 5c and d). Here again, in presence of worms (UT-12), the concentrations were higher and the profile showed a negative peak across the sediment–water interface reflecting consumption of nitrate (Fig. 5b). However, production also occurred in this case but deeper in the sediment. The net diffusive flux was directed towards the overlying water (Fig. 5d).

Remobilisation of uranium from contaminated freshwater sediments

S. Lagauzère et al.

Nitrite – compared to nitrate, the concentrations of nitrite were very lower. Except for the U-0 condition for which PROFILE modelling estimated a clear production of nitrite within sediment, the other profiles indicated very slight diffusive fluxes related rather to consumption in undisturbed sediment (C-0, C-12, U-12) and to production in bioturbated sediment (CT-12, UT-12) (Fig. 6a–d).

3.3 Bioaccumulation in *T. tubifex* worms

The average concentration in uranium determined in the tissues of the *T. tubifex* worms after 12 days of exposure was 37.4 ($\pm$8.3) μg U g^{-1} dry weight. As the concentration of uranium in the surrounding sediment was around ten times higher, it can be concluded that these organisms did not bioconcentrate uranium (Bioconcentration factor BCF $\ll$ 1). However, it can be noted a low bioconcentration by comparing the value of bioaccumulation to the concentration in the water closed to the sediment–water interface (BCF = 1.3 $\pm$ 0.1) or to the porewater concentration in the sediment surrounding worms (BCF = 2.3 $\pm$ 0.1).

3.4 Mass balance of uranium

Table 1 presents the mass balance of uranium between the different compartments (water column, sediment, pore water, organisms) for the initial conditions (day 0) and after 12 days with or without bioturbation. Although equilibrium was not reached after 12 days of experiment, since between treatments U-0 and U-12 the concentration in water continued to rise ($\sim$ 1 %), the results confirmed that uranium did not remain within the sediment and was released through the water column. Bioturbation has a stronger effect on this remobilisation with more than 5 % of uranium being removed from the sediment towards the water phases at the end of the experiment.

4 Discussion

4.1 Bioturbation effects in uncontaminated sediment

Although the main goal of this study was to investigate the distribution and transfers of uranium in bioturbated sediment, the comparison of parameters in uncontaminated aquaria (C-0, C-12, CT-12) have permitted to improve substantially our global knowledge of biogeochemical processes influenced by the bioturbation of *T. tubifex* worms. It is thus important to rapidly discuss these results. The most visible consequence of bioturbation was the changes of the water quality with increasing concentrations of sulfate and nitrate. Since there was not influx of water during the experiment (excepted additions made to compensate evaporation and sampling), these results can be only related to changes occurring within the sediment.

In the absence of uranium contamination, the worms reached the bottom of the aquaria (10 cm) and induced a high upward advection of sediment particles towards the water column (Lagauzère et al., 2009a, c). A fine layer of mucus-bounded faecal pellets appeared at the top of the sediment. The sediment–water interface area moderately increased, the oxygen penetration depth was reduced from 3 to 2 mm, and the diffusive oxygen uptake (DOU) of sediment was enhanced by 14 % (Lagauzère et al., 2009b). In accordance with previous works reported in the literature, it has been suggested that these observations were relative to a global stimulation of microbial activity through notably a supply of labile organic matter, the re-fractioning of sediment particles, and the providing of new microniches for micro-organisms involved in diagenetic processes (Mermillod-Blondin et al., 2013). The upward-bioconveying of sediment particles also induces oxidation of reduced compounds removed from the bottom sediment (i.e. iron sulfide Fe-S), and enhances fluxes of nutrients due to higher diffusion and advection processes (Matisoff, 1995; Mc Call and Fisher, 1980; Mermillod-Blondin et al., 2005; Nogaro et al., 2007; Svensson et al., 2001). In the case of high densities of benthic worms (20 000–70 000 ind m^{-2}), as used in our study, high removal of reduced compounds coupled with intensive aerobic microbial activity in the faecal pellet layer

hampers the oxygen penetration in surface sediments (Pelegri and Blackburn, 1995). These authors suggested that denitrification and sulfate-reduction would be favoured by these suboxic/anoxic conditions whereas nitrification would be limited to a very fine layer under the sediment–water interface. In the present work, the profiles obtained from DET-gel probes partially confirm these assumptions. For instance, the higher sulfate concentrations measured in bioturbated aquaria (CT-12) can be explained by removal of reduced sulfur and its subsequent oxidation in the water. Sulfate ions diffuse therefore towards the sediment where they are rapidly consumed by sulfate-reducers. Inversely, in undisturbed sediment (C-0 and C-12), the concentration profiles show a peak under the sediment–water interface that reflects production of sulfate through iron sulphide oxidation since top sediment was more oxygenated than in bioturbated sediment. This apparent production in sediment can also be due to gypsum dissolution as gypsum particles are commonly present in the Verdon River, the main tributary of the Esparron Lake (E. Viollier, personal communication, 2012). Without upward advection of sediment particles, as induced by worms (see below), the concentrations of sulfate remained low in the water column.

On the other hand, nitrate and nitrite concentration profiles do not directly fit the assumption of an enhanced denitrification and a limited nitrification. In all cases, the concentrations were rather homogeneous with sediment depth that indicates a lower nitrogen turn-over. Nevertheless, the only remarkable profiles correspond to aquaria with bioturbation (CT-12). In this case, concentrations were also more or less constant on the entire profile but much higher than in undisturbed aquaria. As suggested by Stief and De Beer (2002), this result can be explained by a high coupling of denitrification and nitrification processes resulting in a fast turn-over of nitrogen in sediment. Through enhanced organic matter mineralization and their own excretion, the worms lead to the production of ammonium which is in return re-oxidized into nitrite and nitrate. The nitrate concentration profile shows however a low diffusion towards the sediment which can be related to consumption by denitrification.

Finally, it is important to note the downward shift of iron profiles with bioturbation, which indicated a higher dissolutive reduction of Fe(III)-oxi/hydroxides compared to the undisturbed sediment. Here again, the particle reworking of the sediment column was likely to enhance the removal of iron from bottom sediment towards a more reactive zone and then to increase its global turn-over.

4.2 Bioturbation effects in uranium-spiked sediment

As already mentioned, previous experiments conducted in strictly same conditions have permitted to obtain a solid basis to understand the influence of *T. tubifex* bioturbation in uranium-spiked sediments and to choose the most suitable experimental design for the present study (Lagauzère et al., 2009a–c). At the tested concentration of ca. $600\,\mu g\,U\,g^{-1}$ dry sediment (i.e. > 100 times the background level for freshwater sediments), the population of worms was reduced by 10–20 % after 12 days of exposure. Uranium induced several negative effects on *T. tubifex* (e.g. malformations, autotomy, loss of biomass) that became significant only for these higher concentrations. Nevertheless, their bioturbation activity was significantly affected from this level of contamination. The most easily observable effects were a 2-fold reduction of the total length of the gallery network, a net concentration in upper layers of sediments ($< 2\,cm$), a lower maximal penetration depth ($6\,cm$) and asynchronous, disordered and slower movements of sampled individuals. By simulating vertical profiles of particle tracers (microspheres and luminophores) with diagenetic models, it was possible to estimate a decrease of advective (60–70 %) and diffusive transports (25–30 %) induced by bioturbation in contaminated sediments (Lagauzère et al., 2009a). Likewise, in presence of worms the porosity was only enhanced of 10 % in the first cm of uranium-spiked sediments while it reached more than 20 % within 2 cm in uncontaminated sediments. Finally, it is important to note that the lower penetration and dispersal of worms within the sediment column led to a 2-fold higher ingestion rate compared to control sediment, with a peak in the nearest cm under the sediment surface. As a main hypothesis, it was suggested that the behavior of worms resulted in a trade-off between avoiding contaminated sed-

iment and yet remaining within it to meet their physiological needs and to be protected from predators.

Despite the negative effects of uranium on the activity of *T. tubifex* worms, the concentration of uranium in the water column was multiplied by 5 in the course of the three aforementioned studies, a result again confirmed in the present case. As demonstrated for other metals, such a release of uranium can be explained by the removal of particles from anoxic layers to the surface of sediment through the digestive tract of worms. Nevertheless, underlying biogeochemical processes needed to be investigated furthermore to support this hypothesis and to provide additional information on the influence of tubificid worms in contaminated sediments. Previous results relative to DOU (Diffusive oxygen uptake) of sediments, which is a representative parameter of the global functioning of sediment, have shown a net increase due to both uranium contamination (+24 %), *T. tubifex* bioturbation (+14 %), and the combination of these two factors (+53 %). The present study has permitted to confirm and quantify the direct and indirect oxidative loss of uranium initially associated with sediment and to demonstrate a clear impact of uranium and/or bioturbation on microbial-driven diagenetic reactions.

First, it is important to consider the information provided from experimental units without *T. tubifex* worms. As confirmed by DET profiles, uranium released in the water was actually produced in the oxic sediment (< 3 mm). Initially, uranium was added to the sediment in close beakers kept without oxygenation for 4 weeks. In this state, most of uranium would be under insoluble and reduced form U(+IV). After assembling the aquaria, the sediment became in contact with aerated water and uranium could gradually desorbed and be oxidized into its soluble form U(+VI). This result is supported by previous experimental work demonstrating that the oxidation of reduced uranium solid phases is a fast process (Anderson et al., 1989; Cochran et al., 1986). By comparing concentrations of uranium in the water of U-0 and U-12 aquaria, it can be noticed that this process was still on going after 12 days of experiment, so that equilibrium state had been not yet reached. As a consequence, the diffusive flux of uranium towards the sediment increased during the duration of the experiment due to increasing concentra-

tion in the overlying water. Although the direct oxidative loss of uranium could explain the enhanced DOU of sediment (+24 %), it was assumed that uranium could influence several microbial-driven diagenetic processes.

First of all, sulfate concentration profiles show the disappearance of the sulfur oxidation layer in top sediment and only reflect a low diffusion of sulfate from the water to the sediment and then a lower sulfate-reduction rate. In the present case, the microorganisms involved in the sulfur cycle were not stimulated and even rather inhibited by uranium contamination.

In the same manner, profiles of nitrate/nitrite concentrations in the contaminated aquaria show clear differences with the control aquaria. The concentrations in the sediment were higher that could reflect intensive nitrification process. However, these concentrations might be more probably explained by the way of sediment contamination itself since uranyl nitrate was used. Nevertheless, this nutrient supply seemed to not be consumed by denitrification. Here again, the uranium contamination did probably not influence micro-organisms involved in the nitrogen cycle, all the more than they were not already very active in the uncontaminated sediment.

In contrast, uranium has induced slight modifications of the iron cycle as indicated by higher concentrations of dissolved iron in bottom sediment due to potentially enhanced dissolutive reduction of Fe(III) oxi/hydroxides.

Although no strong stimulation of microbial activity linked to sulfur, nitrogen or iron cycles by uranium was put in evidence in this work, some examples have been reported in the literature. Most of these studies deal with the immobilization of uranium in sediment by favoring its reduction in the context of bioremediation of contaminated water. Indeed, uranium can be a potential substrate for anaerobic respiration (Lovley et al., 1991). Most of dissimilatory metal-reducing bacteria capable of conserve energy by coupling organic matter and H_2 oxidation with reduction of metallic ions can also reduce uranyl. As well, some sulfate-reducing bacteria can catalyze the reduction of ferrous ions or uranyl ions without keeping energy or grow up with these ions as sole electron acceptors (Wilkins et al., 2006). In contaminated sites, it was demonstrated that anaerobic

prokaryotes were easily cultivable on nuclear wastes, with a clear dominance of nitrate-reducing organisms (Akob et al., 2007). Besides these reduction processes, oxidation of uranium (uraninite) can also be biotically favored in presence of nitrate or Fe(III) oxides but it remains currently unknown if bacteria turn a gain of energy from this reaction

5 (Borch et al., 2010). Comparatively to these studies, the present experiment represents the first assessment of uranium contamination on microbial communities not previously exposed to pollution. More generally, toxicity of uranium to micro-organisms has been so far poorly investigated and appears to be lower than for other heavy metals (Nies, 1999). A case of resistance has been also reported in an aerobic bacterium capable

10 for detoxification through formation and rejection of intra-cytoplasmic granules (Suzuki and Banfield, 2004). Here, we indirectly demonstrated an inhibition of the activity of micro-organisms involved in sulfur and nitrogen cycles after some weeks of exposure to contaminated sediment. However, from these results, it is not possible to conclude to long-term effects of such a contamination and potential adaptations processes of

15 micro-organisms could not be excluded (Hoostal et al., 2008). Finally, in absence of available estimations of aerobic microbial activity alone, the higher oxygen consumption of sediment in presence of uranium should be mainly attributed to its oxidation that leads to increase its concentration in the water by solubilisation. Without more evident stimulation of metal reducers, the oxidation of uranium may be primarily abiotic.

20 The presence of *T. tubifex* worms introduced another transfer pathway of uranium previously associated with sediment. By conveying particles directly from the depth of maximal ingestion rate (2 cm), which is within the reducing zone, to the sediment surface, oxidative dissolution of uranium was greatly enhanced. In addition, the contact of ingested particles with digestive tract solutions is likely to have contributed to ura-

25 nium dissolution. Already observed in marine environments accumulating authigenic uranium (Zheng et al., 2002), these results confirm what was previously reported for other metals in freshwater sediments (Ciutat and Boudou, 2003; Ciutat et al., 2007; Krantzberg, 1985; Matisoff, 1995). The flux modelling corresponding to UT-12 profile indicates that this process was all the more so efficient that bioturbation also limited

the diffusive flux from the water to the sediment due to the presence of an oxidation layer in top sediment. As well, a low bioaccumulation of sediment-associated uranium during the digestive tract of particles into the worms has favoured its release. Only the bioconcentration factors relative to water were higher than 1, indicating that diffu-
5 sion of dissolved uranium through the tegument of worms may be the dominant way of exposure and accumulation. However, this effect was weak, probably because of the water hardness (152 Eq mg CaCO$_3$ L^{-1}) and the pH (8.6) that considerably limit the bioavailability of uranium (Markich, 2002; Sheppard et al., 2006). Nevertheless, long-term effects need to be assessed furthermore to determine potential adaptation of
10 worm populations or on the contrary increased bioaccumulation and toxic effects due to increasing uranium concentration in the water.

Although the upward particle advection induced by the worm feeding mode was apparently the most influent factor in the present case, the diagenetic behaviour of metallic pollutants can also be indirectly modified by bioturbation-driven changes of sediment
15 properties (e.g. redox boundaries). In presence of *T. tubifex* worms, the DOU of sediment increased of 18 % in comparison with undisturbed aquaria (U-0 and U-12) and of 53 % when sediment was initially not contaminated (C-0 and C-12) (Lagauzère et al., 2009b). From these results it was suggested that bioturbation stimulated aerobic reactions already favoured by uranium. However, the present experiment did not confirm
20 totally this hypothesis since anaerobic reactions were mainly stimulated. Like in control aquaria, sulfate and nitrate concentrations increased in the water due to modifications in the sediment. The profile of sulfate seems to result of combined effect of uranium (i.e. inhibition of micro-organisms involved in sulfur cycle) and bioturbation (i.e. upward-bioconveying of reduced sulfur from bottom sediment, subsequent oxidation in the wa-
25 ter and diffusion towards the sediment where it was consumed by sulfate-reduction), the latter apparently the dominant. For nitrate, the same trend was observed as the profiles were marked by a negative peak around the interface that can be explained by the use of the nitrate supply due to contamination by uranyl nitrate. Although nitrate were not reduced in absence of worms (U-0 and U-12), the bioturbation seemed to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

have stimulated denitrification in UT-12 aquaria, a reaction which was already slightly enhanced in control conditions (CT-12). It is however difficult to explain nitrate concentration increase at depth since the bioturbation activity was damped from 2 cm. The occurrence of transient anaerobic nitrification based on ammonium oxidation by manganese oxides, as proposed in the case of newly deposited sediment (i.e. flood sediments or turbidites) in recent studies (Anschutz et al., 2002; Chaillou et al., 2008; Clément et al., 2005) could be considered for instance. The nitrate profile was particularly complex in contaminated sediment where the interplay with denitrification seems to play an important role. In contrast, the dissolutive reduction of iron oxi/hydroxides did not seem to be modified by the presence of worms.

The higher oxygen consumption of sediment was therefore mainly attributed to oxidation of reduced materials removed from bottom anoxic sediment. Nevertheless, aerobic microbial respiration could have been stimulated by the higher supply of labile organic matter due to toxic effect on worms themselves (i.e. mortality of 10–20 % of the worm population, enhanced mucous production by resistant individuals and lost of the posterior part of their bodies through a detoxification process).

Finally, after only 12 days of bioturbation, around 5 % of uranium initially associated with sediment was removed towards the aqueous phases. Based on estimation of diffusive fluxes in the different experimental treatments and uranium accumulation in water, a conceptual outline is proposed in Fig. 7 to visualize the transfers of uranium in presence of worms in the sediment. Considering a Predicted No-Effect Concentration (PNEC) of $23 \, \text{mg} \, \text{U} \, \text{L}^{-1}$, as estimated from our experimental conditions (pH 8.6, water hardness $152 \, \text{Eq} \, \text{mg} \, \text{CaCO}_3 \, \text{L}^{-1}$), the concentration reached in the water ($\sim 30 \, \text{mg} \, \text{U} \, \text{L}^{-1}$) due to bioturbation represents a serious threat for the aquatic biota (Sheppard et al., 2006). However, the benthic response to increasing concentration in the water corresponds to enhanced downward diffusive fluxes. Until a steady state would be reached, it would account for increasing bioaccumulation of uranium and possible toxic effects slowing down bioturbation activity. In the other hand, long-term

adaptations are likely to occur for a tolerant species such as *T. tubifex* if some populations are gradually or punctually exposed to uranium contamination in the environment.

5   Conclusions

This work confirms the major role of *T. tubifex* bioturbation in the biogeochemistry of freshwater sediments in general (e.g. stimulation of diagenetic processes, remobilisation of reduced materials, redistribution of solutes), and in the remobilization of uranium from the sediment. Despite a lower bioturbation activity in uranium-contaminated sediment, these biogeochemical processes are maintained and some microbial communities are even stimulated (denitrifying and sulfate-reducing bacterial communities) compared to non-bioturbated sediments (Table 2). It remains unclear if these changes indirectly influence the uranium distribution but *T. tubifex* play a key-role in the remobilisation of this metal from the sediment to the water through upward bioconveying of sediment particles. Long-term effects still need to be assessed, microbial diversity and activity have to be investigated more precisely through molecular approach, and experiments should be extended to real contaminated sites. However this study provides the first demonstration of biogeochemical modifications induced by bioturbation in freshwater uranium-contaminated sediment. As regard to the high tolerance of tubificid worms to sediment contamination and the potential risk for aquatic biocenosis exposed to dissolved uranium, it appears crucial to consider bioturbation as an important factor in further studies, notably in the development of bioremediation strategies where the potential key-role of bioturbation is largely overlooked.

References

Akob, D. M., Mills, H. J., and Kostka, J. E.: Metabolically active microbial communities in uranium-contaminated subsurface sediments, FEMS Microbiol. Ecol., 59, 95–107, 2007.

Alfaro-De-la-Torre, M. C. and Tessier, A.: Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake, Geochim. Cosmochim. Ac., 66, 3549–3562, 2002.

Anderson, R. F., Fleisher, M. Q., and Lehuray, A. P.: Concentration, oxidation state, and particulate flux of uranium in the Black Sea, Geochim. Cosmochim. Ac., 53, 2215–2224, 1989.

Anschutz, P., Jorissen, F. J., Chaillou, G., Abu-Zied, R., and Fontanier, C.: Recent turbidite deposition in the eastern Atlantic: Early diagenesis and biotic recovery, J. Mar. Res., 60, 835–854, 2002.

Barlett, M., Zhuang, K., Mahadevan, R., and Lovley, D.: Integrative analysis of *Geobacter* spp. and sulfate-reducing bacteria during uranium bioremediation, Biogeosciences, 9, 1033–1040, doi:10.5194/bg-9-1033-2012, 2012.

Berg, P., Risgaard-Petersen, N., and Rysgaard, S.: Interpretation of measured concentration profiles in sediment pore water, Limnol. Oceanogr., 43, 1500–1510, 1998.

Berner, R. A.: Early Diagenesis: a Theoretical Approach, Princeton University Press, Princeton, USA, 241 pp., 1980.

Borch, T., Kretzschmar, R., Kappler, A., Van Cappellen, P., Ginder-Vogel, M., Voegelin, A., and Campbell, K.: Biogeochemical redox processes and their impact on contaminant dynamics, Environ. Sci. Technol., 44, 15–23, 2010.

Boudreau, B. P.: Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments, Springer-Verlag, Berlin, Germany, 1997.

Budd, G. C.: *Tubifex tubifex*: a Sludge-Worm, Marine Life Information Network: Biology and Sensitivity Key Information Sub-programme (on-line), Marine Biological Association of the UK, Plymouth, available at: www.marlin.ac.uk/species/Tubifextubifex.htm, 2005.

Chaillou, G., Schäfer, J., Blanc, G., and Anschutz, P.: Mobility of Mo, U, As, and Sb within modern turbidites, Mar. Geol., 254, 171–179, 2008.

Ciutat, A. and Boudou, A.: Bioturbation effects on cadmium and zinc transfers from a contaminated sediment and on metal bioavailability to benthic bivalves, Environ. Toxicol. Chem., 22, 1574–1581, 2003.

Remobilisation of uranium from contaminated freshwater sediments

S. Lagauzère et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Ciutat, A., Gerino, M., and Boudou, A.: Remobilization and bioavailability of cadmium from historically contaminated sediments: influence of bioturbation by tubificids, Ecotox. Environ. Safe., 68, 108–117, 2007.

Clément, J.-C., Shrestha, J., Ehrenfeld, J. G., and Jaffé, P. R.: Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils, Soil Biol. Biochem., 37, 2323–2328, 2005.

Cochran, J. K., Carey, A. E., Sholkovitz, E. R., and Surprenant, L. D.: The geochemistry of uranium and thorium in coastal marine sediments and sediment pore waters, Geochim. Cosmochim. Ac., 50, 663–680, 1986.

Curtis, G. P., Davis, J. A., and Naftz, D. L.: Simulation of reactive transport of uranium(VI) in groundwater with variable chemical conditions, Water Resour. Res., 42, W04404, doi:10.1029/2005WR003979, 2006.

Davis, J. A., Payne, T. E., and Waite, T. D.: Simulating the pH and pCO$_2$ dependence of uranium(VI) adsorption by a weathered schist with surface complexation models, in: Geochemistry of Soil Radionuclides, Special Pub. 59, Soil Science Society America, Madison, WI, 61–86, 2002.

Davis, J. A., Meece, D. E., Kohler, M., and Curtis, G. P.: Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments, Geochim. Cosmochim. Ac., 68, 3621–3641, 2004.

Davis, J. A., Curtis, G. P., Wilkins, M. J., Kohler, M., Fox, P., Naftz, D. L., and Lloyd, J. R.: Processes affecting transport of uranium in a suboxic aquifer, Phys. Chem. Earth, 31, 548–555, 2006.

De Haas, E. M., Kraak, M. H. S., Koelmans, A. A., and Admiraal, W.: The impact of sediment reworking by opportunistic chironomids on specialised mayflies, Freshwater Biol., 50, 770–780, 2005.

Denison, F.: Uranium(VI) Speciation: Modelling, Uncertainty and Relevance to Bioavailability Models. Application to Uranium Uptake by the Gills of a Freshwater Bivalve, Thèse de Doctorat de l'Université Aix-Marseille I., 2004.

Gérino, M., Vervier, P., Stora, G., Gilbert, F., Poggiale, J.-C., François-Carcaillet, F., Mermillod-Blondin, F., and Desrosiers, G.: Macro-invertebrate functional groups in freshwater and marine sediments: a common mechanistic classification, Vie Milieu, 53, 221–232, 2003.

Hart, D. R., McKee, P. M., Burt, A. J., and Goffin, M. J.: Benthic community and sediment quality assessment of Port Hope Harbour, Lake Ontario, J. Great Lakes Res., 12, 206–220, 1986.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hoostal, M. J., Bidart-Bouzat, M. G., and Bouzat, J. L.: Local adaptation of microbial communities to heavy metal stress in polluted sediments of Lake Erie, FEMS Microbiol. Ecol., 65, 156–168, 2008.

Komlos, J., Peacock, A., Kukkadapu, R. K., and Jaffé, P. R.: Long-term dynamics of uranium reduction/reoxidation under low sulfate conditions, Geochim. Cosmochim. Ac., 72, 3603–3615, 2008.

Krantzberg, G.: The influence of bioturbation on physical, chemical and biological parameters in aquatic environments: a review, Environ. Pollut., 39, 99–122, 1985.

Kurnaz, A., Küçükömeroglu, B., Keser, R., Okumusoglu, N. T., Korkmaz, F., Karahan, G., and Cevik, U.: Determination of radioactivity levels and hazards of soil and sediment samples in Firtina Valley (Rize, Turkey), Appl. Radiat. Isotopes, 65, 1281–1289, 2007.

Lagauzère, S., Boyer, P., Stora, G., and Bonzom, J. M.: Effect of uranium-contaminated sediment on bioturbation activity of *Chironomus riparius* (Insecta, Diptera) and *Tubifex tubifex* worms (Annelida, Tubificidae), Chemosphere, 76, 324–334, 2009a.

Lagauzère, S., Pischedda, L., Cuny, P., Gilbert, F., Stora, G., and Bonzom, J. M.: Influence of *Chironomus riparius* (Diptera, Chironomidae) and *Tubifex tubifex* (Oligochaeta, Tubificidae) on oxygen uptake by sediments. Consequences of uranium contamination, Environ. Pollut., 157, 1234–1242, 2009b.

Lagauzère, S., Terrail, R., and Bonzom, J. M.: Ecotoxicity of uranium on *Tubifex tubifex* (Annelida, Tubificidae) exposed to contaminated sediment, Ecotox. Environ. Safe., 72, 527–537, 2009c.

Langmuir, D.: Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, Geochim. Cosmochim. Ac., 42, 547–596, 1978.

Li, Y. and Gregory, S.: Diffusion of ions in sea water and in deep-sea sediments, Geochim. Cosmochim. Ac., 38, 703–714, 1974.

Liger, E., Charlet, L., and Van Cappellen, P.: Surface catalysis of uranium(VI) reduction by iron(II), Geochim. Cosmochim. Ac., 63, 2939–2955, 1999.

Lottermoser, B. G. and Ashley, P. M.: Physical dispersion of radioactive mine waste at the rehabilitated Radium Hill uranium mine site, South Australia, Aust. J. Earth Sci., 53, 485–499, 2006.

Lovley, D. R., Phillips, E. J. P., Gorby, Y. A., and Landa, E. R.: Microbial reduction of uranium, Nature, 350, 413–416, 1991.

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Lozano, J. C., Blanco Rodríguez, P., and Vera Tomé, F.: Distribution of long-lived radionuclides of the ^{238}U series in the sediments of a small river in a uranium mineralized region of Spain, J. Environ. Radioactiv., 63, 153–171, 2002.

Marang, L.: Influence de la Matière Organique Naturelle Sur la Spéciation des Radionucléides en Contexte Géochimique, Ph.D. thesis, University Paris Diderot-Paris 7 and IPGP, 178 pp., 2007.

Markich, S. J.: Uranium speciation and bioavailability in aquatic systems: an overview, Scientific World Journal, 2, 707–729, 2002.

Matisoff, G.: Effects of bioturbation on solute and particle transport in sediments, in: Metal Contaminated Aquatic Sediments, edited by: Allen, H. E., Ann Arbor Press, Chelsea, MI, 201–272, 1995.

Mc Call, P. L. and Fisher, J. B.: Effects of tubificid oligochaetes on physical and chemical properties of Lake Erie sediments, in: Aquatic Oligochaete Biology, edited by: Brinkhurt, R. O. and Cook, D. G., Plenum Press, New York, 253–317, 1980.

Mermillod-Blondin, F., Nogaro, G., Datry, T., Malard, F., and Gibert, J.: Do tubificid worms influence the fate of organic matter and pollutants in stormwater sediments?, Environ. Pollut., 134, 57–69, 2005.

Mermillod-Blondin, F., Foulquier, A., Gilbert, F., Navel, S., Montuelle, B., Bellvert, F., Comte, G., Grossi, V., Fourel, F., Lecuyer, C., and Simon, L.: Benzo(a)pyrene inhibits the role of the bioturbator *Tubifex tubifex* in river sediment biogeochemistry, Sci. Total. Environ., 450–451, 230–241, 2013.

Morford, J. L., Martin, W. R., and Carney, C. M.: Uranium diagenesis in sediments underlying bottom waters with high oxygen content, Geochim. Cosmochim. Ac., 73, 2920–2937, 2009.

Motelica-Heino, M., Naylor, C., Zhang, H., and Davison, W.: Simultaneous release of metals and sulfide in lacustrine sediment, Environ. Sci. Technol., 37, 4374–4381, 2003.

Naylor, C., Davison, W., Motelica-Heino, M., Van Den Berg, G. A., and Van Der Heijdt, L. M.: Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulfide DGT probe, Sci. Total. Environ., 328, 275–286, 2004.

Naylor, C., Davison, W., Motelica-Heino, M., Van Den Berg, G. A., and Van Der Heijdt, L. M.: Potential kinetic availability of metals in sulphidic freshwater sediments, Sci. Total. Environ., 357, 208–220, 2006.

Naylor, C., Davison, W., Motelica-Heino, M., Heijdt, L. M., and den Berg, G. A.: Transient release of Ni, Mn and Fe from mixed metal sulphides under oxidising and reducing conditions, Environ. Earth Sci., 65, 2139–2146, 2012.

Neame, P. A., Dean, J. R., and Zytaruk, B. G.: Distribution and concentrations of naturally-occurring radionuclides in sediments in a uranium mining area of northern Saskatchewan, Canada, Hydrobiologia, 91–92, 355–361, 1982.

Nies, D. H.: Microbial heavy-metal resistance, Appl. Microbiol. Biot., 51, 730–750, 1999.

Nogaro, G., Mermillod-Blondin, F., Montuelle, B., Boisson, J. C., Lafont, M., Volat, B., and Gibert, J.: Do tubificid worms influence organic matter processing and fate of pollutants in stormwater sediments deposited at the surface of infiltration systems?, Chemosphere, 70, 315–328, 2007.

Pelegri, S. P. and Blackburn, T. H.: Effects of *Tubifex tubifex* (Oligochaeta: Tubificidae) on N-mineralization in freshwater sediments, measured with ^{15}N isotopes, Aquat. Microb. Ecol., 9, 289–294, 1995.

Petersen, W., Wallmann, K., Pinglin, L., Schroeder, F., and Knauth, H.-D.: Exchange of trace elements at the sediment–water interface during early diagenesis processes, Mar. Freshwater Res., 46, 19–26, 1995.

Phrommavanh, V.: Etude de la Migration de l'Uranium en Milieu Naturel: Approche Experimentale et Modélisation Géochimique, Ph.D thesis, University Joseph Fourier-Grenoble 1, 222 pp., 2008.

Ragnarsdottir, K. V. and Charlet, L.: Uranium behaviour in natural environments, in: Environmental Mineralogy Microbial Interactions. Anthropogenic influences. Contaminated Land and Waste Management, Mineralogical Society of Great Britain and Ireland, 333–377, 2000.

Renshaw, J. C., Lloyd, J. R., and Livens, F. R.: Microbial interactions with actinides and long-lived fission products, C.R. Chim., 10, 1067–1077, 2007.

Schultz, H. D. and Zabel, M.: Marine Geochemistry, Springer, Berlin, New York, 455 pp., 2000.

Sheppard, S. C., Sheppard, M. I., Tait, J. C., and Sanipelli, B. L.: Revision and meta-analysis of selected biosphere parameter values for chlorine, iodine, neptunium, radium, radon and uranium, J. Environ. Radioactiv., 89, 115–137, 2006.

Soster, F. M., Harvey, D. T., Troksa, M. R., and Grooms, T.: The effect of Tubificid oligochaetes on the uptake of zinc by Lake Erie sediments, Hydrobiologia, 248, 249–258, 1992.

Suzuki, Y. and Banfield, J. F.: Resistance to, and accumulation of, uranium by bacteria from a uranium-contaminated site, Geomicrobiol. J., 21, 113–121, 2004.

Svensson, J. M., Enrich-Prast, A., and Leonardson, L.: Nitrification and denitrification in a eutrophic lake sediment bioturbated by oligochaetes, Aquat. Microb. Ecol., 23, 177–186, 2001.

Wilkins, M. J., Livens, F. R., Vaughan, D. J., and Lloyd, J. R.: The impact of Fe(III)-reducing bacteria on uranium mobility, Biogeochemistry, 78, 125–150, 2006.

5 Zheng, Y., Anderson, R., Van Geen, A., and Fleisher, M.: Remobilization of authigenic uranium in marine sediments by bioturbation, Geochim. Cosmochim. Ac., 66, 1759–1772, 2002.

Zoumis, T., Schmidt, A., Grigorova, L., and W, C.: Contaminants in sediments: remobilisation and demobilisation, Sci. Total. Environ., 266, 195–202, 2001.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Mass balance of uranium between the different compartments of the benthic ecosystem reproduced in mesocosms. Means in % ± SD ($N = 3$).

	Preparation of aquaria	Day 0 U-0	Day 12 (−) *Tubifex* U-12	Day 12 (+) *Tubifex* UT-12
Sediment	∼ 100	99.2 (0.21)	98.1 (0.21)	95.5 (0.44)
Porewater	n.a.	0.16 (0.01)	0.37 (0.04)	0.84 (0.22)
Water column	–	0.63 (0.20)	1.53 (0.19)	4.36 (0.44)
T. tubifex worms (bioaccumulation)	–	–	–	0.13 (0.06)

Table 2. Effects of *T. tubifex* and uranium on sediment biogeochemistry.

Parameter	+ Tubifex	+ Uranium	+ Tubifex/uranium
O_2 consumption	Increased (+14 %)[*]	Increased (+24 %)[*]	Increased (+53 %)[*]
	– higher OM mineralization	– oxidative loss of uranium	combined effects + OM supply
	– oxidation of removed reduced compounds	– stimulation of aerobic micro-organisms (?)	
Fe-cycle	Increased dissolutive reduction	Increased dissolutive reduction	Increased dissolutive reduction (no additional effect)
N-cycle	Higher turn-over Increased denitrification	Slightly increased nitrification (?)	Increased denitrification Complex coupling
S-cycle	Increased sulfate-reduction	Decreased sulfate-reduction	Increased sulfate-reduction
Water quality	Increased $[SO_4^{2-}]$ and $[NO_3^-]$	Increased $[NO_3^-]$, $[NO_2^-]$ and [totU]	Increased $[SO_4^{2-}]$, $[NO_3^-]$, $[NO_2^-]$ and [totU]

[*] From Lagauzère et al. (2009b).
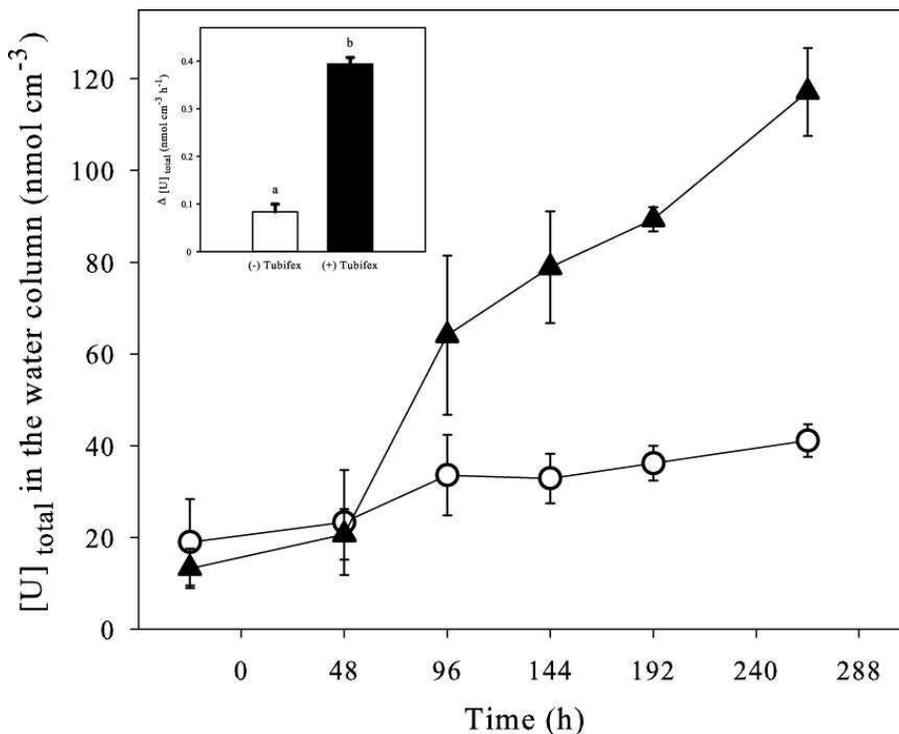
Fig. 1. Temporal variation of the total uranium concentration in the water column, without (○) and with (▲) *T. tubifex* worms inhabiting the sediment. The inset bar chart shows the net accumulation rate of uranium after 12 days. Means ± SD ($N = 3$).
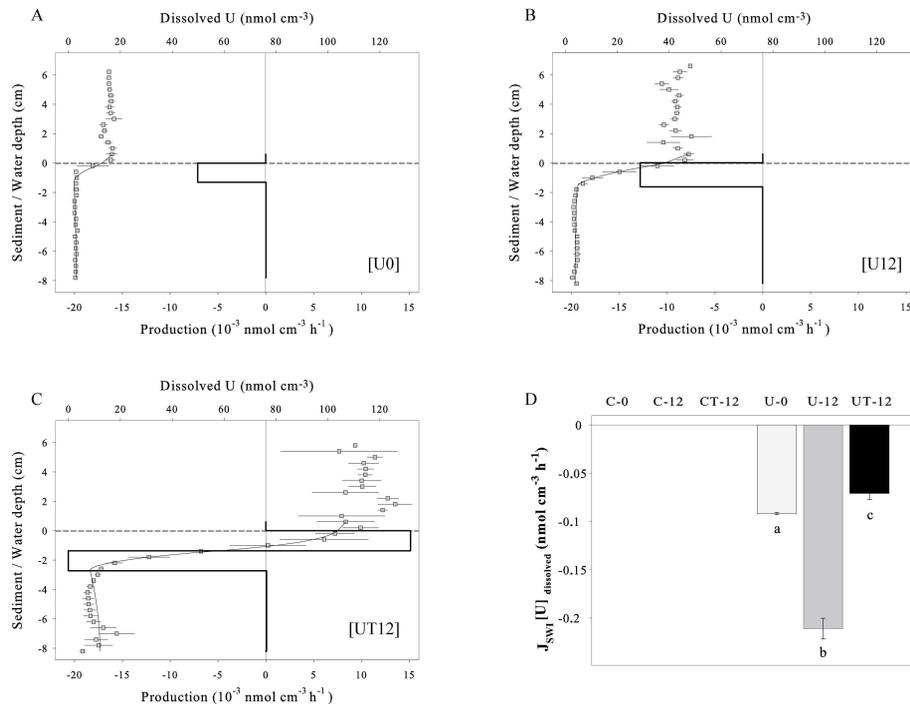
Fig. 2. (A–C) Dissolved uranium concentration profiles and instantaneous consumption/production rates in the sediment estimated in the different treatments (at initial conditions [U-0], and after 12 days without [U-12] or with [UT-12] *T. tubifex worms* in the sediment) using the software PROFILE. Grey dots are measured concentrations (Means ± SD, *N* = 3) and the fine black line the fitted concentration profile. The bold black line shows the production as a function of depth modelled from the concentration profile. The dotted line indicates the sediment–water interface. **(D)** Diffusive downward fluxes (integrated with the height of overlying water) of dissolved uranium in the different treatments estimated from concentration profiles. Means ± SD (*N* = 3). Different letters correspond to significant differences between treatments.

Full Screen / Esc
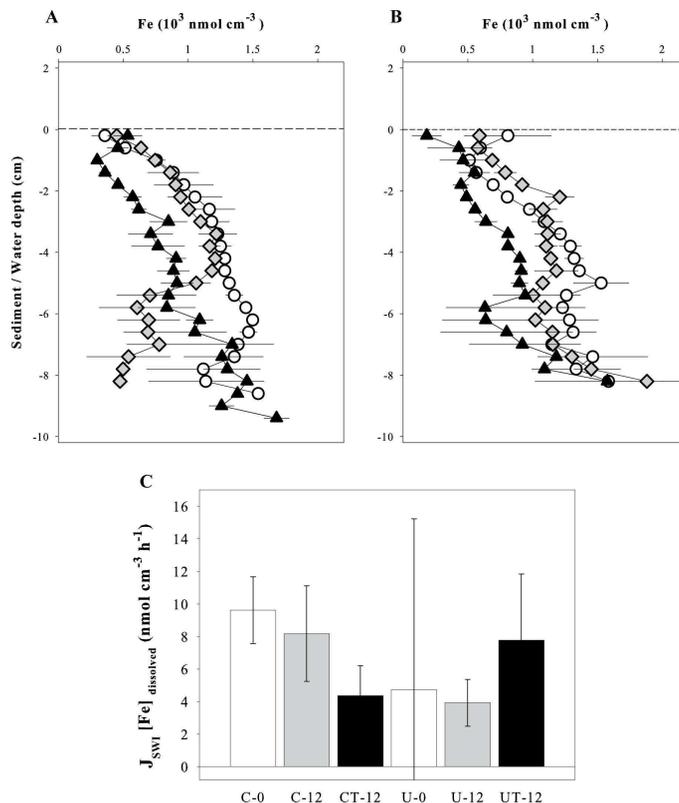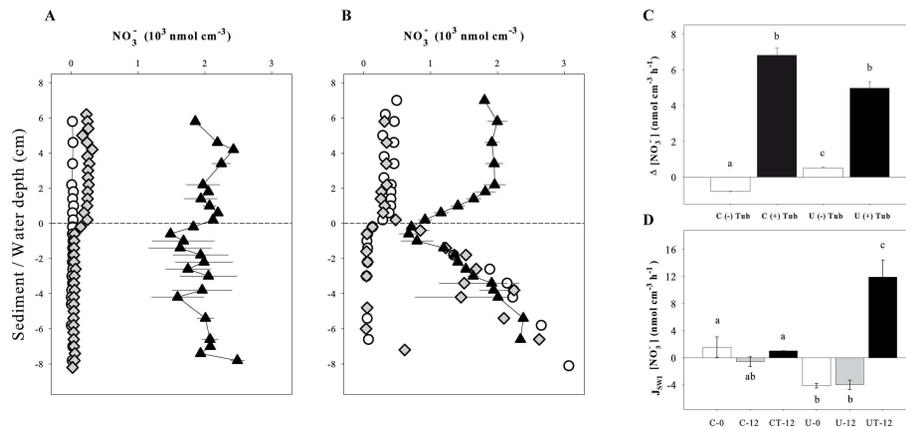
Fig. 3. Dissolved total Fe concentration profiles in uncontaminated **(A)** and uranium-spiked sediment **(B)** in the different treatments: at initial conditions [C-0] and [U-0] (○), and after 12 days without [U-12] (◇) or with [UT-12] (▲) *T. tubifex worms* in the sediment. The bar chart **(C)** indicates the corresponding integrated outward diffusive fluxes at the sediment–water interface estimated using the software PROFILE. Means ± SD ($N = 3$). No significant difference was detected between treatments.
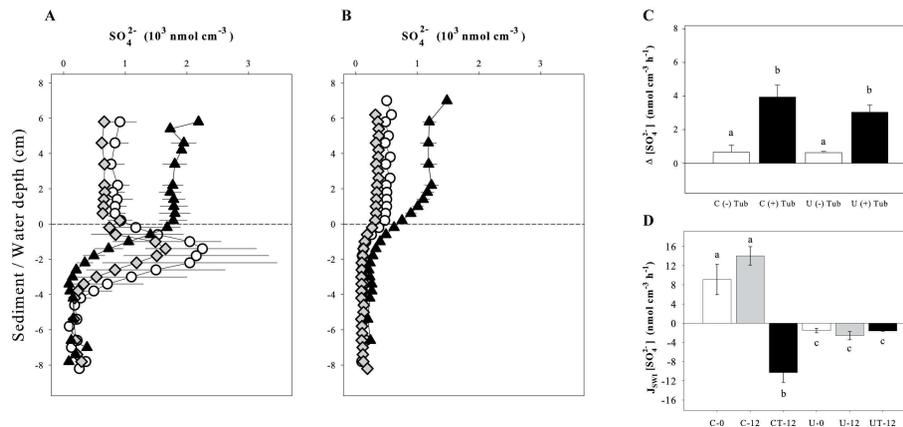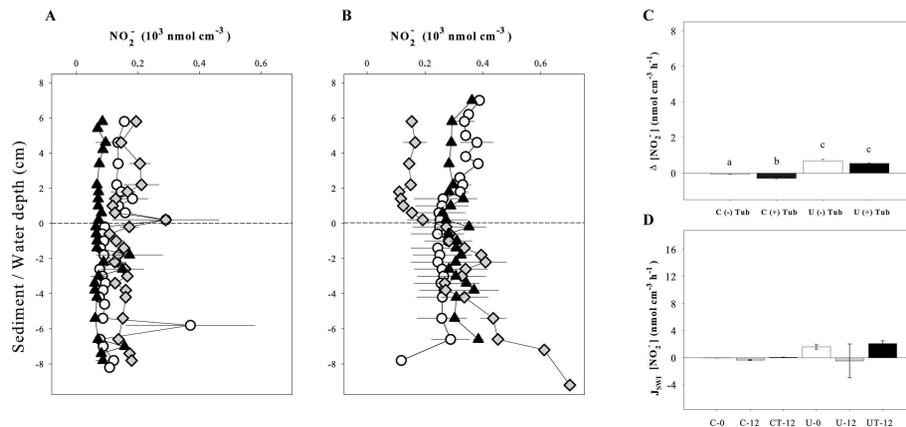
Fig. 4. Dissolved sulfate concentration profiles in uncontaminated **(A)** and uranium-spiked sediment **(B)** in the different treatments: at initial conditions [C-0] and [U-0] (○), and after 12 days without [U-12] (◇) or with [UT-12] (▲) *T. tubifex worms* in the sediment. The bar chart **(C)** corresponds to the net accumulation rate in the water column after 12 days. The bar chart **(D)** shows the integrated diffusive fluxes at the sediment–water interface estimated using the software PROFILE. Means ± SD (*N* = 3). Different letters correspond to significant differences between treatments.

Fig. 5. Dissolved nitrate concentration profiles in uncontaminated **(A)** and uranium-spiked sediment **(B)** in the different treatments: at initial conditions [C-0] and [U-0] (○), and after 12 days without [U-12] (◇) or with [UT-12] (▲) *T. tubifex worms* in the sediment. The bar chart **(C)** corresponds to the net accumulation rates in the water column after 12 days. The bar chart **(D)** indicates the integrated diffusive fluxes at the sediment–water interface estimated using the software PROFILE. Means ± SD ($N = 3$). Different letters correspond to significant differences between treatments.

Fig. 6. Dissolved nitrite concentration profiles in uncontaminated **(A)** and uranium-spiked sediment **(B)** in the different treatments: at initial conditions [C-0] and [U-0] (○), and after 12 days without [U-12] (◇) or with [UT-12] (▲) *T. tubifex worms* in the sediment. The bar chart **(C)** corresponds to the net outward flux in the water column after 12 days. The bar chart **(D)** indicates the corresponding diffusive fluxes at the sediment–water interface estimated using the software PROFILE. Means ± SD ($N = 3$). Different letters correspond to significant differences between treatments (no significant differences detected on **D**).
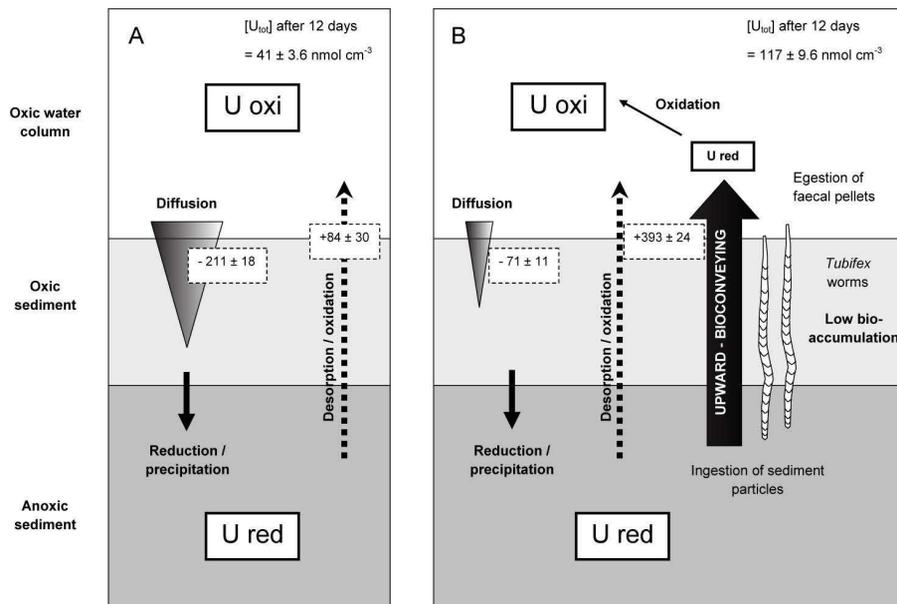
Fig. 7. Conceptual outline of the repartition and transfers of uranium within a sediment without macro-invertebrate **(A)** or bioturbated by *T. tubifex* worms **(B)** under an oxygenated water column (U oxi = uranium under its oxidized form, U red = uranium under its reduced form). Framed values indicate the estimated fluxes of uranium over the 12 days of experiment (10^{-3} nmol cm^{-3} h^{-1}): diffusion values correspond to diffusive fluxes estimated with profile; outward flux values, i.e. desorption/oxidation ± removal by bioturbation, correspond to variation of uranium concentration in water column in [U-12] and [UT-12] aquaria, respectively.