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THE EFFECTS OF BIOTURBATION ON CADMIUM TRANSFER AND DISTRIBUTION INTO FRESHWATER SEDIMENTS

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Abstract—To investigate bioturbation effects on cadmium (Cd) fluxes from overlying water to sediments, indoor microcosms were developed. The bioturbating organisms were freshwater tubificid worms. Three experimental conditions were studied during 56 d. The three conditions were contaminated water column ([Cd]: 20 μg/L) with or without worms and uncontaminated water column with worms. Cadmium vertical profiles were determined in the pore water and in the sediments, based on six layers (0–0.5, 0.5–1, 1–2, 2–3, 3–5, 5–12 cm). Dissolved oxygen, manganese, sulfate, and particulate manganese were measured. Bioturbation was analyzed using conservative fluorescent particulate tracers. Bioturbation increased Cd flux into the sediments by close to a factor of two. Scavenging of Cd was more efficient in the bioturbated sediments because particles and adsorption sites for Cd were renewed at the sediment–water interface. Tubificids also increased the thickness of the Cd-enriched layer. Metals adsorbed on particles at the sediment surface were distributed by bioadvection, which predominated the mixing processes. Bioturbation also modified the vertical profiles of dissolved and particulate manganese and dissolved sulfate but not the profiles of dissolved oxygen. These results indicate that the advective transport of particles by bioturbation and their subsequent modification by redox reactions accelerates the trapping of metals in sediments.

Keywords—Bioturbation Sediment Cadmium Tubificids Redox species

INTRODUCTION

Sediments constitute the most important storage reservoir for anthropogenic metals in freshwater ecosystems. These metals originate via diffusion from the water column and mainly from the deposit of suspended particles, which are characterized by a strong metal-binding capacity [1,2]. Metal distribution in sediments, chemical speciation reactions, and exchange capacities are the result of a complex set of physical, chemical, and biological processes that are not fully understood. Although nearly all freshwater benthic environments are inhabited by macro- and microinvertebrates, only a limited number of studies has been devoted to the effects of bioturbation on metal storage and release processes. Bioturbation results from the activity of animal species living at the surface and/or within the sediment superficial layers [3]. This activity causes sediment mixing and solute transport across the sediment–water interface [4,5]. The physical and chemical properties of the sediment can be altered. Former studies have investigated the effects of freshwater infaunal invertebrates on sediment transport [6–10] and solute composition [8,11–14]. Bioturbation can modify trace-metals profiles in the sediment, their distribution between particulate and interstitial phases [15], and their transfer between the water column and the sediment. Bioturbation induces a significant release of metals from the sediment to the overlying waters mostly in the particulate form [16], but these metals are poorly bioavailable for benthic or pelagic species [17,18]. Soster et al. [19] and Petersen et al. [20] showed that bioturbation increases the cadmium (Cd) and zinc (Zn) flux from overlying water to uncontaminated estuarine or freshwater sediments. Peterson et al. [21] demonstrated that tubificid oligochaetes significantly reduce acid-volatile sulfide concentrations in sediments, which results in an increase of interstitial Cd concentration and metal accumulation by worms.

The links between bioturbation, redox state of sediment, and metal behavior have been previously poorly studied. The aim of this study was to investigate the role of bioturbation on redistribution of Cd from the overlying water into the sediment, together with an analysis of the effects on the geochemical properties of the sediment. A kinetic approach was developed using indoor microcosms comprised of a mixed biotope (water/natural sediment). The bioturbating organisms were tubificid worms; these worms are one of the major bioturbation agents in freshwater environments [7]. Several species from this Oligochaetes group are used for toxicity testing and for bioaccumulation studies; they are also used as benthic indicators of freshwater pollution. These worms feed head down in muddy sediments, consume sediments at depth, and deposit undigested material at the sediment–water interface. causing the downward sediment migration [7]. Such sediments could be recycled through the feeding zone many times before ultimate burial below the deepest feeding zone [9]. Tubificids are, in the lexicon of Rhoads [3], conveyor-belt deposit feeders. This bioturbation mode, called bioadvection, leads to a direct link between two sediment layers that are very different geochemically, i.e., the oxidized superficial layer and the reduced profundal layer [7]. This study aims to better understand how bioadvection modifies Cd fluxes from overlying water to the sediments. Bioturbation intensity, the redox state of the sediment, and the quantification of Cd trapping and distribution in the sediment were studied during a 56-d experiment. Three

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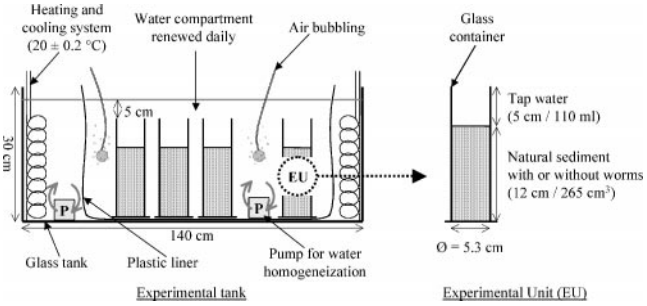

Fig. 1. Experimental systems used in the present study. For both +Cd+Tub, water column contaminated with Cd and Tubificidae (Tub) added to the sediment, and −Cd+Tub, no Cd added to the water column and Tubificidae in the sediment, conditions, each tank held 45 experimental units (EUs) with 60 L of water at the beginning of the experiments. For +Cd−Tub condition, water column contaminated with Cd and no Tubificidae added to the sediment, the experimental tank held 18 EUs and 24 L of water.

experimental conditions were analyzed, contaminated water column with or without worms and uncontaminated water column with worms. Results allow examination of the effects of worms on metal fluxes between the water column and sediment compartments. The vertical distribution of some major redox species was measured. Bioturbation activity was also analyzed using particulate tracers to establish links between bioturbation and Cd transfer and distribution in the sediment.

MATERIALS AND METHODS

Three distinct experimental conditions were run. In the first, ?5 −Cd+Tub (where Tub represents tubificid worms), defined as the control condition; tubificid worms were added to a noncontaminated sediment–water column. In the second, +Cd−Tub, the water column was contaminated with Cd but no worms were added; and in the third, +Cd+Tub, worms were added to a Cd-contaminated system.

Microcosm structure and experimental design

Experiments were performed in experimental units (EUs), comprised of sediment and water, enclosed in a glass container (see Fig. 1). The sediment was taken from the Garonne riverbank, upstream from Bordeaux (Gironde, southwest France). Approximately 50 kg of sediment were collected and stored at 4°C in the dark. The sediment was then sieved through a 1-mm mesh to remove macrofauna and frozen to −20°C to kill organisms. When needed, the sediment was defrosted and homogenized by mechanical mixing. Its main characteristics were defined with 10 samples collected after the mixing stage. The grain-size spectrum of sediment particles was as follows: 46.4% < 15 μm in diameter, 27.7% between 15 and 30 μm, 20.0% between 30 and 63 μm, 4.4% between 63 and 125 μm, 1.4% between 125 and 250 μm, and 0.1% between 250 and 500 μm. The fresh weight (fresh wt) to dry weight (dry wt) ratio (fresh wt:dry wt) after 72 h of desiccation at 60°C was 2.05 ± 0.01 and the organic carbon content was 6.9%. The background Cd concentration was found to be 0.75 ± 0.02 μg/g. An amount of 425 g of homogenized sediment were introduced into each EU. An amount of 110 ml of dechlorinated tap water (water saturated with dissolved oxygen; pH [20°C] = 8.15; conductivity [20°C] = 310 μS/cm; total dry salt content = 131 mg/L) was then added to each EU, avoiding disturbances at the sediment surface. The sediment and the water were left to equilibrate for 48 h before adding the worms.

Tubificid worms were used as the bioturbating organisms. Worms consisted of a mixture of three species, which are closely related from a taxonomical, biological, and ecological point of view, *Tubifex tubifex* (50%), *Limnodrilus hoffmeisteri* (45%), and *Limnodrilus claparedeianus* (5%). The worms were collected from natural ponds (Grebil, Arry, France) and were acclimatized for 15 d at 20°C in breeding tanks containing Garonne River sediment. Before the experiments, the sediment from the breeding tanks was sieved under running water to collect worms. Worm batches of 250 ± 0.5 mg (fresh wt) were constituted and added to each EU. No prior sorting of worms was made with respect to the heterogeneous size distribution of natural communities. In total, 133 ± 5 worms, or about 60,000 worms/m^2 were added to each EU. This is close to densities that can be found in natural environments [11]. Additional worms were collected to determine their fresh wt to dry wt ratio, which was 5.6 ± 0.1, dry wt after 72 h at 60°C. To avoid any nonmonitored changes in Cd complexation by the food particles, food was not added during the experiments. Preliminary experiments demonstrated that the organic carbon content of the sediment was sufficient for worms to feed during 56 d.

The bioturbation activity of tubificids within the sediment was analyzed using conservative fluorescent particulate tracers. These tracers consisted of two types of particles, luminophores and microspheres. Luminophores were natural sand particles coated with fluorescent paint. They were present in two different sizes, Ø = 63 to 100 μm and Ø = 100 to 315 μm [22,23]. Microspheres were fluorescent balls of latex (Ø = 1 μm) within a liquid phase (Fluoresbrite YG Microspheres, Polysciences Europe, Eppelheim, Germany). In each EU, a mixture of 10.6 g of Garonne sediment with 0.45 g and 0.6 g of the two types of luminophores and 0.3 ml of microspheres suspension was deposited in 3-mm-thick frozen mud cakes at the sediment surface 24 h after the introduction of the worms.

The EUs were placed into three experimental tanks, one for each experimental condition (see Fig. 1). For the two contaminated tanks (+Cd−Tub and +Cd+Tub), the nominal Cd contamination level in the water was fixed at 20 μg/L ($CdCl_2$; Merck, Darmstadt, Germany). To maintain the contamination pressure throughout the experiments and to limit variations between the two contaminated conditions, the water in each tank was replaced daily. The water in the uncontaminated tank (−Cd+Tub) was also replaced daily, so that all the EUs underwent identical disturbances.

The experiments lasted 56 d, with five sampling times, which were 7, 14, 21, 28, and 56 d. For the −Cd+Tub and +Cd+Tub conditions and for each exposure duration, nine EUs were set up, including three replicates for the bioturbation study, three for Cd analysis and major redox species distribution in the sediment, and three for Cd determination in worms. Cadmium bioaccumulation in worms, relative to metal distribution in sediment and bioturbation intensity, has been reported in a previous publication [24]. For the +Cd−Tub condition, three EUs were prepared for each duration to quantify Cd transfer in the sediment, with three supplementary EUs for the last sampling period for the comparative bioturbation study. In total, 108 EUs were prepared. At each sampling period, EUs were removed from the experimental tanks and sacrificed to collect water, sediment, and worm samples. The volume of water of each tank was then adjusted to the number of remaining EUs, so the ratio of volume between the water and the EUs was maintained constant.

Physico-chemical measurements, sampling procedure, and cadmium determination

Temperature (EverSafe Thermometer; Fisher Bioblock Scientific, Illkirch, France), turbidity (HI 93703 turbidity meter; Hanna Instruments, Ann Arbor, MI, USA), pH (MP120 pH Meter; Mettler-Toledo, Greifensee, Switzerland), and dissolved oxygen concentrations (MO128 dissolved oxygen meter; Mettler-Toledo) were measured daily in the central part of the three experimental tanks before replacing the water. Cadmium concentration in the waters was measured at the beginning and end of each renewal cycle. Ten milliliters of unfiltered water were sampled from each experimental tank with a polypropylene syringe, then acidified with 200 μl of Merck 65% HNO_3, stored at 4°C in 12-ml prewashed polypropylene tubes, and analyzed for total Cd within 3 d. One or two times a week, 10 ml of filtered water was also sampled from each experimental tank with a polypropylene syringe and 0.2-μm surfactant-free cellulose acetate membrane syringe filters (Nalgene, Rochester, NY, USA), then acidified and analyzed for dissolved Cd.

Vertical distribution of Cd, manganese (Mn), and sulfate in the sediment was analyzed for the three experimental conditions at five distinct times. The water column of the EUs was removed with a syringe and then the sediment was pushed out of the EUs using a piston. The sediment was sliced into six horizontal layers (0–0.5, 0.5–1, 1–2, 2–3, 3–5, and 5–12 cm) with plastic knifes under nitrogen atmosphere. Each layer was placed in a 50-ml centrifugal polypropylene tube (Bibby Sterilin, Stone, UK) with nitrogen atmosphere, weighed, and centrifuged (centrifuge 3K12; Sigma-Aldrich, St. Louis, MO, USA) for 20 min at 2,627 *g* at 20°C to collect pore waters. The supernatant was collected with a 10-ml polypropylene syringe (Terumo, Tokyo, Japan) and filtered with a SFCA membrane 0.2-μm filter. One hundred microliters of HNO_3 were added to the filtrate, which was stored at +4°C in a 5-ml polypropylene tube (Porex Bio Products, Petaluma, CA, USA) before Cd and Mn determination. Another subsample was stored without acidification for sulfate analysis. The solid fraction was lyophilized and weighed to determine the fresh weight to dry weight ratio (fresh wt:dry wt) for each sediment layer. A 60- to 80-mg subsample of lyophilized sediment was digested in Merck 65% HNO_3 at 100°C for 3 h under pressurized conditions. The digest was diluted up to 20 ml with MilliQ® plus ultrapure water (Millipore, Billerica, MA, USA) before Cd and Mn determination. Digestion blanks were also performed.

Cadmium was determined by atomic absorption spectrophotometry using a Varian AA 400 spectrophotometer equipped with a graphite tube atomizer (GTA 96), autosampler, and Zeeman correction (Varian Instruments, Palo Alto, CA, USA). Samples of water or sediment digestates (10 μl) were mixed before atomization with 4 μl of a 0.2 g/L Pd and 0.5 g/L $Mg(NO_3)_2$ mixture, to avoid interference. The detection limit was 0.1 μg/L (detection limit: 3× standard deviation of the reagent blanks). The accuracy of the analytical procedure was monitored by analysis of National Research Council Canada (Ottawa, ON, Canada) standard reference marine sediments (PACS-2 and MESS-3). Values were consistently within the certified ranges (data not shown). Pore water and particulate Mn were measured by flame atomic absorption spectrometry. Sulfate was measured with a nephelometric method, with a precision better than 2%. The volume of pore waters extracted from the sediment was less than 2 ml for some samples. Therefore, it was not possible to measure dissolved Mn or sulfate in all the samples or in all sediment units.

A voltammetric gold amalgam minielectrode [25,26] was used to measure the dissolved oxygen profiles. The voltammetric electrode was constructed and used according to the method of Anschutz et al. [27]. A DLK-100 AIS electrochemical analyzer (Analytical Instrument Systems, Flemington, NJ, USA) was used for all measurements. Oxygen was determined with linear sweep voltammetry, scanning from −0.1 to −1.7 V at a rate of 200 mV/s after 10 s of equilibration at −0.1 V. Profiling was carried out just before the cores were sliced.

To analyze vertical distribution of luminophores and microspheres in the sediment, the same sampling procedure was applied as for Cd, Mn, and sulfate. Three samples of 100 ± 0.5 mg of each lyophilized sediment layer were analyzed using an Olympus Optical epifluorescence ultraviolet-microscope at 360 nm with a reflected light fluorescence attachment. Luminophores were counted at ×4 magnification and microspheres at ×20 magnification. All tracer concentrations were standardized for homogenizing graph scales and expressed in percentages (luminophores or microspheres counted in a sediment layer versus their total in each sediment column).

Data treatment

Statistical computations were performed with Statistica 5.1 (StatSoft, Tulsa, OK, USA), using two- or three-way analysis of variance followed by a least-significant-difference test. The check of normality and homeoscedasticity of the error term, based on residue analysis, was done both graphically and using the Kolmogorov–Smirnov goodness-of-fit test and the Levene test. When the assumptions were not checked, we used a BOX–COX data transformation. Significance of the observed effects was assessed at the $p < 0.05$ level.

RESULTS

The temperature, pH, and dissolved oxygen concentration were constant throughout the experiments and equal to 19.8 ± 0.1°C, 8.4 ± 0.2, and 8.1 ± 0.3 mg/L, respectively. Significant differences were observed, however, in turbidity measured at the end of the renewal cycles. The mean turbidity values during the experiments were 10.3 ± 1.3 formazine turbidity units for the +Cd+Tub and −Cd+Tub conditions and 0.2 ± 0.1 formazine turbidity units for the +Cd−Tub condition.

Cadmium concentrations measured in unfiltered-water samples are shown in Figure 2, at the beginning and at the end of each renewal cycle. For the +Cd+Tub and +Cd−Tub conditions, the mean Cd concentrations were 13.9 and 18.3 μg/L, respectively. The decrease in Cd concentration in the water column during the renewal cycles was, on average, 57 and 13%, respectively. Mean dissolved Cd concentration for the +Cd−Tub condition represented 98.4 ± 0.6% of total Cd. For the +Cd+Tub condition, the mean dissolved Cd concentration represented 78.7 ± 2.4% of total Cd between 0 and 25 d and 96.1 ± 1.6% of total Cd between 26 and 56 d. For the −Cd+Tub condition, dissolved Cd was below the detection limit (0.1 μg/L).

The temporal evolution of the Cd dissolved vertical distribution in the pore waters and in the particulate fraction of the six sediment layers is shown in Figure 3. For more clarity, only the profiles determined after 7, 21, and 56 d are shown on the graphs. In the −Cd+Tub condition, the dissolved Cd

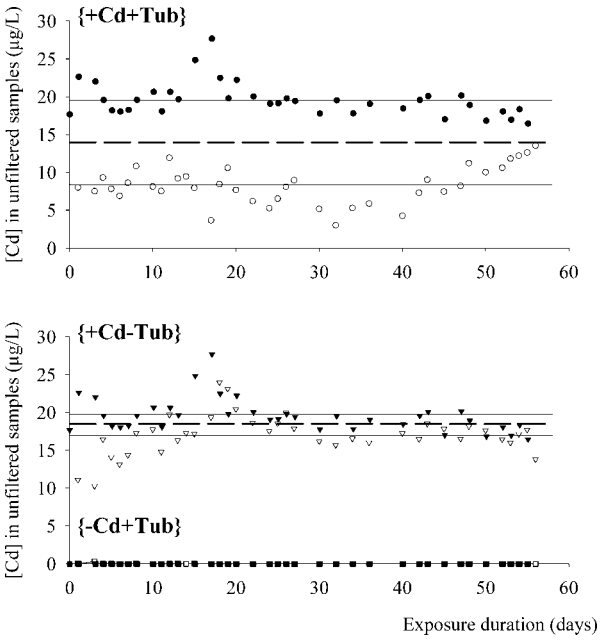

Fig. 2. Cadmium concentrations measured in unfiltered water samples during the experiments for the three experimental conditions: −Cd+Tub, no Cd added to the water column and Tubificidae (Tub) in the sediment; +Cd−Tub, water column contaminated with Cd and no Tubificidae added to the sediment; +Cd+Tub, water column contaminated with Cd and Tubificidae added to the sediment. Solid line, mean Cd concentration at the beginning and at the end of renewal cycles; dashed line, mean Cd concentration determined from the [Cd] measured during the duration of the experiment. Black circles, +Cd+Tub, beginning of renewal cycles; white circles, +Cd+Tub, end of renewal cycles; black triangles, +Cd−Tub, beginning of renewal cycles; white triangles, +Cd−Tub, end of renewal cycles; black squares, −Cd+Tub, beginning of renewal cycles; white squares, −Cd+Tub, end of renewal cycles.

concentration was below the detection limit. Corresponding Cd concentrations in the particulate fraction did not differ significantly from the background level. For the +Cd−Tub condition, a significant Cd concentration peak was observed in the top centimeter of the sediment, which increased during the experiments. Maximum Cd concentrations, 5.5 ± 0.7 µg/L and 39.8 ± 13.4 µg/g, were observed in the 0 to 0.5 cm layer in the dissolved pore water and in the particulate fraction, respectively, at the end of the experiments. A marked increase in Cd concentration was observed deeper in the sediment for the +Cd+Tub condition, and this affected the 3- to 5-cm layer, but the maximum contamination levels in the surface layer were lower than those measured for the +Cd−Tub condition, 3.1 ± 0.4 µg/L and 20.9 ± 0.6 µg/g dry weight, respectively, after 56 d.

The amount of Cd transferred from the water to the sediment was determined from the average Cd concentrations measured in the different sediment layers, after correction for background Cd (Fig. 4A). After 7 d, no significant difference was observed whether or not worms were present. After 56 d, Cd burdens increased notably in the sediment and significant differences were observed between the +Cd−Tub and +Cd+Tub conditions, with 318 ± 103 µg and 671 ± 21 µg, respectively. The Cd flux from the water to the sediment (Fig. 4B) was nearly independent of time for the +Cd−Tub condition. The Cd flux in the +Cd+Tub condition was similar to that of the +Cd−Tub condition after 7 d but nearly twice as high later in the experiments.

The concentration of dissolved oxygen shown in Figure 5A decreased with depth, from values close to saturation just above the sediment–water interface to zero between 3 and 5 mm below this interface. The penetration depth of O_2 remained similar for all conditions (+Cd−Tub, −Cd+Tub, and +Cd+Tub). Deeper dissolved oxygen due to bioirrigation was not observed. Dissolved Mn(II) (Fig. 5B) was measured below the oxygen penetration depth in all conditions, indicating that the majority of the sediment was anoxic. The vertical profiles of dissolved Mn remained fairly constant during time from 14 to 56 d for all conditions. The Mn(II) concentration ranged between 150 and 200 µmol/L at the bottom of the units without worms and decreased upward. The Mn(II) concentrations were close to the detection limit of 1 µmol/L in the oxic sediments. In the units with worms, Mn(II) concentrations were between 120 and 170 µmol/L at the bottom, the lowest values corresponding to the end of the experiment, and between 0 and 10 µmol/L at the top. The amount of dissolved Mn and the concentration gradient just below the oxic layer was always higher in the worm-free units. The concentration gradient was, on average, 65 nmol/cm⁴ for the +Cd−Tub condition and 25 nmol/cm⁴ for the +Cd+Tub and −Cd+Tub conditions. The profiles of particulate Mn showed maximum values in the top sediments (0–0.5 cm) of the worm-free units. The maximum concentration increased with time, from 17 ± 0.5 µmol/g at 7 d to 21.5 ±1 µmol/g at 56 d. The Mn(II) concentrations decreased abruptly below the oxic layer to a constant background value of 15.5 µmol/g. The profiles also showed a minimum concentration, between 13 and 15 µmol/g, just below the oxic layer at 56 d. Particulate Mn concentrations in the worm-present condition remained fairly constant with depth and time. The average concentrations were 15 µmol/g at 7 and 21 d, and 13 to 14 µmol/g at 56 d. The concentration of dissolved sulfate in the water column changed during time, from 170 µmol/L at 7 d to 70 µmol/L at 56 d (see Fig. 5C). These concentrations were higher than the concentration of the sediment pore water at the beginning of the experiments, which was close to 40 µmol/L. The dissolved sulfate concentrations at the top of the units decreased with time. For all conditions, the dissolved sulfate concentration at the bottom of the EUs also decreased with time, from about 40 µmol/L at 7 d to less than 15 µmol/L at 56 d. The dissolved sulfate evolution at intermediate depths, between 1 and 5 cm, depended on the presence of worms. In the absence of worms, the sulfate concentrations decreased with time. Dissolved sulfide was not detected at any depth in the sediment column with the polarographic electrode, which had a detection limit of 0.1 µmol/L.

The vertical distribution of luminophores and microspheres in the sediment after 7, 21, and 56 d is illustrated in Figure 6. Each graph corresponds to one EU, which is representative of the three EUs analyzed for each time. In the +Cd−Tub condition, luminophores and microspheres were confined to the upper sediment layers. About 75% were recovered in the top 0- to 0.5-cm layer and 25% just below, in the 0.5- to 1.0-cm layer. In the +Cd+Tub condition, the distribution of tracers changed with time. The maximum luminophore content deepened progressively from the 0.5- to 1-cm layer after 7 d to the 3- to 5-cm layer after 21 d, to below 5 cm at the end of the experiment. The average advection velocity of luminophores, assuming migration from 0 cm to 3 to 5 cm during 21 d, was 0.14 to 0.24 cm/d. Microsphere distribution was different. The microspheres were also buried during the experiment, but they

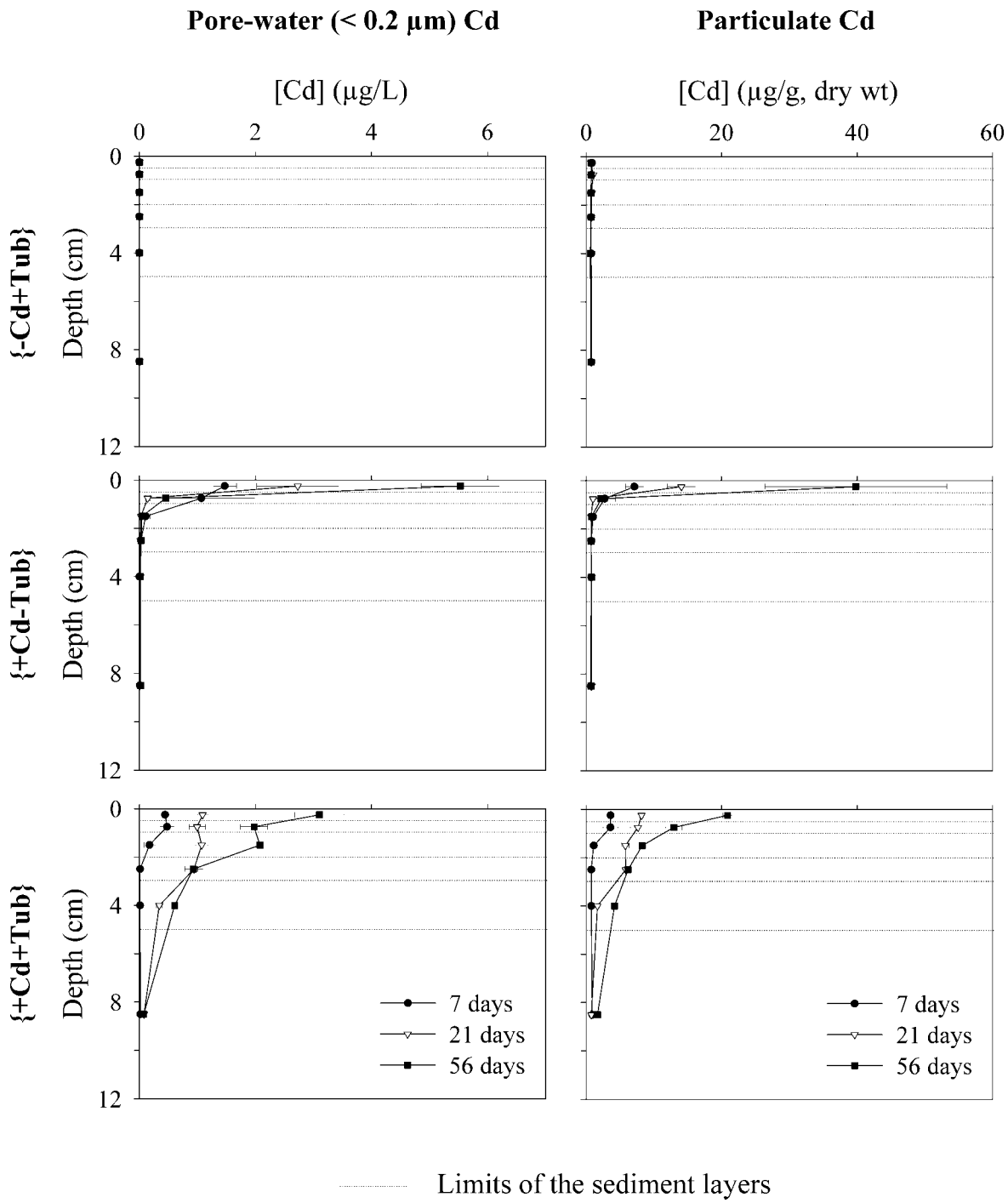

Fig. 3. Vertical profiles of pore water (<0.2 μm) and particulate Cd concentrations in the sediment after 7, 21, and 56 d for the three experimental conditions studied: −Cd+Tub, no Cd added to the water column and Tubificidae (Tub) in the sediment; +Cd−Tub, water column contaminated with Cd and no Tubificidae in the sediment; +Cd+Tub, water column contaminated with Cd and Tubificidae in the sediment. Dry weight (dry wt) after lyophilization. Mean ± standard deviation (n = 3).

were still also observed in the top sediment layer throughout the experiments. After 56 d, the highest concentration of microspheres was observed in the bottom layer (5–12 cm), but this maximum did not represent a marked peak. The vertical distribution of microspheres became more or less homogeneous throughout the sediment column with time.

DISCUSSION

Results show that tubificid worms can increase significantly metal loads in sediments. The worms also changed the vertical metal distribution within the sediment by increasing the thickness of the Cd-enriched layer. Worms' activity affected particle mixing and diagenetic reactions, which both contribute to the Cd distribution.

Particle mixing

In the absence of bioturbation, luminophores should have been recovered at the top of the sediment pile. Some luminophores and some microspheres were recovered in the 0.5- to 1.0-cm layer of the +Cd−Tub condition (see Fig. 6), prob-

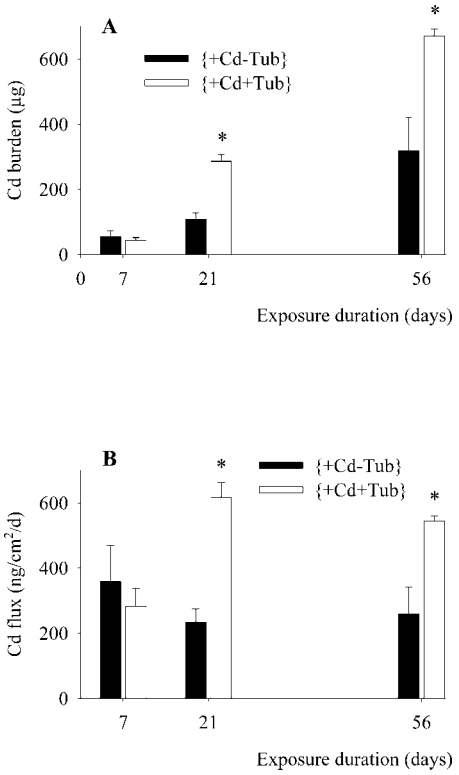

Fig. 4. (**A**) Cadmium burden measured in the sediment compartment at the experimental unit level for the two experimental conditions: +Cd−Tub, water column contaminated with Cd and no Tubificidae (Tub) in the sediment; +Cd+Tub, water column contaminated with Cd and Tubificidae in the sediment, at time 0, 7, 21, and 56 d. The background level of the −Cd+Tub condition (0.75 ± 0.02 µg Cd/g, dry wt) was deducted. Mean ± standard deviation (n = 3). (**B**) Estimated mean Cd fluxes from the water column to the sediment compartment of EUs for the two experimental conditions: +Cd−Tub, water column contaminated with Cd and no Tubificidae in the sediment; +Cd+Tub, water column contaminated with Cd and Tubificidae in the sediment, over a period of time equal to 7, 21 and 56 d. Mean ± standard deviation (n = 3). * indicates a significant difference between the two experimental conditions ($p < 0.05$).

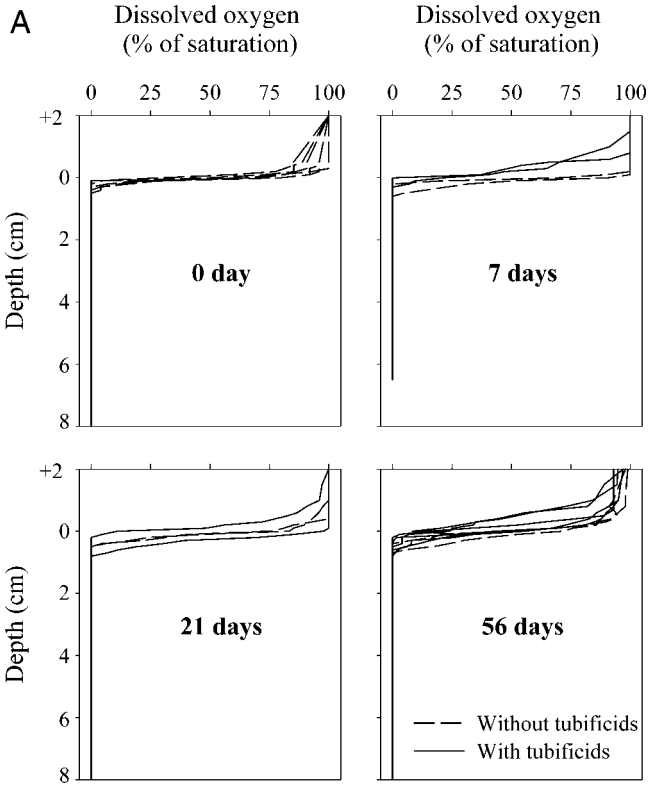

Fig. 5. (**A**) Dissolved oxygen profiles measured above the sediment–water interface and in the sediment pore water at time 0 and after 7, 21, and 56 d.

ably because the sediment surface was not exactly horizontal and also because the sediment layer containing the two particulate tracers was almost as thick as the first sampled sediment layer.

Results from the +Cd+Tub condition show marked differences. Tracer distribution illustrates the effect of bioadvection and biodiffusion on the sediment. Biodiffusion is not the major effect of worm bioturbation but certainly occurs as evidenced by tracers' dispersion. Tubificids are known to ingest anoxic sediment at depth and reject it at the sediment surface. This process is called bioadvection because it generates the rapid burial of surface sediment by accumulation of fecal pellets at the sediment surface. Luminophores, which are too coarse to be ingested by tubificids [28,29], migrate vertically in the sediment as far as the ingestion zone, where they remain in the absence of physical accumulation. In our experiments, the average bioadvection velocity was between 0.14 and 0.24 cm/d, with a tubificid density of 60,000 worms/m^2. This rate is similar to previous bioadvection rates estimated in the literature. The bioadvection rate was estimated to be between 0.23 and 0.68 cm/d for 100,000 worms/m^2 for *Limnodrilus hoffmeisteri* at temperatures between 20 and 22°C and between 0.12 and 0.64 cm/d for 100,000 worms/m^2 for *Tubifex tubifex* [7,11,30].

The behavior of microspheres provides further insight into the bioturbation process. These smaller tracers are easily ingested by the three species of tubificids present in our experiments that preferentially feed on particles smaller than 63 µm [29]. The presence of microspheres in the top layer as early as 7 d after the beginning of the experiment can be explained by this ingestion (see Fig. 6). This result suggests sediment ingestion by worms at a shallow depth of between 0.5 and 2 cm. The heterogeneity of length of worms leads to a progressive homogenization of microsphere distribution in this zone, the depth of which is limited by the maximal ingestion depth. The occurrence of luminophores in the 5- to 12-cm layer at 28 d indicates that the maximal ingestion depth is located in this layer.

Diagenetic redox species

The concentration of dissolved oxygen decreased from saturation in the water column to zero at a few millimeters depth below the sediment–water interface (see Fig. 5A). The rapid consumption of O_2 is due to oxic respiration by microorganisms and oxidation of reduced products that diffuse from below. In the worm-present experiments, worm respiration also contributed to the oxygen consumption. Tubificids do not irrigate their burrows with water currents [11] nor pump oxygen at depth. Their respiratory exchanges are achieved by cutaneous diffusion across the surface of the posterior end of the body, which often remains in the water column. The contribution of reduced species oxidation was probably high because the worms transferred particles from the anoxic sediment to the surface. Some of the particles advected to the surface likely

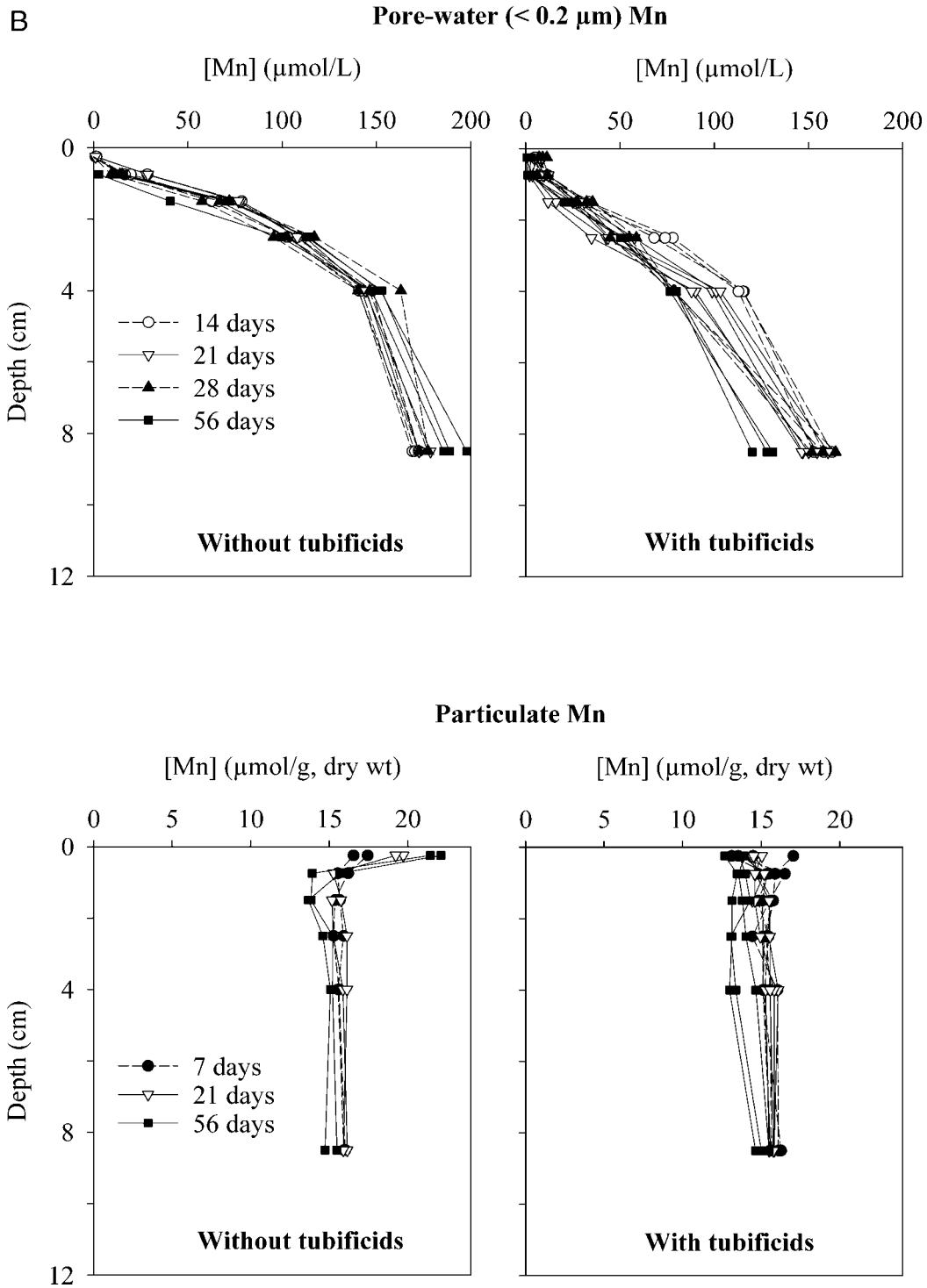

Fig. 5. (**B**) Vertical profiles of pore water and particulate manganese (Mn) concentrations in the sediment after 7, 21, and 56 d. Dry weight (dry wt) after lyophilization.

reacted with oxygen. McCall and Fisher [11] observed that the oxygen consumption of tubificid-inhabited sediment is twice as high as the simple sum of worm respiration and sediment oxidation. This difference was attributed to the oxidation of FeS transferred to the surface by worms and to enhanced microbial activity.

Dissolved Mn, as Mn(II), is one of the reduced products that is oxidized in the oxic layer and precipitates as insoluble Mn(III) or Mn(IV). In our EUs, dissolved Mn concentrations were close to zero just below the sediment–water interface, in both worms and worm-free experimental units, and particulate Mn concentrations increased with time in the worm-free experiments. The profiles of dissolved Mn are close to steady state after 14 d in the presence or absence of worms (see Fig. 5B), indicating an equilibrium between the precipitation rate of Mn(II) in the oxic layer and its production rate in the anoxic layers. The presence of a particulate Mn maximum in the oxic layer is commonly observed in modern sediments [31] as well as in our EUs without bioturbation. This Mn-oxide accumulation results from the oxidation of dissolved Mn(II) diffusing

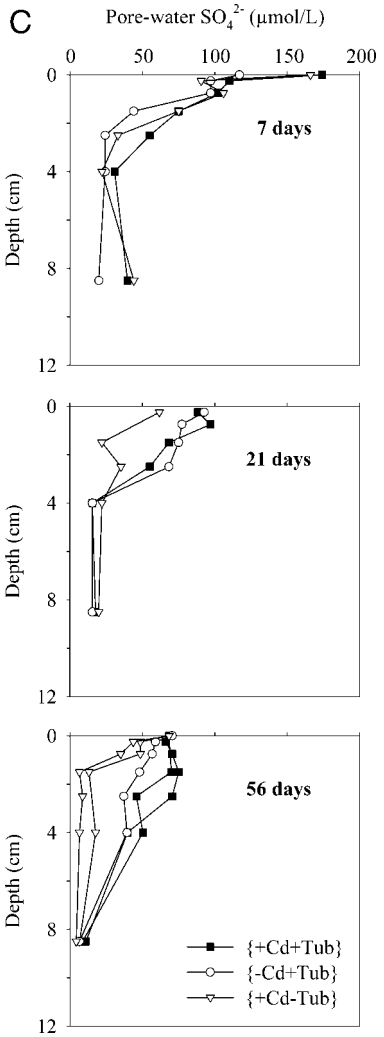

Fig. 5. (**C**) Dissolved sulfate (SO_4^{2-}) profiles in the sediment pore water after 7, 21, and 56 d. Measurements in the water column at times 7 and 56 d are figured at the 0-cm depth. The values plotted on each graph correspond to single measurements.

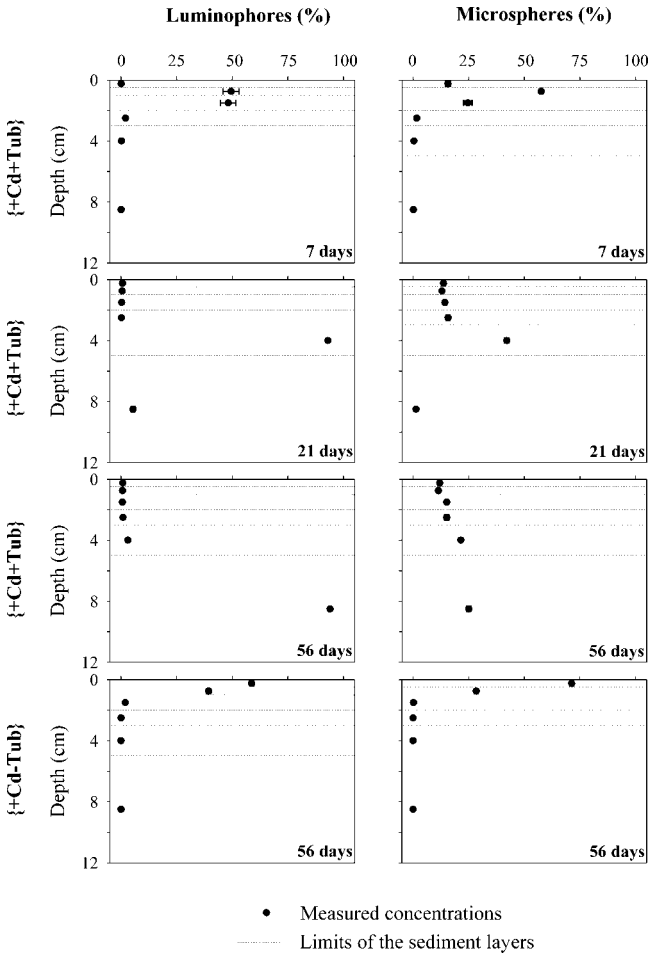

Fig. 6. Vertical profiles of fluorescent particles: Measured concentrations after 56 d for the +Cd−Tub condition (no worms) and after 7, 21 and 56 d for the +Cd+Tub condition (water column contaminated with Cd and Tubificidae (Tub) in the sediment). Each profile corresponds to one experimental unit (EU), which is representative of the three EUs analyzed per condition. Luminophores (63–315 μm) and microspheres (1 μm) values are means ± standard deviation from three tracer countings; % represents the percentage of luminophores or microspheres counted in a sediment layer versus their total in each EU.

upward from the anoxic sediment. Therefore, the diffusive flux of Mn should equal the accumulation of oxides. Assuming transport by molecular diffusion and a constant gradient of dissolved Mn during time, this flux can be calculated using Fick's first law, $J = -\phi D_s dC/dX$. J is the flux, ϕ is the porosity, dC/dX is the concentration gradient, and D_s is the bulk sediment diffusion coefficient corrected for tortuosity, i.e., $D_s = D_o/\theta^2$, where θ is the tortuosity and D_o is the diffusion coefficient in water [4,32]. The D_o values were obtained from Li and Gregory [33] and the value of θ^2 is assumed to equal to $1 - \ln(\phi^2)$ [34]. The dC/dX for dissolved Mn was 65 nmol/cm^4 at the top of the anoxic layer in the worm-free experiments. The D_s for Mn is calculated to be 3.43×10^{-6} cm^2/s. So J for dissolved Mn was 0.156 pmol/cm^2/s^1, or 0.47 μmol/cm^2 in 35 d. The top 0- to 0.5-cm layer contained 270 mg of particles per cm^2. In this section, the particulate Mn content increased from 5.27 μmol/cm^2 at 21 d to 5.86 μmol/cm^2 at 56 d, which indicates an input of about 0.59 μmol/cm^2 in 35 d. The increase of particulate Mn is close to the diffusive flux of dissolved Mn.

In the presence of worms, the shape of the dissolved Mn profile suggests that Mn(II) is oxidized in the oxic layer, but Mn oxides did not accumulate in this layer. The bioadvection velocity (0.14–0.24 cm/d) deduced from the distribution of the luminophores suggests that oxidized Mn would be readily transported back to the anoxic layers below.

The dissolved sulfate concentrations in the pore water decreased from the top to the bottom, indicating a downward diffusive sulfate flux (see Fig. 5C). The sulfate concentration decreased with time at the bottom of the units, indicating that sulfate was consumed in the anoxic sediment, probably by bacterial sulfate reduction. Sulphate reduction produces dissolved sulfide, which can rapidly react with iron oxides, and precipitates as iron sulfide [35]. Metal-sulfide precipitation probably occurred in our experiments because we did not detect any dissolved sulfide with the microelectrodes. Between 1- and 4-cm depth, the sulfate concentration in the worm-free units decreased with time, whereas they increased in the presence of worms. This indicates that sulfate reduction occurs just below the oxic layer in the units without worms but not in the worm-present units. The most probable source of sulfate in the bioturbated units is particulate sulfide oxidation. In these sediments, worms transported sulfide particles to the surface.

Some of the sulfide must have been oxidized in the oxic layer but, because the bioadvection velocity was high, a significant fraction of sulfide probably reached the anoxic sediment. Sulfide oxidation in the anoxic sediment may have occurred in the presence of the oxidized particles, such as the Mn oxides that were advected together with the sulfide. As Mn oxides are a more favorable electron acceptor than sulfate for the dissimilatory oxidation of organic matter, they have probably decreased the sulfate reduction rate.

Cadmium behavior without bioturbation

Dissolved and particulate Cd were detected only in the first centimeter below the sediment–water interface in the worm-free units (see Fig. 3), with a maximum in the top 0 to 0.5 cm. In the oxic layer, Cd can be removed from water by adsorption on organic matter and on Mn and Fe oxides [36,37]. In the anoxic sediment, Cd can precipitate as CdS in the presence of sulfide. We did not detect sulfide in the experiments, but this does not imply that sulfide was not produced. Sulfide can be trapped immediately as acid-volatile sulfide. The maximal depth of oxygen penetration below the sediment–water interface was measured by polarographic electrode at 0.5 cm. Therefore, the oxic layer, and probably the top of the anoxic sediment, was included within the 0- to 0.5-cm sediment sample. Consequently, the sample resolution is insufficient to determine directly the location of Cd precipitation. The trapping of the Cd in sulfide mineral in the experiments implies that most of the dissolved Cd was transported by molecular diffusion through the oxic layer to the anoxic sediment, where it precipitated. The diffusive Cd flux through the oxic layer must be similar to the observed accumulation of particulate Cd during the experiment. That can be estimated from the dissolved Cd concentration gradients with Fick's first law. The calculated diffusion coefficient in the surface sediment (D_s) of Cd is 4.48×10^{-6} cm^2/s. The concentration gradient is difficult to determine accurately from our data set. Yet, assuming a dissolved Cd concentration of zero at the oxicline located at a depth of 0.5 cm and a mean dissolved Cd concentration in the water column of 18 μmol/L, a maximum value for dC/dX of 36 ng/cm^4 is obtained. This concentration gradient excludes the occurrence of a diffusive boundary layer. The calculated diffusive flux is 11.1 ng/cm^2/d, which corresponds to an input of 13.7 μg of Cd to the anoxic sediment for each EU during the experiments. The average Cd load measured in the sediments was 318 μg, which is more than 20 times higher than the calculated Cd flux. This poor correspondence illustrates that Cd diffusion through the oxic layer cannot explain the observed Cd accumulation. The dissolved Cd gradient may be much greater than that used in the preceding calculation, i.e., that the Cd is trapped at the very top of the sediment, within the oxic layer, and/or the oxicline is less than 0.5 cm in depth. Cadmium is probably adsorbed on metal oxides and organic matter at the sediment–water interface. Cadmium may be transported from the water column to the surface sediment by diffusion through a thin diffusive boundary layer where the Cd concentration gradient is high. Our results show an increase in particulate Cd concentration within the superficial sediment layers throughout the entire experiment, which indicates that the adsorption sites did not become saturated during the experiments. However, we observe also that the dissolved Cd in the 0- to 0.5-cm layer increased with time. This could result from a slowing down of the adsorption kinetics of Cd onto particles while the adsorption sites became more and more saturated during the experiment.

The Einstein–Smoluchowski equation enables us to calculate the propagation depth, d, of Cd that diffuses in the sediment as a function of time: $d = (2D_s t)^{1/2}$ [4]. This equation indicates that the pore water should be contaminated in dissolved Cd down to 6.6 cm after 56 d, whereas we only observed increasing Cd concentration down to 1 cm. This indicates that the top sediments are an efficient barrier to Cd diffusion.

Cadmium behavior with bioturbation

The temporal evolution of the Cd concentration profiles was similar for both particulate and dissolved Cd in the +Cd+Tub condition (see Fig. 3). The concentration increased over 56 d, and a migration of the Cd anomaly down to 5 cm was observed. This differs from Cd distribution in the +Cd−Tub condition. These results are in agreement with those of Soster et al. [19], who measured an increase in particulate and pore-water Zn concentrations to a depth of 3 cm after 139 d in tubificid-present experiments, while Zn concentration was limited to the first centimeter of sediment in tubificid-free condition. Petersen et al. [20] showed also that bioturbation enhanced Cd transport into uncontaminated estuarine sediments. Their experiments with *Arenicola marina* indicated an increase in pore-water and particulate Cd concentrations at depth in the sediment.

In nonbioturbated units, the diffusive Cd flux to the anoxic sediment represented less than 5% of the total Cd flux. In the presence of worms, the dissolved Cd gradient was even smaller. Here again, the diffusive Cd flux toward the anoxic sediments and its subsequent precipitation as CdS contributed little to particulate Cd accumulation. Adsorption on oxic sediments was probably the most efficient Cd-enrichment process. These sediments were then buried by bioturbation, as were fluorescent tracers.

In the +Cd+Tub experiments, Cd enrichment must reach the deepest layer of sediment ingestion, which occurred in the 5- to 12-cm sediment layer, as shown in the luminophore profile after 56 d (see Fig. 6). We did not observe a significant increase in particulate Cd concentration in this layer relative to the background, probably because few particles that contained Cd reached this level. Most of these particles may have been reingested during their burial. Several cycles of Cd-bearing particle reingestion at depth and Cd accumulation at the surface can explain the Cd particulate enrichment at the top of the sediment. The profiles of particulate Cd and microspheres are not similar because the production of particulate Cd at the surface is continuous, unlike the microsphere input. Soster et al. [19] also concluded that the higher level of Zn found in the upper 3 cm of tubificid-inhabited sediments was probably caused by adsorption and bioadvective particle movement rather than by solute diffusion. Petersen et al. [20] suggest also that the enhanced transport of Cd from the water column into sediments with infaunal burrows is driven in part by adsorption to iron and manganese oxides.

The distribution of luminophores and microspheres indicates that, throughout the experiment, bioadvective transport by tubificids led to the continuous transport of small particles ingested at different depths to the surface. Therefore, the residence time of non- or low-contaminated particles at the sediment surface and the contact time of particles with contaminated water were low. The concentration of solid Cd in the

0- to 0.5-cm sample was then always lower in the +Cd+Tub experiment than in the +Cd−Tub experiment.

The overall Cd flux was higher when worms were present. Therefore, the renewal of particles at the surface promoted a greater Cd flux to the sediment than stagnant particles. Because the residence time of particles at the surface was short in the presence of bioturbation, Cd adsorption sites were continuously renewed and fresh and unsaturated surfaces were brought into contact with contaminated waters. For example, we showed that fresh Mn oxides, which are efficient Cd scavengers, precipitated close to the surface and were rapidly buried in the anoxic sediment.

Dissolved Cd concentration increased with time in the oxic sediment in both the presence and absence of worms and also exceeded the background level in the anoxic sediments in the presence of worms. The first hypothesis that can explain these observations is that the Cd measurements were influenced by the presence of a <0.2-μm colloid fraction. If this is not the case, then the Cd in the anoxic part of the bioturbated sediments may originate from the release of adsorbed Cd when particulate Fe and Mn oxides are reduced at depth; or the desorption of Cd, according to a desorption/adsorption equilibrium; or the diffusion of Cd from the overlying water column. The similarity of the particulate and dissolved Cd profiles suggests that desorption occurred. The Einstein–Smoluchowski equation indicates that the pore waters should be contaminated with dissolved Cd down to 6.6 cm after 56 d, which is similar to what we observed. In the +Cd−Tub condition, we suggest that dissolved Cd was absent from the anoxic sediment because it was trapped in the oxic layer or precipitated as CdS just below the oxic/anoxic interface. This implies that sulfide was produced from sulfate reduction during the experiments. Cadmium-sulfide precipitation can occur in the presence of very low sulfide concentration, as observed by Lapp and Balzer [38] and Chaillou et al. [39]. In the presence of worms, Cd did not precipitate in the anoxic sediments. The dissolved-sulfate profiles show that sulfate concentrations did not decrease in the bioturbated part of the sediment. Therefore, the dissolved sulfide production was lower than the flux of dissolved Cd into the anoxic zone of the bioturbated units. Peterson et al. [21] also observed that bioturbation by the oligochaete *Lumbriculus variegatus* reduced significantly acid-volatile sulfide concentrations in surficial sediments, resulting in high dissolved Cd concentrations. Sulphate reduction is an anaerobic process of organic-matter oxidation. It is favored only when more thermodynamically favorable oxidants, such as oxygen, nitrates, Mn oxides, or reactive Fe oxides, have been consumed [40]. The lower amount of sulfate reduction at the top of the anoxic zone of +Cd+Tub experiments could result from the bioadvection of reactive oxides, which could have been preferentially used as electron acceptors for the bacterially mediated degradation of organic matter.

CONCLUSION

The present study indicates that uncontaminated sediments adsorbed Cd originally dissolved in the overlying water. During this 56-d experiment, Cd was primarily adsorbed on particles present in the oxic layer, below the sediment–water interface. Tubificids worms increased this Cd scavenging into the sediment by a factor of two because particles and Cd adsorption sites were constantly renewed at the sediment–water interface by their bioadvection activity. Metals adsorbed onto oxide particles were then distributed throughout the biologically mixed layer. This mechanism led to higher metal concentrations at depth in the worm-present experiments.

Even though our experimental design did not attempt to perfectly simulate field conditions, this study provides valuable information on transport patterns and Cd distribution of Cd in sediment under the direct (transport) and indirect (early diagenesis) effects of bioturbating infauna. As bioadvective processes are found to increase substantially metal adsorption onto sediments, such processes should be taken into account in realistic biogeochemical models.

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