Bioturbation effects on metal release from contaminated sediments are metal-dependent☆

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ABSTRACT

Metal flux measurements inform the mobility, potential bioavailability and risk of toxicity for metals in contaminated sediments and therefore is an important approach for sediment quality assessment. The binding and release of metals that contribute to the net flux is strongly influenced by the presence and behaviors of benthic organisms. Here we studied the effects of bioturbation on the mobility and efflux of metals from multi-metal contaminated sediments that inhabited by oligochaete worms or both worms and bivalves. Presence of bivalves enhanced the release of Mn, Co, Ni and Zn but not for copper and chromium, which is likely due to the high affinities of copper and chromium for the solid phase. Metals in the overlying water were primarily associated with fractions smaller than 10 kDa, and the fractionation of all metals were not affected by the presence of the bivalve. Metal fluxes attributed to different processes were also distinguished, and the bioturbation induced effluxes were substantially higher than the diffusive effluxes. Temporal variabilities in the total net effluxes of Mn, Co, Ni and Zn were also observed and were attributed to the biological activities of the bivalves. Overall, the present study demonstrated that the response of different metals to the same bioturbation behavior was different, resulting in distinct mobility and fate of the metal contaminants.

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1. Introduction

Historic discharges of poorly treated or untreated industrial and domestic sewage into aquatic environments frequently result in the accumulation of metal contaminants in sediments. These legacy contaminants are not permanently immobilized in the sediment, but instead are often being released to the aquatic environment (Apell et al., 2018; Warnken et al., 2001; Xie et al., 2015). Sediments are recognized as an extremely complex system, and the fate of metals in sediment is regulated by a wide range of processes (e.g. sediment biogeochemistry, flow hydrodynamics, bioturbation, etc.) and factors (dissolved oxygen, pH, redox potential, etc.) (Chapman et al., 1998; Eggleton and Thomas, 2004; Xie et al., 2019; Xie et al., 2015; Xie et al., 2018). The mobility of metals within and their efflux from sediments will strongly influence the bioavailability and toxicity of metals to aquatic organisms (Amato et al., 2016; Simpson

et al., 2012). Consequently, identifying key controls on the behavior of metals and assessing their importance to the efflux of metals are essential to evaluating the ecological risk the sediments pose to the environment (Burton and Nedrich, 2018; Simpson and Batley, 2016).

The chemical evolution of metals in sediments is regulated by an interrelated suite of redox reactions that mineralize the labile organic matter (Aller, 2014). Metals are either directly involved in these biogeochemical reactions (e.g. Fe and Mn) or interact with the reaction products (e.g. iron and manganese oxy-hydroxides, and sulfide) via adsorption and/or co-precipitation (Gaillard et al., 1986). Along with these biogeochemical processes, the behavior and fate of metals may be further influenced by the activities of benthic organisms that rework and reorganize the sediments. Due to the inherent physiological difference, the activities of various organism species are distinct (Aller, 1994). Tubificid oligochaete worms, such as *Limnodrilus hoffmeisteri*, have been classified as deposit feeders (Fisher et al., 1980; Matisoff et al., 1999). These tubificid worms feed head down in the sediment and egest fecal particles at the sediment water interface (SWI), leading to turnover of surficial sediments on an ongoing basis. As the depth of the

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feeding zones is mainly restricted by the body length of the worms, the cyclical mixing of the surficial sediments may thus occur over a restricted depth range (Matisoff et al., 1999). In contrast, bivalve clams, such as *Corbicula fluminea*, can harvest food sources both from the suspended particles as well as from the ambient sediment bed and are therefore often classified as filter-feeders and/or deposit-feeders (Hakenkamp and Palmer, 1999; Vaughn and Hakenkamp, 2001; Way et al., 1990). Ventilation of oxygenated overlying water into deep anoxic sediment modifies the redox conditions and the repartition of many metals due to their redox sensitivity (Aller, 2014). Accordingly, the behavior of metals within the sediments and release of metals across the SWI are strongly regulated by the coupling between sediment biogeochemistry and the activities of larger organisms within the sediments.

Characterizing the release and measuring the fluxes of metals are important approaches to identifying the sources of contamination, evaluating the fate of metals, and assessing the bioavailability and toxicity of metals in sediments (Simpson and Batley, 2016; Warnken et al., 2001). Greater efflux of metals generally represents greater bioavailability and higher risk of toxicity to aquatic biota (Remaili et al., 2016; Simpson and Batley, 2016). Fluxes of metals across the SWI are determined in two ways — by determining the rate of change of metal concentrations in the overlying water within a closed system and by inferring from porewater metal concentration gradients near the SWI (Berner, 1980; Simpson and Batley, 2016; Wang and Wang, 2017; Xie et al., 2016). Diffusive gradients in thin films (DGT) is a well-developed *in situ* technique that provides time-integrated measurements of metal concentrations (Davison and Zhang, 1994). The DGT unit comprises a membrane filter (0.45 μm pores), a porous polyacrylamide gel (2—5 nm pores), and a metal binding resin (Chelex-100) (Davison and Zhang, 1994; Zhang et al., 1995). When deployed in sediments, metals dissolved in sediment porewater rapidly diffuse through the membrane filter and the hydrogel layer and accumulate on the binding layer. The localized decline of metals in porewater is then supplied by metals weakly associated with sediment particles. Following retrieval, the DGT unit is disassembled, the binding resin layer sectioned, and metal concentrations in each section determined. The time-integrated metal concentration profiles in porewater are then derived based on a series of well-established equations that consider the deployment time and the diffusion coefficients of metals in the DGT gel (Zhang et al., 1995). Conventional porewater sampling approach, which involves sediment core sectioning and centrifugation, may cause inadvertent artefacts during the sample processing, such as mixing of porewater solutes or/and chemical reactions of the analytes (Arsic et al., 2018; Rathnayake et al., 2017). Using DGT can avoid such artefacts and yield metal concentration profiles across the SWI at greater spatial resolution (Peijnenburg et al., 2014). Diffusive metal fluxes can then be derived from the concentration profile based on the Fick's first law of diffusion (Gao et al., 2010; Wang and Wang, 2017; Xu et al., 2016).

While many studies have focused on the net metal-mobilization effects by a certain single functional group of organisms (Amato et al., 2015; Cardoso et al., 2008; Reible et al., 1996), natural aquatic system typically contain multiple functional groups of organisms that interact. Further, urban river sediments receive sewage drainage from diverse sources, leading to contamination of sediments by multiple metals. The response of different metals to the same perturbation (by aquatic organisms) under similar biogeochemical conditions is still not well understood, yet these perturbations may alter the outcome of ecological risk assessment programs (Burton and Nedrich, 2018; Burton, 2018; Remaili et al., 2016). Accordingly, the primary goal of the present study is to improve understanding of how bioturbation and sediment biogeochemistry influence the mobility and efflux of metals across the SWI, with particular focus on characterizing the contribution of different processes on metal fluxes across the SWI. We conducted laboratory experiments harboring different species and densities of organisms. We evaluated the effects of bioturbation on metals efflux by comparing the total fluxes measured from metals in the overlying water and diffusive fluxes derived from porewater metal concentration profiles.

2. Materials and methods

2.1. Source and collection of sediment and organisms

Metal-contaminated sediments were obtained from an intertidal river — Dongbao River (Fig. S1, Supporting Information), a branch river that discharges into the upper Pearl River Estuary. The catchment area of Dongbao River was severely polluted by the historical discharge of industrial sewage for several decades and this river has been recognized as one of the most contaminated urban rivers in China (Wu et al., 2016). Sediments were collected from a single inter-tidal site at low tide during the wet season in June 2017, and salinity in the sediment porewater was close to 0‰. Fine-grained surficial sediments (~10 cm depth) were collected with a plastic shovel, immediately transported to the laboratory and stored at room temperature for less than 24 h before placement into the experimental system.

The sediments were also colonized predominantly by tubificid worms that were identified as *L. hoffmeisteri* ($12,000 \pm 1000$ worms/m², n = 4). These worms were intended to remain present as part of the study. As it was not feasible to remove all the worms without significantly modifying the physical, and biogeochemical properties of sediments, they remained present in the sediments prepared for the experiments and chemical analyses. The sediments were gently, but thoroughly homogenized using a plastic spoon with care not to damage the worms. A subsample of sediment was taken for analyses and the remainder placed into the experimental setup without additional manipulation.

The bivalve clams used in the study were *C. fluminea*, and bivalves with a body length between 1 and 1.5 cm and collected in a river in Guangdong Province (23° 28′40.74″ N, 113° 49′46.34″ W).

2.2. Experimental setup

Bioturbation chambers were used to study the effects of bioturbation by two species of benthic organisms on mobilization of metals. To minimize metal contamination, all parts of the experimental system were made of polypropylene. The experimental system was a closed system, consisting of a bioturbation chamber connected to a water reservoir bottle via a recirculation system (Fig. S2, Supporting Information). The bioturbation chamber was cylindrical, with diameter of 20 cm and height of 19 cm (6 L), containing a 10 cm depth of the homogenized sediments and 2 L of reconstituted freshwater (RFW) (depth = 6.4 cm) (Smith et al., 1997). A round-bottom polypropylene bottle containing 2 L of RFW served as a water reservoir was connected to the bioturbation chamber by silicone tubing and two peristaltic pumps. The total 4-L volume of overlying water was constantly circulated at a rate of 3.6 L/h within the system. To keep the overlying water oxygenated, air was supplied to both the bioturbation chamber and the reservoir bottle via aquarium air stones. The air supply rate in the bioturbation chamber was adjusted to provide water mixing without suspending the sediment particles. A magnetic stirrer was also used in the reservoir bottle to maintain a homogeneous distribution of solutes in the circulating water.

A control treatment (Ctrl) contained only the native

oligochaetes worms, providing a frame of reference for the other two treatments which contained both *in situ* worms and additional bivalve clams, *C. fluminea*. Ten and twenty bivalves, were added to form bivalve densities of 318 and 636 individuals/m^2. These treatments were denoted as low density (LD) and high density (HD), respectively. Each treatment was duplicated.

2.3. Experimental procedures

Once sediment (containing only *in situ* oligochaete worms), and water was present, all treatments were allowed to stabilize for 3 months before experiments started in order to develop near-equilibrium geochemical conditions within the sediment bed (Simpson et al., 2000). Before experiments commenced, the overlying water within the bioturbation chamber was renewed with 2 L RFW and the water reservoir bottle containing an additional 2 L of RFW was connected. In the LD and HD treatments, the bivalves were added into the bioturbation chamber and evenly distributed at the sediment surface. Experiments were run continuously for 8 days, and 16 mL of overlying water was collected daily for dissolved metal analyses. Following sample acquisition, the same volume of clean RFW was added into each chamber to maintain a constant volume of the overlying water. On the 8th day, overlying water in the bioturbation chamber was drained to a few mm above the SWI, and DGT devices were inserted into the center of each chamber to determine metal concentrations in porewater and overlying water. The 4 L of overlying water was then renewed in the bioturbation chamber (with care to avoid sediment resuspension) and in the reservoir bottle. The experiments then continued for a further two days. At the end of the experiments (10 days), the overlying water was drained, DGT samplers retrieved for analysis (after 48 h), and sediment minicores were removed for porewater extraction and determining the oligochaete density (described below).

2.4. Sampling and analysis

All plasticwares used in the study were pre-cleaned by soaking in 10% HNO$_3$ (v/v) for at least 24 h and thoroughly rinsed three times with Milli-Q water (18.2 MΩ·cm).

Bulk sediments were characterized for particle size distribution (wet-sieving at 64 and 106 μm), total metal concentrations (homogenized sediments were freeze dried and then subject to microwave assisted digestion following USEPA Method 3051A), and total organic carbon (Flash*Smart*™ elemental analyzer).

For dissolved metal analyses, 16 mL of the overlying waters were filtered (0.2 μm, nylon, Sartorius™) and divided into 4 aliquots (4 mL in each aliquot). One aliquot was acidified with concentrated HNO$_3$ (Puriss.p.a, Sigma-Aldrich) to pH < 2 and then stored at 4 °C before metal concentrations determination (referred to as dissolved metal concentrations). The three other aliquots were used to characterize colloidal metals by ultrafiltration-based fractionation techniques. The aliquots of filtered water samples were ultrafiltered using centrifugal filters (Millipore) with three different molecular weight cutoff values (3, 10 and 100 kDa). The ultrafiltrate was also acidified to pH < 2 and stored for metal concentrations determination. The combined filtration techniques enabled colloidal metal fractions to be described as [Me]$_{<3kDa}$, [Me]$_{3-10kDa}$, [Me]$_{10-100kDa}$, and [Me]$_{100kDa-0.2\mu m}$, as subfractions of dissolved metals (total <0.2 μm), where [Me] represents the concentrations of various metals.

DGT sediment probes were deployed for the determination of labile metal concentrations in porewaters and overlying water. The membrane filter, diffusive gel and the metal binding resin were purchased from DGT® Research Ltd and assembled into a self-manufactured plastic housing with a sampling window of 120 mm height × 18 mm width. Before deployment, the DGT probes were deoxygenated by bubbling nitrogen gas through 0.01 M NaNO$_3$ solution where they were submerged in overnight. The DGT probes were inserted vertically into sediment for 48 h, and then cleaned with Milli-Q water to remove attached sediment particles upon retrieval. The rectangular sampling window was sectioned into 0.5 cm intervals, and each slide was eluted in separate acid-washed vials in 1 mL of a 1 M HNO$_3$ solution for 24 h and then diluted for metal analyses. A single DGT sampler subject to the same treatment procedures but not deployed in the sediment was used as a control blank. The mass of metals accumulated in each DGT section was then converted to time integrated concentrations of each metal ([Me]$_{DGT}$) following the prescribed methods and using diffusional coefficients of metals in the literature (Wang et al., 2016; Zhang and Davison, 1995).

Sediment minicores were taken using a modified 100 mL plastic syringe (3.2 cm in diameter) with the end cut off to create an open cylinder. For porewater extraction, one minicore from each chamber was transferred to an anaerobic chamber (3% H$_2$ and 97% N$_2$), sectioned at 0.5 cm intervals and centrifuged at 7400 g for 10 min. The supernatant (porewater) was then filtered through a 0.2 μm filter and acidified to pH < 2 for metal analyses. For worm density calculation, the sediments in each of three minicores were wet sieved through a 64 μm nylon mesh, the number of worms retained on the mesh counted, and the worm density in each treatment determined by dividing the number with the area of the sediment core (8.04 cm^2).

The bivalves were recovered from each experiment and the percent survival determined. The surviving bivalves were depurated in clean RFW for a period of 2 days. The bivalves were then dissected, with the soft tissues freeze-dried, and digested in 1 mL concentrated HNO$_3$ at 80 °C for 12 h. Metal concentrations in 20 unexposed bivalves were also measured to determine the baseline (BL) concentrations.

Metal concentrations in overlying water, porewaters, sediment and biota digests, and acid extracts of DGTs were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800). Mn, Fe, Cu, Zn, Co, Cr and Ni were analyzed. ^{45}Sc and ^{72}Ge were used as internal standards to correct sample matrix effects and instrument drift. As part of quality control, repeat analyses were made on 5% of all samples. Certified reference material IAEA 158 (sediment) and SRM 1566b (oyster) were also subject to the same digestion and analytical procedures during the analysis of metal concentrations in sediment samples and bivalve tissue samples.

2.5. Modeling of metal effluxes

In a closed system, molecular diffusion and bioturbation both contribute to the release of metals into the overlying water (Aller, 2001). A mass conservation equation (1) relating these processes to the release of dissolved metals is:

$$Flux_{net} = Flux_{diff} + Flux_{bio} \tag{1}$$

where $Flux_{net}$ is the total net flux of metals into the overlying water, while $Flux_{diff}$ and $Flux_{bio}$ represent metal fluxes attributed to diffusion and bioturbation, respectively.

The total net fluxes were calculated using the changes in the dissolved metal concentrations within the total 4-L volume of recirculating overlying water and the area of the SWI:

$$Flux_{net} = \frac{V}{A} \frac{dC_{ow}(t)}{dt} \tag{2}$$

where t is time, $C_{ow}(t)$ the concentrations of dissolved metals in the

overlying water, A the area of the SWI, and V the volume of overlying water. $\frac{dC_{ow}(t)}{dt}$ was calculated by linear least-squares fitting of dissolved metal concentrations over successive 2-day periods (Xie et al., 2016).

The diffusive fluxes were quantified based on the Fick's first law of diffusion using the metal concentration profiles derived from DGT measurements over the last two days (Boudreau, 1997; Gaillard et al., 1986; Wang and Wang, 2017):

$$Flux_{diff} = -D_b \frac{\Delta C_{spw}}{\Delta z} \qquad (3)$$

where D_b is the bulk sediment diffusion coefficient and approximately equals $10^{-5} cm^2/s$ for all metals (Gaillard et al., 1986), C_{spw} is metal concentrations in the surficial porewater and z is the porewater depth. $\frac{\Delta C_{spw}}{\Delta z}$ represents the porewater metal concentration gradient near the SWI which was calculated using metal concentrations measured in the overlying water (0–0.5 cm above SWI) and porewater (0 to −1 cm below SWI).

The bioturbation induced metal effluxes $Flux_{bio}$ were quantified as the difference between the total net fluxes and the diffusive fluxes, as described below.

3. Results and discussions

3.1. Sediment characteristics and the density of worms

Sediments were silty and clayish in nature and contained on average 1.3% of organic carbon. Sediments were primarily composed of fine particles, with ~90% of particles passing through a <64 μm sieve. The sediments were severely contaminated with multiple metals, particularly Cu, Cr, Ni, and Zn (1900 ± 130, 690 ± 40, 340 ± 20, and 1050 ± 70 mg/kg dry sediment, respectively) (Table S1, Supporting Information). These metals were 5–30 times higher than the corresponding sediment quality guideline values (SQGVs) (Table S1) (Burton, 2002; Simpson and Batley, 2016).

Sediment minicores retrieved from the chambers also recovered worms at densities ranging from 10,000 to 15,000 worms/m² in the sediments, but were not statistically different between treatments (p > 0.05, paired *t*-test).

3.2. In situ measurement of metals in the porewater using DGT

Metal concentrations in the blank DGT were low for all metals except for zinc. The equivalent concentrations in the blank DGT were below the detection limits for Cr, Mn, Ni, and Cu, 0.036 ± 0.007 μg/L for cobalt, but 6.6 ± 0.9 μg/L for zinc. Metal concentrations derived from other DGT units were corrected for cobalt and zinc only by subtracting these values.

Porewater metal concentration profiles derived by DGT measurements in each treatment are shown in Fig. 1. The distribution, forms and mobilization of metals within the sediment bed are controlled by a series of diagenetic reactions (Van Cappellen and Gaillard, 1996). The [Mn]$_{DGT}$ and [Fe]$_{DGT}$ in porewater of all treatments followed typical diagenetic product profiles (Aller, 2014). [Mn]$_{DGT}$ at depths greater than 1.25 cm were substantially higher than those observed near the SWI, i.e. within the first centimeter and above the SWI, and consistent with release of dissolved manganese at depth while oxidation and precipitation of dissolved manganese occurred near the SWI. This resulted in steep gradients of dissolved manganese across the SWI and drove efflux of [Mn]$_{DGT}$ into the overlying water. Dissolved iron profiles were similar to manganese, but with the maximum concentrations located deeper relative to the dissolved manganese profiles. This was consistent

with the reported theoretical diagenetic reaction sequences, where thermodynamics dictates that manganese oxides are consumed before iron oxides as terminal electron acceptors for oxidation of organic carbon (Aller, 2014). Contrary to the [Mn]$_{DGT}$, which resulted in release across the SWI, [Fe]$_{DGT}$ was depleted within the first centimeter below the SWI, and therefore [Fe]$_{DGT}$ were not detected in the overlying water. The production and removal of dissolved iron in porewater also yielded sharp gradients of [Fe]$_{DGT}$ below the SWI, consistent with an upward flux of dissolved iron towards the surficial layer of sediment, where oxidation and precipitation occurred.

The presence of the bivalves greatly enhanced the release of manganese and iron to the porewater (LD and HD treatments, Fig. 1). The maximum concentrations of [Mn]$_{DGT}$ in the Ctrl treatment were 150 ± 10 μg/L whereas those in the LD and HD treatments were 210 ± 50 and 290 ± 50 μg/L, respectively. Similarly, the maximum [Fe]$_{DGT}$ for LD and HD were 1.6 ± 0.4 and 2.4 ± 0.4 times higher than the maximum [Fe]$_{DGT}$ of experiment Ctrl. This observation was consistent with the finding of Chen et al. (2016), in which the release of soluble and DGT-labile Fe(II) were also promoted when bivalves were present and they attributed this to the depletion of oxygen in surficial porewater as a result of bivalve respiration.

[Co]$_{DGT}$ and [Ni]$_{DGT}$ showed maxima from 0.75 to 1.25 cm below the SWI and gradually declined towards and across the SWI, reflecting upward efflux to the overlying water. The distribution of [Co]$_{DGT}$ and [Ni]$_{DGT}$ were highly correlated ($R^2 > 0.97$), suggesting that the release of cobalt and nickel in porewater shared similar biogeochemical processes.

Mobilization of zinc also occurred near the SWI, with the [Zn]$_{DGT}$ maximum also located ~ 1 cm below the SWI (Fig. 1e). Dissolved copper concentrations measured by DGTs were lower than 1.5 μg/L throughout the sediment depth of all three treatments (Fig. 1f). The [Cr]$_{DGT}$ concentrations increased slightly with increasing depth (Fig. 1g). In different environments chromium exists in two oxidation states — Cr$^{(III)}$ and Cr$^{(VI)}$, and the Chelex resin within the DGT probe exclusively accumulates the reduced Cr$^{(III)}$ species (Ernstberger et al., 2002). The increasing [Cr]$_{DGT}$ concentrations with increasing depth indicate that reduction and/or release of Cr$^{(III)}$ was occurring within deeper sediments.

3.3. Ex situ measurement of porewater metal concentrations

The broad features of metal concentrations in porewater obtained from the minicores (Fig. S3, Supporting Information) were similar to those obtained using the DGT samplers (Fig. 1). The most significant differences were the depths of the concentration maxima derived by the two methods, particularly in the case of Co, Ni, Zn, and Cu. While the [Me]$_{DGT}$ porewater profiles often displayed clear concentration gradients below the SWI, the minicore profiles could not provide such a high level of resolution in concentrations with depth. For the minicores, there was evidence of maximum concentrations of Co, Ni, Zn and Cu in the 0–0.5 cm depth range, but no clear peaks below the SWI. A plausible explanation for these discrepancies is artefacts associated with the coring and subsequent porewater extraction by centrifugation. As the sediment minicores were retrieved from the experimental system and transferred to the anaerobic chamber, metal concentration gradients near the SWI may disappear as upward effluxes ceased. Mixing of porewater solutes from different depths during porewater extraction may also contribute to the elimination of concentration gradients (Rathnayake et al., 2017).

The maximum porewater metal concentrations determined from the minicores were substantially higher than the metal concentrations in overlying waters (cf. the following section). This
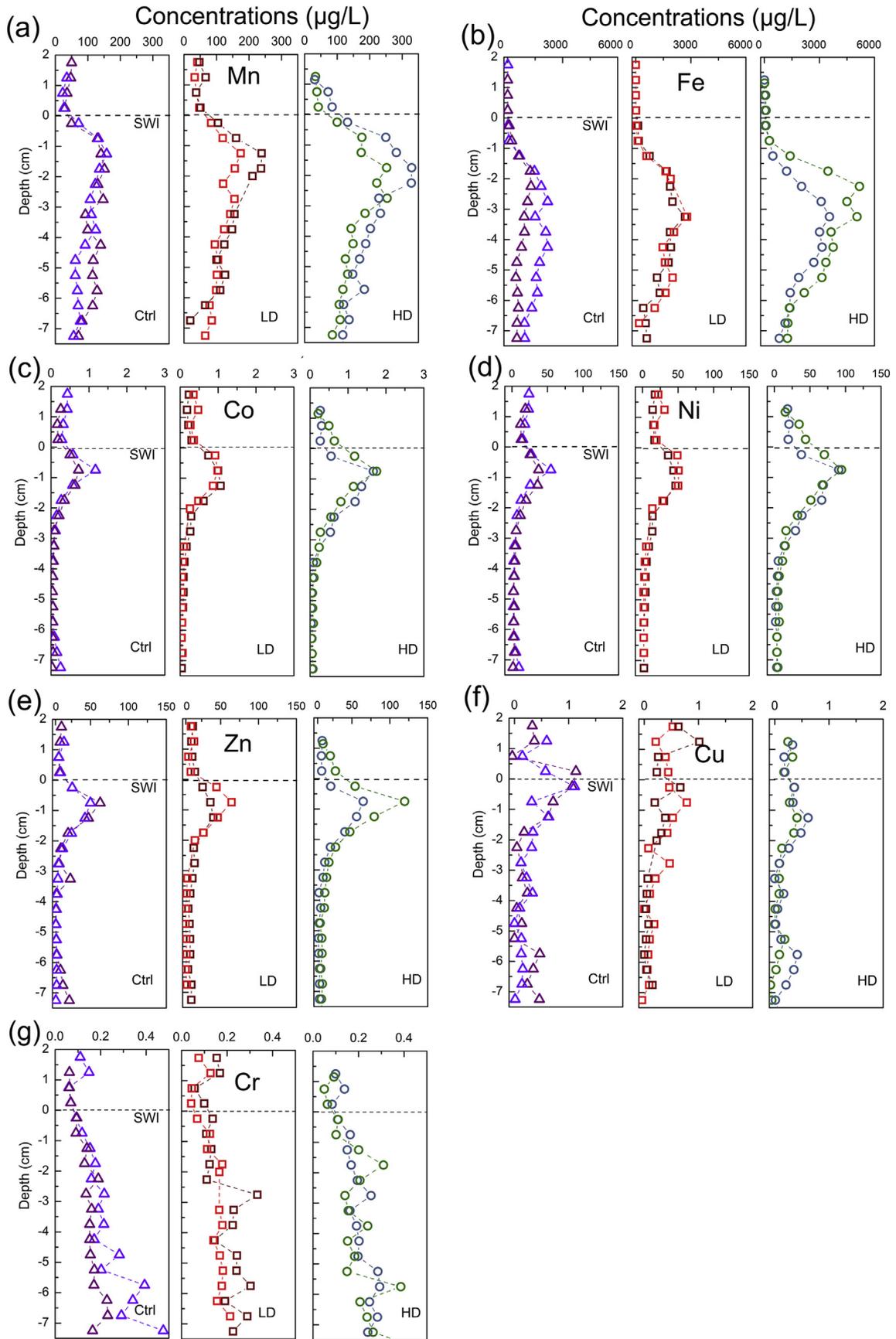
Fig. 1. Metal concentrations in porewater measured using DGT. The treatments with no, low and high densities of added bivalves are designated as Ctrl, LD and HD, respectively. The two series represent metal concentration profiles from duplicate experiments for each condition. The dashed lines (y = 0) represent the sediment water interface (SWI).

indicates the surficial porewater is a source of metals to the overlying water. It is rational to compare the maximum metal concentrations obtained from the minicores with those derived by DGT in terms of a R ratio (Harper et al., 1998; Martine et al., 2006; Wang and Wang, 2017). The R value is defined here as the ratio of the maximum metal concentrations derived by DGT to the maximum metal concentrations obtained from the minicores (Table S2). The average R values for the three treatments decreased in the order of Fe (0.66) > Zn (0.55) > Ni (0.50) > Co (0.46) > Mn (0.43) > Cu (0.20) > Cr (0.19). The differences in the R ratio reflect the degree that the different metals in the porewater are sustained as a result of mobilization/release from the sediments. The magnitude of the R ratios indicates that Fe, Zn, Ni, Co, and Mn in porewaters were resupplied (released from sediment particles) at considerably higher rates relative to copper and chromium.

3.4. Metals in the overlying water

The presence of the bivalves in the system strongly promoted the release of Mn, Co, Ni, and Zn into the overlying waters, but did not influence the release of copper and chromium. In the Ctrl treatment, dissolved manganese rapidly increased from 2.7 to 77 μg/L during the first two days and then gradually increased to 105 μg/L over the remaining 6 days. The presence of the bivalves greatly enhanced the release of manganese to the overlying water ($p < 0.05$, paired t-test). Over the 8-day experiment, dissolved manganese concentrations increased from 11 to 270 μg/L and from 2.4 to 340 μg/L for the LD and HD treatments, respectively. Release of dissolved cobalt showed similar trends as dissolved manganese. In the Ctrl treatment, dissolved cobalt concentrations increased from <0.1 to 0.7 μg/L during the first two days and then gradually approach 0.8 μg/L over the remaining 6 days. In LD and HD treatments, dissolved cobalt gradually increased from 0.1 to 2.5 μg/L and from <0.1 to 3.6 μg/L for LD and HD experiments, respectively. Strong correlations between dissolved manganese and cobalt were observed in all three treatments ($R^2 > 0.96$), suggesting release of manganese and cobalt were closely associated.

The concentrations of dissolved nickel gradually increased from 11 to 91, 180, and 210 μg/L for Ctrl, LD and HD treatments, respectively. Release of dissolved zinc in all three treatments showed a lag of 2–3 days (compared to the other metals) with limited release initially, followed by a more rapid release. The lag was likely caused by the sequestering of zinc in sediments by adsorption, owing to its higher affinity to hydrous iron oxides relative to other metals (nickel and cobalt) (Jeon et al., 2003; Tessier et al., 1985). The increasing rates in dissolved zinc concentrations were greater in the presence of the bivalves (i.e. LD and HD relative to Ctrl treatments) ($p < 0.05$, paired t-test).

Release of dissolved copper and chromium were not significantly different between all three experimental conditions ($p > 0.05$, paired t-test). Copper concentrations started from 0.8, 0.6 and 0.7 μg/L and gradually approached to 8.4, 8.0 and 6.2 μg/L for Ctrl, LD and HD treatments, respectively. Chromium concentrations remained at low concentrations, but also gradually increased, from <0.1 μg/L to 0.3, 0.3 and 0.4 μg/L for Ctrl, LD and HD treatments, respectively.

3.5. Metal fractionation in the overlying water

The ultrafiltration-based fractionation of metals revealed speciation of metals in the overlying waters. Overall, the dissolved concentrations of Mn, Co, Ni, Zn and Cr were primarily associated with fractions <10 kDa over the course of the experiment (>80%) (Fig. S4). This was consistent with previous studies that showed metals were primarily associated to small size aquatic colloids (<10 kDa) (Stolpe et al., 2010; Wang et al., 2017). Dissolved manganese and cobalt were strongly correlated in all size fractions ($R^2 > 0.9$), indicating association of manganese and cobalt when released from the sediments. The high correlation between manganese and cobalt is likely due to the catalytic oxidation reaction of Co(II) to Co(III) at the surface of manganese oxide, where precipitation of Co(III) occurred (Manceau et al., 1992). The proportion of manganese and cobalt smaller than 3 kDa for all three treatments increased for the first 2–3 days and remained high (80–90%) over the remaining 5–6 days of experiments. Ni, Zn and Cr were also abundant in the small size fractions (<3 kDa) throughout the experiments. While the presence of bivalves influenced the release of Mn, Co, Ni, and Zn into the overlying water (Fig. 2), the fractionation of these metals however remained unaffected ($p > 0.05$, paired t-test). Dissolved copper exhibited distinct size fractionation. $[Cu]_{<3kDa}$ primarily comprised 20–40% of the dissolved copper while the remaining proportions of dissolved copper were present in the larger size fractions. Distributions of copper in all size fractions were approximately constant throughout the experiments and also remained unvaried when the bivalves were present ($p > 0.05$, paired t-test). Collectively, the distribution of all metals in
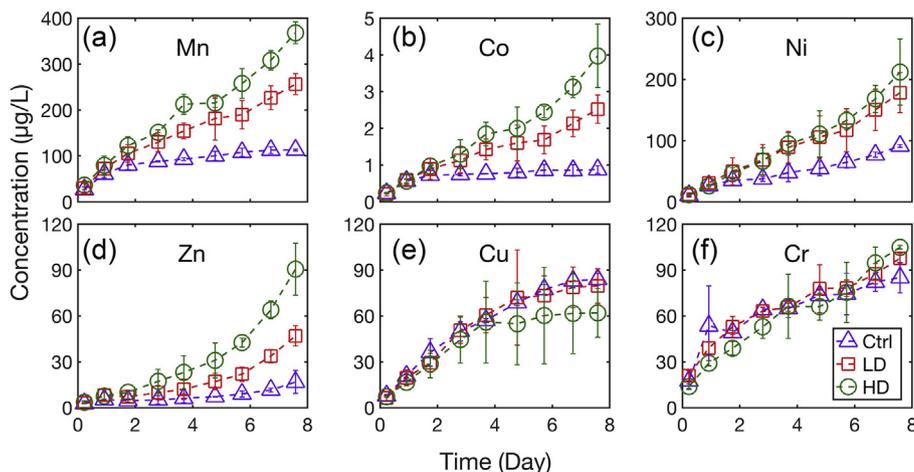

Fig. 2. Temporal change of dissolved metal concentrations in the overlying water. Iron was not detected in the overlying water. Error bars represent standard deviation from duplicate experiment results. The treatments with no, low and high densities of added bivalves are designated as Ctrl, LD and HD, respectively.

different size fractions may suggest that the additional bioturbation by the bivalves did not change the composition of these metals in the overlying water.

DGT samplers passively accumulate labile dissolved metals in the water, while some strong metal-ligand complexes are non-labile and large colloids are excluded by the polyacrylamide gel (Davison and Zhang, 1994). When deployed, the section of samplers above the SWI accumulated metals from the water and provided DGT-labile metal concentrations in the overlying water. Filtered samples (0.2 μm) from the overlying water collected concurrently during the deployment of DGT samplers also provided time-averaged metal concentrations in the overlying water (Supporting Information). The ratios between the DGT-labile metal concentrations and the time-averaged metal concentrations were defined as DGT extraction coefficients, which also partially revealed metal speciation in the overlying water. The DGT extraction coefficients were substantially higher for Mn, Co, Ni, Zn and Cr (from 0.50 to 0.93) relative to Cu (from 0.17 to 0.27) (Table S3, Supporting Information), suggesting a large fraction of copper was present in forms not available for accumulation by the DGT samplers. The size fractionation results of different metals in the overlying water may partially explain this (Fig. S4, Supporting Information). The small pore size of the polyacrylamide gel (2–5 nm, approximately equivalent to 2.4–50 kDa) may impede the transport of larger colloids through the diffusive gel of the DGT samplers (Davison and Zhang, 2012). Mn, Co, Ni, Zn and Cr were more abundant in the small size fraction (<3 kDa) relative to copper, resulting in a greater portion of these five metals being in forms that should diffuse freely through the diffusive gel and be retained by the binding resin.

3.6. Temporal variation of total net fluxes observed in the overlying water

Temporal variations of the total net fluxes of metals are shown in Fig. 3. Nearly all metal fluxes were positive, indicating upward release of all metals from the sediments. Effluxes of Mn, Co and Ni showed similar trends. In the Ctrl treatment, the effluxes initially decreased and then remained low. In the LD and HD treatments, the effluxes decreased initially, but then gradually increased. Effluxes in the LD and HD treatments were consistently higher than those in the Ctrl treatments, indicating presence of the bivalves promoted the release of Mn, Co and Ni from the sediments. Effluxes of zinc for all three treatments were similar and low initially, but the effluxes in LD and HD treatments substantially increased after day 5, suggesting enhanced release of zinc in presence of the bivalves. Effluxes of copper and chromium generally decreased with increasing time, however effluxes for the three treatments were not statistically different from each other ($p > 0.05$, paired t-test), suggesting that release of dissolved copper and chromium from the sediments were not affected in presence of the bivalves.

3.7. Metal fluxes attributed to diffusion and bioturbation

Metal fluxes determined at the end of the experiments (over the last two days) comprise (i) the diffusive fluxes derived from DGT-labile metal concentration profiles, and (ii) the total net fluxes quantified from metal concentrations in the overlying waters measured concurrently during the deployment of DGT samplers (refer to Supporting Information).

The diffusive fluxes were of similar magnitudes between treatments for all metals (Fig. 4, Table S3, Supporting Information), indicating consistency in the diffusive transport of metals near the SWI. The total net fluxes for all metals except for zinc were substantially higher than the diffusive fluxes (Table S3). Considering that the DGT samplers accumulate only the labile fraction of
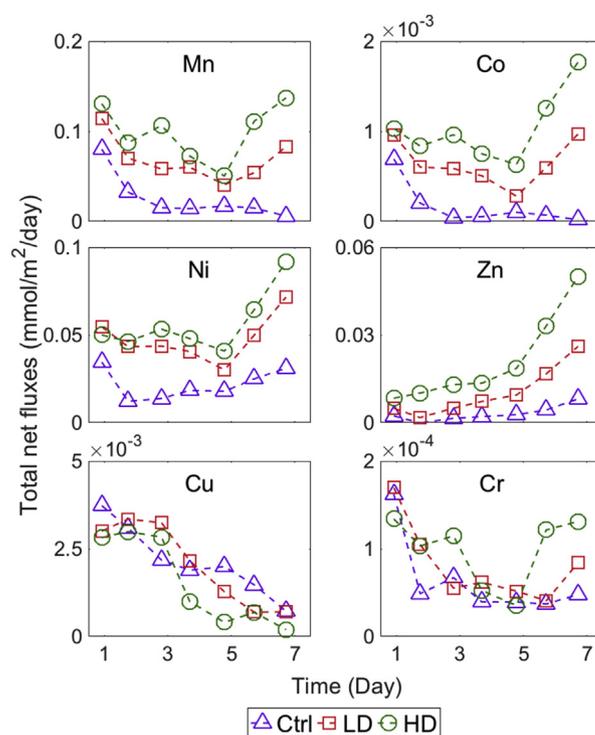

Fig. 3. Temporal variations of total net fluxes of metals into the overlying water. The treatments with no, low and high densities of added bivalves are designated as Ctrl, LD and HD, respectively.

dissolved metals, the total net fluxes were adjusted by multiplying by the DGT extraction coefficients (Table S4) (denoted as corrected total net fluxes) and compared with the diffusive fluxes (Fig. 4, Table S3). The bioturbation fluxes were calculated as the difference between these corrected total net fluxes and the diffusive fluxes. The bioturbation fluxes of Mn, Co, Ni, Cu and Cr were much higher than the corresponding diffusive fluxes, suggesting that bioturbation governed the release of these metals from the sediments in all treatments. Zinc fluxes were different, with the diffusive fluxes being higher than the corresponding total net fluxes. This yielded negative bioturbation fluxes for zinc, which suggest that zinc released in the porewater was likely being sequestered in the sediment close to the SWI, and this inhibited the total net flux to the overlying water.

Comparison between the diffusive effluxes with the bioturbation effluxes suggested that bioturbation was the dominant factor influencing the release of metals (Fig. 4). This was congruent with other studies that affirm bioturbation being an important process that controls the bioavailability and toxicity of metals from the sediments (Remaili et al., 2016; Remaili et al., 2018). While this comparison provided a snapshot of the relative contribution of metal fluxes induced by different processes, it is also worth noting that the total net fluxes exhibited strong temporal variations when both organisms were present (Fig. 3). Total net fluxes of Mn, Co, Ni and Zn over the last three days in LD and HD treatments (bivalves and worms) were substantially higher than those in the Ctrl treatment (worms only) (Fig. 3). In closed system where overlying water is not replaced, continuous exchange of metals will eventually result in equilibrium in metal concentrations between overlying water and surficial porewater (Simpson and Batley, 2016). The net release of metals then ceases and the net effluxes of metals approach to zero (e.g. the Ctrl treatment in Fig. 3). Presence of the bivalves in the system (LD and HD treatments) clearly caused
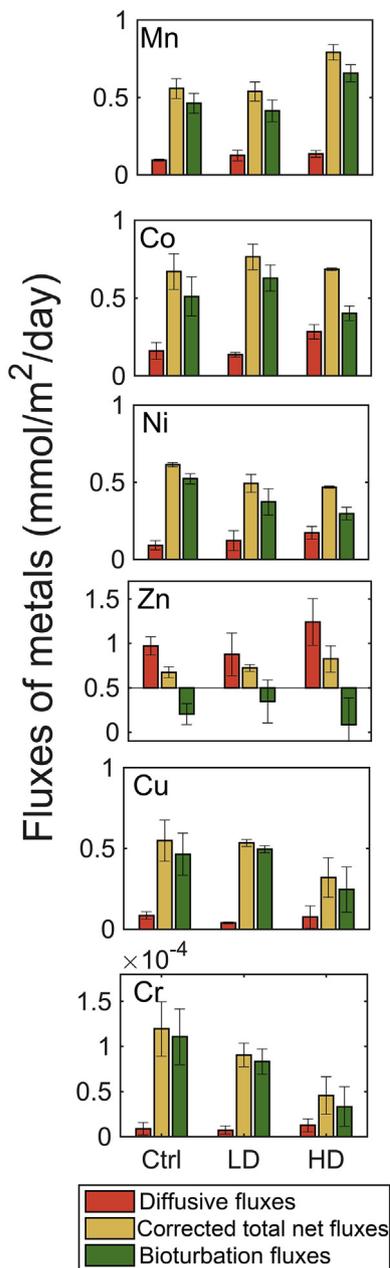
Fig. 4. Fluxes of metals attributed to different processes. Bioturbation fluxes were quantified as the difference between the corrected total net fluxes and the diffusive fluxes. Error bars represent standard deviation from duplicate experiment results. The treatments with no, low and high densities of added bivalves are designated as Ctrl, LD and HD, respectively.

additional release of metals (Mn, Co, Ni, Zn) and increased total net effluxes of these metals (Fig. 3). This suggest that bioturbation activities by the bivalves (burrowing and irrigation) produced additional sources of metals to the overlying water. The probable activities may be linked to the burrowing and irrigation activities of the bivalves. *C. fluminea* constructs burrows in anoxic sediments, and pedal feeds to harvest the buried organic matter using its cilia on the food (Vaughn and Hakenkamp, 2001). Exposure of the anoxic sediments to oxygenated water may liberate metals to the porewater within and in vicinity to the burrows. Ventilation of the burrows to supply oxygen and expel metabolites and (pseudo) faeces out of the burrows by the bivalves may promote the

liberation of metals deep in the sediments and facilitate the release of metals to the overlying water (Remaili et al., 2018).

3.8. Coupling between biogeochemical and biological processes controlling mobility of metals

Biogeochemical processes and bioturbation by large benthic organisms act in concert to control the release of metals from the sediment. The response of different metals to the same perturbation (by benthic organisms) under similar biogeochemical conditions were distinct. In experiments with the bivalve (LD and HD), the release rates of Mn, Co, Ni and Zn were initially higher, maintained for longer, and generally increased over the course of experiments (Fig. 2). This clearly indicated the release of these metals was substantially enhanced by the presence and increased density of the bivalves. In contrast, the release of copper and chromium were not affected by the presence of bivalves (Figs. 2 and 3). One possible explanation for the distinction in the release behavior among the various metals may be attributed to their affinities for the solid phase. Exchange of metals between overlying water and porewater is a dynamic process, and surficial porewater often serves as source of metals to the overlying water in low permeability sediments (Arsic et al., 2018; Packman and Brooks, 2001; Xie et al., 2015). Transport of metals across the SWI may result in decline of metal concentrations in surficial porewater, which is then supplied by metals associated with the sediment particles. The calculated R ratios are indicative of the extent to which metals in porewater are sustained (Harper et al., 1998). The magnitude of R values for copper and chromium were much lower than Zn, Ni, Co and Mn (Table S2, Supporting Information), suggesting that porewater concentrations of copper and chromium were not well sustained by resupply from the solid phase relative to other metals. And therefore, the release of copper and chromium to the overlying water may be kinetically controlled by the liberation of metals from sediment particles to the adjacent porewater, and the mobility and release of these two metals were affected to a much lesser extent when sediments were perturbed by bioturbation.

3.9. Implications for metal bioavailability and sediment quality assessment

Measurement of metal fluxes from sediments can be useful for describing the potential exposure of organisms to bioavailable metals, and therefore can provide a useful line of evidence for sediment quality assessments (Simpson and Batley, 2016). Typically, higher fluxes indicate greater bioavailability of metals and represent a greater risk of toxicity to benthic biota (Amato et al., 2014). An important component of sediment quality assessment programs is the preparation of a conceptual model that describes the key processes controlling the mobility and exposure of bioavailable contaminants which may result in toxicity to aquatic organisms. In the present study, by comparing the diffusive fluxes determined from DGT measurements and the total fluxes into the overlying water, we identified that bioturbation induced metal efflux represent a major constituent of the total net efflux from the sediments. In sediments occupied by organisms belonging to different functional groups (having different behaviors), fluxes can be variable with time. Short sampling periods for assessing fluxes will therefore result in great uncertainty and the assessment of contaminant mobility and the associated risk could be greatly biased.

We also observed that the effects of bioturbation on the release of metals were not uniform, but metal-dependent. Metals with higher affinities for the solid phase (copper and chromium with lower R values) were less mobile and their releases were affected to

a much lesser extent in presence of the bivalves relative to metals with lower affinities (Mn, Co, Ni and Zn with higher R values). Therefore, using R ratios to classify the mobility of different metals may be a feasible approach and this needs validation in future studies.

4. Conclusions

In the present study, the release of metals from contaminated sediments under the perturbation by aquatic organisms and similar biogeochemical conditions was investigated. Both biogeochemical processes and bioturbation act in concert to control the mobility of metals. Diagenetic reactions mobilized metals into porewaters which were then released across the SWI into overlying waters. Discrimination of fluxes from different processes revealed that bioturbation-induced metal effluxes were dominant relative to the molecular diffusion-induced effluxes. Presence of bioturbating organisms exerted complex effects on the release of different metals. The release of Mn, Co, Ni, and Zn were greatly enhanced when the bivalves were present; whereas the release of copper and chromium were lesser affected. This is possibly explained by the affinity of different metals to sediment particles. The total release was greater for metals whose porewater concentrations were sustained by resupply occurring through release from sediments. Temporal variabilities were also observed in the total net fluxes and were likely attributed to the ventilation behavior of the bivalves, which highlights the need to consider bioturbation when assessing the exposure and risks of adverse effect from contaminants in sediments.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.04.003.

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