Relationship between heavy metals and dissolved organic matter released from sediment by bioturbation/bioirrigation

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ABSTRACT

Organic matter (OM) is an important component of sediment. Bioturbation/bioirrigation can remobilize OM and heavy metals that were previously buried in the sediment. The remobilization of buried organic matter, thallium (Tl), cadmium (Cd), copper (Cu) and zinc (Zn) from sediment was studied in a laboratory experiment with three organisms: tubificid, chironomid larvae and loach. Results showed that bioturbation/bioirrigation promoted the release of dissolved organic matter (DOM) and dissolved Tl, Cd, Cu and Zn, but only dissolved Zn concentrations decreased with exposure time in overlying water. The presence of organisms altered the compositions of DOM released from sediment, considerably increasing the percentage of fulvic acid-like materials (FA) and humic acid-like materials (HA). In addition, bioturbation/bioirrigation accelerated the growth and reproduction of bacteria to enhance the proportion of soluble microbial byproduct-like materials (SMP). The DOM was divided into five regions in the three-dimensional excitation emission matrix (3D-EEM), and each part had different correlation with the dissolved heavy metal concentrations. Dissolved Cu had the best correlation with each of the DOM compositions, indicating that Cu in the sediment was in the organic-bound form. Furthermore, the organism type and heavy metal characteristics both played a role in influencing the remobilization of heavy metal.

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Introduction

Sediment is a natural reservoir of nutrients, organic compounds and various dissolved substances in aquatic ecosystems (Boehler et al., 2017; Miller et al., 2014; Skierszkan et al., 2013; Watmough, 2017; Woodruff et al., 1999; Yu et al., 2017; Zhou et al., 2017; Zhu et al., 2017). In the aquatic environment, heavy metals from natural and anthropogenic sources find their way into surface water and generally accumulate in sediment (Ciutat et al., 2005; Xiong et al., 2017; Zhao et al., 2017). In recent years, with development of the scale of mining and heavy metal smelting, pollution due to heavy metals has become a serious problem in the water environment (Singh and Kumar, 2017). In one example, the wastewater discharge from a Zn/Pb smelter caused a sudden spike in Tl pollution in the nearby waters (0.18–1.03 Tl μg/L) (NCNA, 2010). More than 10 poisoning events involving Tl have occurred in China since 1997 (Xiao et al., 2012). In addition, Cd, Cu and Zn are commonly occurring heavy metals. Cd and Zn mines are intermixed due to their similar chemical properties (Gu et al., 2013; Moore et al., 2011). Both Cu (Hopkin, 1989) and Zn

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(Christensen, 1995) are microelements needed for animal growth, but high accumulation of these metals is harmful to health. Organic matter (OM) and heavy metals coexist in sediment, and OM in sediment has been found to have important implications for heavy metal speciation, transport, and bioavailability (Bianchi, 2007; Blankson and Klerks, 2017; Dong et al., 2017). OM and heavy metal in sediment were found to combine into simple or mixed ligand complexes through adsorption or complexation, which affect their environmental behaviors in sediment (Drouillard et al., 1996; Szokan-Emilson et al., 2014; Wallschlager et al., 1998). Researchers found that decrease of Ni and Zn in the overlying water was more likely related to an association with the organic carbon in the sediment due to disturbance (Collins and Kinsela, 2010; Schroeder et al., 2017), while the association of metals with dissolved organic matter (DOM) increased significantly due to the loss of reactive Mn-oxide and Fe-oxyhydroxide sorption phases during reduction (Vink et al., 2010). However, research on the relationship between remobilization of OM and heavy metals is lacking.

Furthermore, the activities of benthic organisms have been found to influence the exchange of dissolved substances in sediment in different ways (Zhang et al., 2010). This includes the mediation of flux, which is due to direct interception by benthic organisms, such as the sediment particle re-suspension by the movement of the organisms, ingestion and biological sedimentation. Also, indirect effects of change on the physical properties of sediment are caused by building pipelines and depressions with bioturbation/bioirrigation, which also change the physical and chemical condition of water simultaneously (Graf and Rosenberg, 1997; Svensson, 1998). In addition, bioturbation/bioirrigation causes the transport of particulate matter in the highest redox reduction zones to enhance the oxidation and reduction for OM remineralization (Aller, 1994). Bioturbation/bioirrigation also could alter the speciation and distribution of heavy metals in the sediment to encourage their release. Several studies have demonstrated that bioturbation/bioirrigation has an effect on the transport of heavy metals across the interface of sediment and water (Blankson and Klerks, 2016, 2017; Brumbaugh et al., 2013; He et al., 2015, 2017; Men et al., 2016; Schaller, 2014).

The aim of this study was to investigate the effect of bioturbation/bioirrigation by different types of organisms on the transport of DOM and heavy metals from sediment into the overlying water. We studied the effect of different species, the molecular weight distribution of the OM and the correlation between these organic substances and concentrations of heavy metals in the overlying water respectively. Four experimental conditions were set up simultaneously in this paper: control (without organisms), with tubificid (Limnodrilus hoffmeisteri), with chironomid larvae (Chironomus plumosus larvae) and with loach (Misgurnus bipartitus).

1. Materials and methods

1.1. Preparation of contaminated sediments and aquariums

Sediment and water were collected from uncontaminated surface sediment (0–30 cm) in the Ming Tombs Reservoir in north China. The sediment was sieved with a mesh of 0.5 mm aperture to remove gravel, plants, organisms and other impurities. The percentage of sediment particle sizes below 60 μm, pH value and loss on ignition of the sediment was 85.7%, 7.6 and 7.9%, respectively. Then both the sediment and water were preserved after pretreatment (He et al., 2015). The sediment was spiked with TlNO₃, Cd(NO₃)₂·4H₂O, CuSO₄·5H₂O and ZnSO₄·7H₂O (AR) successively to obtain nominal Tl(III), Cd (II), Cu(II) and Zn(II) concentrations of 11.7 ± 0.3 mg/kg, 11.3 ± 1.4 mg/kg, 587.1 ± 5.2 mg/kg and 715.3 ± 8.8 mg/kg in the sediment on a dry weight basis, respectively. Before being added to the experimental units, the contaminated sediment was aged in a dark environment for 2 months. Five hundred grams of the contaminated sediment was placed in plastic aquaria (height 13.8 cm, diameter 10 cm), and 500 mL aerated reservoir water was used as the overlying water. The units were left to stand for 24 hr to settle sediment particles that were re-suspended when the overlying water was introduced. The three organisms were cultivated under the experimental conditions for one week. The tubificids were cultivated in pump tap water, chironomid larvae were in a wet container with changing water daily and loach were kept in an aerated water.

1.2. Experimental setup

A total of 16 aquaria were randomly assigned to one of four different treatments: without organisms for control, with tubificid, with chironomid larvae or with loach. The design included 4 parallel units in each treatment. Five hundred individuals of tubificid, 62 individuals of chironomid larvae, or 1 individual loach were introduced into each biological unit, respectively. All 16 units were placed in an artificial climate chamber (RXZ intelligent, Ningbo Jiangnan Instrument Factory). The temperature was maintained at 23°C, humidity remained at 50% and the daily period of light:dark was 16:8 hr throughout the entire experiment.

1.3. Sampling and analysis

Twenty milliliters of overlying water was sampled with a polypropylene syringe at days 1, 3, 5, and 7 after addition of animals, and filtered through a 0.45 μm mixed cellulose ester membrane filter (0.45 μm, d = 25 mm, Millipore, USA). Each sample was put into a brown glass bottle and placed in a dark environment at 4°C. The DOM concentration was detected by a total organic carbon analyzer (TOC-VPCH, Shimadzu, Japan). The composition of DOM was determined by three-dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy (F-4500, Hitachi, Japan). Heavy metal concentrations were detected by inductively coupled plasma mass spectrometry (ICP-MS, 7500a, Agilent, USA). The molecular weight distribution of DOM was characterized by the high-performance size exclusion chromatography (HPSEC) method, using a high-performance liquid chromatography system (Waters 1525, Waters, USA) coupled with a size exclusion chromatography column (Shodex Protein KW-802.5, Shoko, Japan). Samples were filtered through a 0.22 μm mixed cellulose ester membrane filter (0.22 μm, d = 25 mm, Millipore, USA) before analysis by HPSEC.
1.4. Data analysis

The data were prepared using Excel 2007. Statistical analyses were performed using Origin 9.0 and SPSS Base 15.0 software. Pearson correlation coefficients were determined between compositions of DOM and Tl, Cd, Cu and Zn concentrations in the overlying water. All samples were measured in triplicate. The method detection limits for the DOM and heavy metals were $\mu$g/L and ng/L. The ICP-MS was based on standard quality control procedures using internal standards (yttrium and indium).

2. Results

2.1. The concentration and molecular weight distribution of DOM

The concentrations of DOM in the overlying water are shown in Fig. 1a. During the exposure time, the DOM concentration increased slowly from 9.4 to 10.3 mg/L in the control group and from 13.5 to 16.2 mg/L in the tubificid group. At the beginning of exposure, the DOM concentration was 11.8 mg/L and increased to 14.4 mg/L on the 3rd day, then the concentration maintained a steady state in the chironomid larvae group. DOM concentrations ranged from 16.1 to 18.0 mg/L in the loach group. As shown in Fig. 1b, the molecular weight distributions of DOM in the overlying water were similar among the control, tubificid and chironomid larvae groups. In the early exposure, the DOM was mainly composed of micromolecules, and the molecular weight was $100–1000$ Da. After 5 days of exposure, the molecular weight of DOM was $1000–10,000$ Da. In the loach group, the DOM molecular weight was $1000–10,000$ Da on the third day of exposure, and later the DOM was dominated by macromolecules.

2.2. The composition of DOM

EEM results for the DOM in the overlying water are shown in Fig. 2. The DOM in the overlying water included abundant protein-like materials (APN I and APN II), soluble microbial byproduct-like materials (SMP), humic acid-like materials (HA), and a small amount of fulvic acid-like materials (FA) in the four treatments. The fluorescence regional integration (FRI) (Table 1) (Chen et al., 2003) showed that, at the end of the exposure, the FRI of APN I decreased 7%, while the FRI of APN II, SMP, FA and HA increased 34%, 41%, 71% and 73% in the control group, respectively. In the tubificid group, the FRI of APN I, APN II, SMP, FA and HA increased 49%, 82%, 49%, 164% and 149%, respectively. In the chironomid larvae group, the FRI of APN I, APN II, SMP, FA and HA increased 79%, 48%, 38%, 135% and 117%, respectively. In the loach group, the FRI of APN I, APN II, SMP, FA and HA increased 30%, 58%, 51%, 91% and 83%, respectively.

2.3. The concentrations of dissolved heavy metals

The concentrations of dissolved heavy metals in the overlying water are shown in Fig. 3. At the beginning of exposure, the dissolved Tl concentration was 4.3, 4.5, 4.4 and 6.2 $\mu$g/L in the control, tubificid, chironomid larvae and loach groups, respectively. Only the control group showed a decrease in the dissolved Tl concentration at the end of exposure. The dissolved Cd concentrations in the overlying water ranged from 1.3 to 1.9 $\mu$g/L, 1.4 to 2.5 $\mu$g/L, 1.6 to 2.5 $\mu$g/L and 1.8 to 2.1 $\mu$g/L in the control, tubificid, chironomid larvae and loach groups, respectively. The dissolved Cu concentrations reached a maximum on the 5th day at 41.0, 50.2, 53.0 and 44.0 $\mu$g/L in the control, tubificid, chironomid larvae and loach groups, respectively. The dissolved Zn concentrations were highest on the 1st day of the exposure. The values were 3.1, 3.6, 4.6 and 3.3 $\mu$g/L in the control, tubificid, chironomid larvae and loach groups, respectively. These values decreased with exposure time, reaching 1.4, 1.9, 1.2 and 2.1 $\mu$g/L at the end of exposure, respectively.

3. Discussion

The concentrations of DOM in the overlying water increased during the exposure time. These DOM mainly resulted from the photodegradation of phytoplankton (Vodacek et al., 1995), bacterial degradation (Nelson et al., 2004) and the cell leakage...
of plankton and planktonic bacteria (Henderson et al., 2008; Tzortziou et al., 2008). DOM concentrations in the biological groups were higher than in the control group. This may be because the material exchange may be enhanced significantly by bioturbation/bioirrigation compared to molecular diffusion (Benoit et al., 2009), the biological waste contained many DOM (Qin et al., 2010; Vanni, 2002), and the bioturbation/bioirrigation enhanced the introduction of O₂ to strengthen the heterotrophic processes that promoted the decomposition of OM in sediment (Gessner et al., 2010). The concentrations of heavy metals at the sediment–water interface were partly linked to the degradation of OM (Amato et al., 2016; Furrer and Wehrli, 1993), and the increased release of heavy metals by higher bioturbation/bioirrigation (in the loach group) may be attributed to the same reason (Amato et al., 2016). In addition, bioturbation/bioirrigation resulted in re-suspension of some sediment particles (Atkinson et al., 2007) to release dissolved Tl, Cd, Cu and Zn into overlying water, as well as changes in the particle size of the suspended sediment, affecting DOM release (Dong et al., 2016). The adsorbed DOM on the sediment particles also released due to the oscillation of redox, which was magnified by bioturbation/bioirrigation in the sediment (Skoog and Arias-Esquivel, 2009; Valdes et al., 2009). However, the characteristics of heavy metals also affected their release from sediment. Tl(I) had a strong tendency to easily diffuse from the sediment to the overlying water (He et al., 2015). Due to the stable forms of Cd in the sediment, its concentrations were lower than those of Tl in the overlying water. Only the concentrations of dissolved Zn declined with the exposure time. Apart from the Fe/Mn oxides and metal sulfides adsorbing and coprecipitating with dissolved Zn to remove it from the overlying water (Chapman et al., 1998; Goldberg, 1954; Lewandowski and Hupfer, 2005; Luan and Vadas, 2015; Tankere-Muller et al., 2007), there was also association with the organic matter (Collins and Kinsela, 2010; Schroeder et al., 2017). Organic ions acted as ligands for the metals, which reduced the concentration of free metal cations (Sanchez-Marin et al., 2007), so the increase of DOM in the overlying water contributed to part of the decrease in the dissolved Zn concentration. The result was consistent with a previous study (He et al., 2017).
Furthermore, bioturbation/bioirrigation by different types of organisms also affected the release of DOM and heavy metals. Tubificid and chironomid larvae dug into the sediment as a consequence of building channels in the sediment, and promoted the exchange of dissolved materials between pores and overlying water. These activities increased the speed and amplitude of the decrease in the redox potential through respiration and aerobic decomposition of their metabolites; as a result, the flux of DOM between sediment and water increased (Fanjul et al., 2015), and also changed the forms of heavy metals in the sediment and enhanced their migration to the water (Calmano et al., 1993; Du Laing et al., 2009; Hare et al., 1994; Huerta-Diaz et al., 1998; Peterson et al., 1996; Qiao, 2011; Zoumis et al., 2001). In more detail, tubificids could rapidly rework the deposits (Anschutz et al., 2012) and through selective ingestion of the organic materials in sediment (Ciutat et al., 2006; Rhoads, 1974; Wu, 2010) to influence the release of DOM, and they have been shown to enhance OM processing (Mermillod-Blondin et al., 2000). Consistent with a previous study, the bioturbation/bioirrigation by chironomid larvae accelerated the release of DOM and heavy metals from sediment to water (Schaller, 2014). The burrowing activities of chironomid larvae tripled the oxygen uptake of sediment, to promote the decomposition and mineralization of OM in surface sediments (Lagauzere et al., 2011). Additionally, the feeding activities of the larvae caused a net downward transport of carbon (Adámek and Maršálek, 2012). In the absence of large organisms, molecular oxygen permeated only a few millimeters into sediment (Revsbech et al., 1980); however, in the presence of loach, the material exchange between the

| Table 1 – EEM FRI of organic matter in the overlying water (unit: mg/L). |
|---------------------------------|-----|-----|-----|-----|-----|
| Exposure time (day) | APN I | APN II | SMP | FA | HA |
| Control | 1 | 0.85 | 0.92 | 2.18 | 1.12 | 5.16 |
| | 3 | 0.74 | 1.15 | 2.58 | 1.55 | 7.00 |
| | 5 | 0.80 | 1.21 | 2.78 | 1.70 | 7.69 |
| | 7 | 0.71 | 1.11 | 2.75 | 1.71 | 8.00 |
| Tubificid | 1 | 0.96 | 1.09 | 2.22 | 1.01 | 4.11 |
| | 3 | 1.29 | 1.66 | 3.06 | 1.73 | 7.31 |
| | 5 | 1.87 | 2.04 | 3.18 | 2.13 | 8.13 |
| | 7 | 1.34 | 1.84 | 3.06 | 2.46 | 9.44 |
| Chironomid larvae | 1 | 0.87 | 1.42 | 2.46 | 1.17 | 4.91 |
| | 3 | 1.24 | 1.71 | 3.31 | 2.16 | 9.38 |
| | 5 | 0.76 | 1.21 | 2.59 | 1.91 | 8.64 |
| | 7 | 1.16 | 1.57 | 2.53 | 2.06 | 7.96 |
| Loach | 1 | 1.05 | 1.25 | 2.81 | 1.51 | 6.83 |
| | 3 | 1.02 | 1.26 | 2.72 | 1.56 | 6.89 |
| | 5 | 0.89 | 1.25 | 2.69 | 1.71 | 7.69 |
| | 7 | 1.09 | 1.58 | 3.38 | 2.30 | 9.97 |

EEM: excitation emission matrix; FRI: fluorescence regional integration; APN I: aromatic protein I; APN II: aromatic protein II; SMP: soluble microbial byproduct-like materials; FA: fulvic acid-like materials; HA: humic acid-like materials.

![Fig. 3 – The concentrations of dissolved Tl, Cd, Cu and Zn in the overlying water during the exposure time (p < 0.05). Control, without organisms; Tubificid, presence of tubificid; Chironomid larvae, presence of chironomid larvae; Loach, presence of loach.](image-url)
surface sediments and the overlying water was rapidly balanced with their strong activities, so the concentration of DOM was basically in equilibrium in the loach group. This would explain the release of large-molecular-weight OM to the overlying water by the bioturbation/bioirrigation of loach.

During the exposure, the five EEM regions of DOM increased, especially those corresponding to the FA and HA. The increase of SMP suggested that the presence of organisms also stimulated the growth and reproduction of bacteria. The bioturbation/bioirrigation by tubificid substantially influenced major microbial-driven biogeochemical reactions in sediment (Lagauzere et al., 2014), as did the chironomid larvae and loach. Although some researchers found that Cu and Zn had poor affinity for organic carbon because of their higher deposition patterns in riverine aquatic ecosystem (Croot, 2003). The present study demonstrated that the dissolved Cu was mainly in organic-bound forms (Du Laing et al., 2009), which was supported by the correlation between the dissolved heavy metal concentrations and FRI of DOM in the five regions. In the control group, the FRI of APN II, SMP, FA and HA had good correlation with the dissolved Cu concentrations, and the dissolved Zn concentrations had good correlation with dissolved Tl and Cd concentrations. In the chironomid larvae group, however, the FRI of APN II, SMP, FA and HA had good correlation with dissolved Tl and Cu concentrations, and the dissolved Zn concentrations were significantly negatively correlated to the FRI of FA and HA. In the loach group, the FRI of APN II, SMP, FA and HA was only correlated to dissolved Cu concentrations (Table 2).

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### 4. Conclusions

Bioturbation/bioirrigation could accelerate the DOM release from sediment to overlying water, and the DOM was mainly composed of HA and FA. The composition of DOM changed with bioturbation/bioirrigation exposure time, such as the increase of SMP, which was the result of the boom of bacterial growth and propagation by bioturbation/bioirrigation. The release of DOM was influenced by the bioturbation/bioirrigation of different organism types. Furthermore, the DOM gradually became dominated by macromolecules, especially in the loach group. The types of organisms affected the bioturbation/bioirrigation results regarding the heavy metals. Tubificid increased the dissolved Tl, Cd and Cu release to overlying water, chironomid larvae increased Tl and Cu, and loach Tl, Cu and Zn.

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| Table 2 – The correlation between heavy metals concentrations and EEM FRI of organic matter in the overlying water. |
|--------|--------|--------|--------|--------|
|        |        |        |        |        |
| Control | Tl     | 0.0636 | 0.1555 | 0.0244 | 0.0401 |
|         | Cd     | −0.0254| 0.4870 | 0.7196 | 0.4968 |
|         | Cu     | 0.0114 | 0.7348 | 0.7255 | 0.8345 |
|         | Zn     | 0.2392 | 0.0281 | −0.082 | −0.2939 |
|         | Tl     | 0.6940 | 0.7926 | 0.8131 | 0.7887 |
|         | Cd     | 0.7343 | 0.8772 | 0.9199 | 0.8956 |
|         | Cu     | 0.7185 | 0.8582 | 0.7711 | 0.8771 |
|         | Zn     | −0.1005| −0.2353| −0.1555| −0.4710 |
| Tubificid | Tl    | 0.2943 | 0.2859 | 0.6740 | 0.8348 |
|          | Cd     | −0.2001| 0.2525 | 0.2450 | 0.1875 |
|          | Cu     | 0.2460 | 0.1624 | 0.6611 | 0.7690 |
|          | Zn     | −0.1753| −0.4330| −0.4705| 0.7501 |
| Chironomid larvae | Tl | 0.2111 | 0.1985 | 0.4183 | 0.2057 |
|           | Cd     | −0.1535| −0.1559| 0.1472 | −0.1194 |
|           | Cu     | 0.4120 | 0.7606 | 0.8923 | 0.7916 |
|           | Zn     | 0.2017 | −0.3980| −0.3243| −0.4779 |

* p < 0.05.
** p < 0.01.


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