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Dissolved oxygen drives the environmental behavior of heavy metals in coastal sediments

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Abstract In this study, the impacts of dissolved oxygen (DO) on dynamics concentrations of heavy metals (Cu, Cd, Cr, and Pb) from estuary sediments were investigated in a 49-day laboratory simulation. The exchange flux method, Bureau Communautaire de Référence (BCR) sequential extraction procedure, and risk assessment code (RAC) were used to analyze the behavior of heavy metals. The results indicated that oxic environments promoted the concentrations of Cu and Cd in overlying water compared to the anoxic environments. The exchange fluxes showed that the diffusion of Cu, Cd, Cr, and Pb from sediments was the predominant process in the first 9 days, and a metastable equilibrium state was gradually reached in the later period under anoxic conditions. However, oxic conditions extended the time required to reach metastable equilibrium for Cu over the sediment–water (overlying water) interface (SWI). Although the reducible fractions of Cu, Cd, and Pb accounted for a large proportion of their total levels, the release ability of Cu, Cd, and Pb was limited by the high content of sulfide under anoxic conditions. The RAC values indicated that anoxic environments increased the proportion of acid-soluble fraction. The information obtained from this study highlights the potential risk for re-release of heavy metal from sediments under different redox conditions.

Keywords Sediments · Heavy metals · Dissolved oxygen · Exchange fluxes

Introduction

Heavy metal contamination has aroused increasingly serious concern worldwide since heavy metals are highly biotoxic and persistent and easily accumulate in the food chain (Eren et al., 2021; Ji et al., 2019). Heavy metals are directly or indirectly discharged into the water column through surface runoff and atmospheric deposition (Villen-Guzman et al., 2021). Most heavy metals discharged into the water column are associated with suspended particle matter (approximately 85%) and eventually accumulate in sediments (Chou et al., 2018). As the sink of various pollutants in the water column, sediments play a crucial role in transporting and accumulating potentially toxic and harmful pollutants (Joksimovic et al., 2020). Due to

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the change in physicochemical properties over the sediment–water (overlying water) interface (SWI), heavy metals accumulated in sediments can be released into overlying water, further deteriorating the water quality. Sediments, therefore, serve as both sinks and potential sources of heavy metals in the water environment (Li et al., 2019).

The continuous discharge of various pollutants, especially organic pollutants and nutrients, into estuaries may create a long-term reduced state in estuarine areas (Madadi et al., 2021). Redox and pH are considered to be significant factors affecting re-released the desorption of heavy metals from sediments (Yuan et al., 2020). Variations in dissolved oxygen (DO) may strongly affect metal fractionation and mobility. Dissolved heavy metals are easily absorbed by aquatic organisms and then have the potential to transfer to higher trophic levels via food chain. Although studies on the mobility of heavy metals under oxic and anoxic envionments have been reported (Madadi et al., 2021; Shaheen et al., 2017), different trends for heavy metals have been observed to be related to differences in hydrochemistry and sediment properties. Madadi et al. (2021) showed that heavy metals (Cr and Cu, etc.) had high mobility under anoxic conditions. Shaheen et al. (2017) found that anoxic conditions were conducive to the release of Zn, while oxic conditions were conducive to the release of Cu. Hence, there is no uniform rule governing the behavior of heavy metals under varied redox conditions, which emphasizes the necessity of investigating the variation in redox conditions in different environments. Furthermore, previous studies on heavy metals in aquatic environments have mainly concentrated on the analysis of total contents and fractions. However, the adsorption/desorption of heavy metals over the SWI is still unclear and is of great significance for evaluating aquatic environment under different redox conditions. Additionally, both ex situ remediation and in situ remediation directly or inadvertently expose sediments to oxygenated environments, inevitably changing the binding pattern of heavy metals in sediments and releasing them into the overlying water. Therefore, it is crucial to predict the mobility and bioavailability of heavy metals in estuarine sediments under different DO level of overlying water to guide further environmental management.

In a laboratory study, simulated oxic and anoxic environments were used to assess the release of Cu, Cr, Cd, and Pb and to investigate the mechanisms responsible for their behavior. Specifically, the aims of this study were (1) to evaluate the variations in the release mechanisms of Cu, Pb, Cd, and Cr under oxic and anoxic environments for estuary sediments, (2) to determinate the changes of metals in the geochemical fractions, and (3) to analyze the ecological risk posed by heavy metals after being submitted to oxic and anoxic environments.

Materials and methods

Sediment sampling

Surface sediments (0–10 cm) were sampled in the estuary of the Guangdang River (Yantai, China) (Fig. 1). The Guangdang River, which originates from Fenghuang Lake, flows northeast into the Yellow Sea. The Guangdang River receives domestic sewage and industrial wastewater, resulting in serious heavy metal pollution (Jiang et al., 2021). After sampling, large stones and other debris were removed from the samples, which were then placed in polyethylene plastic bags. In the laboratory, the sediment was carefully homogenized under the protection of N_2 and then stored in a 4 °C. Part of the sediment was freeze-dried and then passed through a 100-mesh nylon sieve to determine the pH, particle size, total organic carbon (TOC), and organic matter (OM) and other basic physicochemical properties of the raw sediments. The detailed physicochemical properties determination methods of the raw sediments are presented in Text S1 of supplementary information (SI) and the results are presented in Table S1.

Experimental setup

In the laboratory, 49-day incubation experiment was conducted at room temperature. 500 g (wet weight) of sediments was added to a reactor (1.1-L plastic bottle, 20 cm × 8.5 cm), followed by 600 g of artificial seawater. The composition of the artificial seawater was based on Shene et al. (2016). Detailed configurations are provided in Table S2. By adding deionized water to dilute, the salinity of artificial seawater was maintained at 25.4 PSU (the salinity of the overlying water at the sampling site). In this

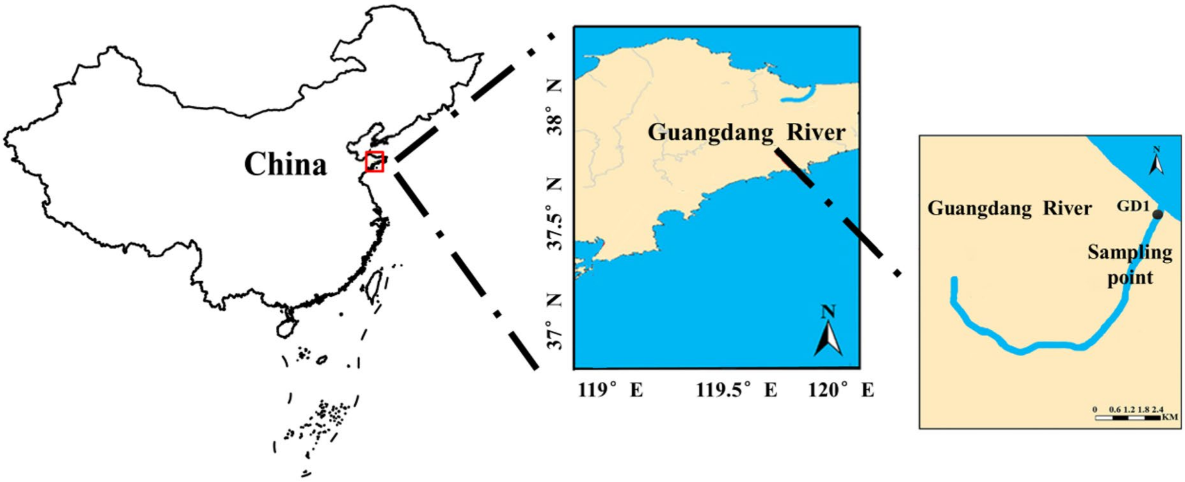

Fig. 1 Sampling location in the study area

work, oxic and anoxic environments were created by adding N_2 to decrease the DO level or adding O_2 to increase DO level. The experimental device is provided in Fig. 2. According to previously published studies (Chen et al., 2021; Li et al., 2019, 2013), the DO levels in the reactors were maintained at about 10–12 mg·L^{-1} and 1–2 mg·L^{-1} using an intermittent aeration device throughout the incubation period. By adjusting the size of the aeration airflow to maintain, the DO level but did not disturb the sediments. The two treatments were named as oxic treatments and anoxic treatments, respectively. When the DO in oxic treatments and anoxic treatments reached the desired concentrations, the incubation time was recorded as day 0. During the incubation period, the overlying water was gently mixed once a day to prevent stratification. Two replicates were carried out for each treatment in the incubation experiments.

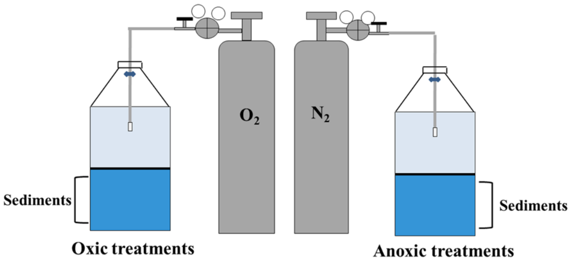

Fig. 2 Diagram of the experimental setup

Sampling and analysis

At the 8 scheduled time points (1, 3, 5, 9, 13, 21, 33, and 49 days), 2 mL of the overlying water in the reactors was collected. The collected water samples were filtered through a 0.45-μm filter, acidified (pH$<$2), and then analyzed for dissolved heavy metals using inductively coupled plasma mass spectrometry (ICP-MS, Optima 7000 DV, Perkin Elmer, USA). The pH, DO, and redox potential (Eh) of the overlying water in the reactors were also determined at each sampling time. pH was measured using a pH meter (FE28, Mettler Toledo, Switzerland) (pH range: 0–14; Reference system: Ag/AgCl). DO was determined by a portable dissolved oxygen analyzer (JPB-607A, REX, China) (DO range: 0.0–20.0 mg·L^{-1}). Eh was determined by an oxidation–reduction potential analyzer (Eh30, Twinno, China). Additionally, the exchange fluxes over the SWI were calculated by a previously reported approach (Gillan et al., 2012; Liu et al., 2019). The detailed calculation information is provided in Text S1. The fluxes are given in μmol m^{-2} day^{-1}.

Chemical analysis of sediments after incubation

The pH, AVS, and TOC of the sediments were determined after the incubation experiment. AVS were determined by an improved cold diffusion method (Sheng et al., 2015). Detailed determination methods are provided in Text S1.

BCR sequential extraction procedure

In this work, a modified Bureau Communautaire de Référence (BCR) sequential extraction procedure was applied to measure the heavy metal fractions in sediments (Guillen et al., 2012). The detailed extraction procedure is presented in Table S3. The heavy metals in sediments were classified into four parts: the acid-soluble fraction (F1), the reducible fraction (F2), the oxidizable fraction (F3), and the residual fraction (F4). The sediment standard reference materials GBW 40,376 and GBW 07,311 (GSD-11) were used for quality assurance in the analysis of the total concentration and fraction of heavy metals. The recoveries of Cu were 82–98%. The recoveries of Cd were 104–105%. The recoveries of Cr were 93–109%. The recoveries of Pb were 95–107%. The relative deviations were < 3%.

Risk assessment code

Acid-soluble heavy metals (F1) are known to be more bioavailable and pose greater health risks than the other fractions. The risk assessment code (RAC), based on the ratio of F1 to the total heavy metal content, has become a crucial metric for assessing the ecotoxicity of heavy metals in sediments (Shaaban et al., 2021). A RAC of 1% or less represents no risk, low risk ranges from 1–10%, medium risk ranges from 11–30%, high risk ranges from 31–50%, and extremely high risk ranges from over 50%.

Results and discussion

Physicochemical properties of the raw sediments

Generally, the properties of sediments are critical determinants of the environmental behavior and bioavailability of heavy metals (Liu et al., 2020). The basic characteristics of the sediments are displayed in Table S1. The grain size of the raw sediments was mainly sand (58.92%), followed by silt and clay. The organic matter (OM) content was 9.24%. Studies have shown that sediments with high OM showed very high microbial activities (Schaller et al., 2011). Table 1 compares the mean concentrations of heavy metals (Pb, Cu, Cr, and Cd) in the raw sediments with those from other regions of the world. From Table 1, the Cu, Cr, Cd, and Pb levels in this study area were higher compared to those in other coastal sediments. Additionally, the content of Cu and Cd in the raw sediments was between class I and class II of The Marine Sediment Quality Standard (GB 18,668–2002) (Table S4). The contents of Pb and Cr in the raw sediments were below of the class I. The above results indicated the severity of heavy metal contamination in the sampled sediments and the necessity of a secondary pollution risk assessment.

Changes of pH, AVS, and TOC in sediments after incubation

After incubation, the pH, AVS, and TOC of the sediments in each treatment are displayed in Fig. 3. The pH was 7.7 in oxic treatments and 8.12 in anoxic treatments. The AVS decreased from 50.50 to 22.70 $\mu mol \cdot g^{-1}$ in oxic treatments but increased in anoxic treatments, with a maximum of 55.97 $\mu mol \cdot g^{-1}$. Moreover, the TOC dropped from 3.74 (GD1) to 3.44% and 3.51% in the case of oxic and anoxic treatments, respectively.

The pH of sediments has an important effect on the mobility of heavy metals (Liu et al., 2021a, b). Compared to the control, pH decreased under both oxic and anoxic treatments, but pH was much lower in oxic treatments. Various oxidation reactions, such as sulfide oxidation, produced protons (H^+), causing a low pH (Miao et al., 2006). Additionally, AVS mainly consists

Table 1 Comparison of Cu, Cd, Cr, and Pb in the studied areas with other estuaries sediments

	Cu	Cd	Cr	Pb	Reference
Present study (mean value)	85.35	1.53	76.97	39.24	
Meghna River, Bangladesh	6.22	0.28	10.59	12.48	(Siddique et al., 2021)
JieHe, China	10.57	0.33	–	14.05	(Liu et al., 2020)
Haizhou Bay, China	14.187	0.08	43.6	21.73	(Liu et al., 2021a, b)
Jiaozhou Bay, China	29.8	0.334	77.4	21	(Liang et al., 2018)
Yangtze River Estuary, China	24.3	0.25	84.7	21	(He et al., 2019)

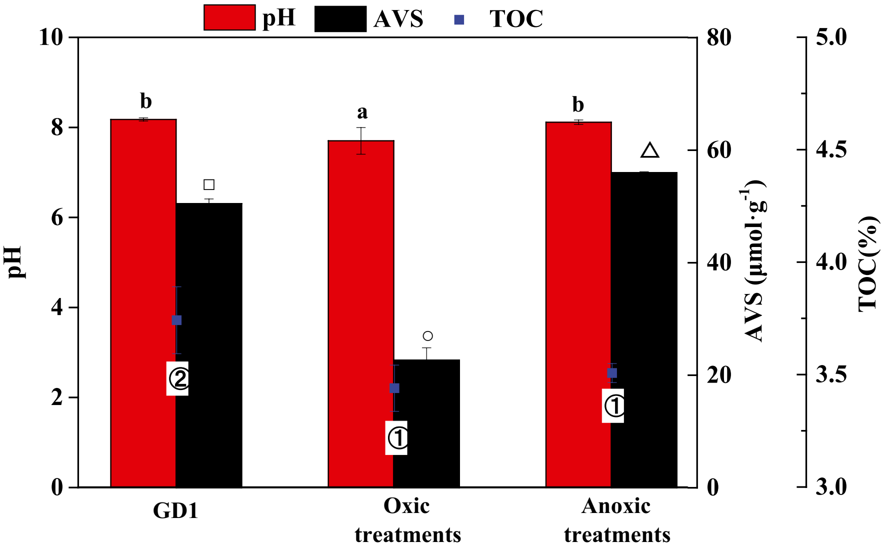

Fig. 3 The pH, acid volatile sulfide (AVS), and total organic carbon (TOC) of sediments after incubation (GD1 represents pre-incubation sediments) (different letters or symbols (**a** and **b** for pH, □, ○, and △ for AVS, and ① and ② for TOC) on the bars indicated significant differences among groups ($P < 0.05$))

of iron sulfide (FeS), which plays an important role in heavy metal adsorption (Rickard & Morse, 2005). The AVS in the raw sediments reached 50.50 μmol·g^{-1}, far exceeding that in river sediments in other areas (Jiang et al., 2021; Pignotti et al., 2018), indicating that the sediments had been in a reduced environment for long periods. The oxic environments may adverse to the activity of anoxic sulfate-reducing bacteria but facilitate the activity of nitrate-reducing and sulfide-oxidizing bacteria, which can oxidize sulfur compounds through nitric acid reduction (Kang et al., 2019) Under anoxic conditions, the activity of sulfate-reducing bacteria may increase, using sulfates as electron acceptors to decompose OM and produce sulfides. Therefore, the content of AVS decreased in oxic treatments but increased in anoxic treatments. TOC serves a crucial function in controlling the distribution of heavy metals due to its large surface-to-volume ratio (Yao et al., 2021). Specifically, humus in organic carbon has strong adsorption and chelation of heavy metals (Ranjbar Jafarabadi et al., 2020). Although TOC decreased under both oxic and anoxic treatments, the former decreased more. Totally, the changes in physicochemical properties of sediments in oxic treatments were conducive to the release of heavy metals.

pH, DO, and Eh variations in the overlying water

The pH, DO, and Eh in the overlying water during the incubation experiment are illustrated in Fig. 4. The pH values in oxic treatments reached the peak values of 8.05 at day 5. Then, the pH decreased in oxic treatments but continuously increased in anoxic treatments. The DO was slightly unstable during the incubation period. The DO values in oxic treatments and anoxic treatments remained at 0.90–1.80 and 9.95–12.40 mg·L^{-1}, respectively. A downward trend in Eh from −118 to −252 mV was noticeable in anoxic treatments while an increase trend from 38 to 194 mV in oxic treatments.

Overall, pH of the overlying water decreased in oxic treatments and increased in anoxic treatments, which was consistent with the change of pH in the sediments. The reducing environment in anoxic treatments was conducive to the reduction of species such NO_3^- and Fe^{3+}. Studies have found that the reduction of NO_3^-, SO_4^{2-}, and Fe^{3+} requires the consumption of H^+, which may result in a higher pH (Madadi et al., 2021). Additionally, the supply of O_2 in oxic treatments achieved oxidizing conditions and resulted in higher Eh and DO in the overlying water. On the contrary, the input of N_2 in anoxic treatments reached a reduction condition with low Eh and DO.

Dynamic concentrations of heavy metals in the overlying water

The dynamic concentrations of Cu, Cd, Cr, and Pb in the overlying water are presented in Fig. 5. Totally, the peak concentrations of Cu, Cd, Cr, and Pb in oxic treatments were higher than that in anoxic treatments.

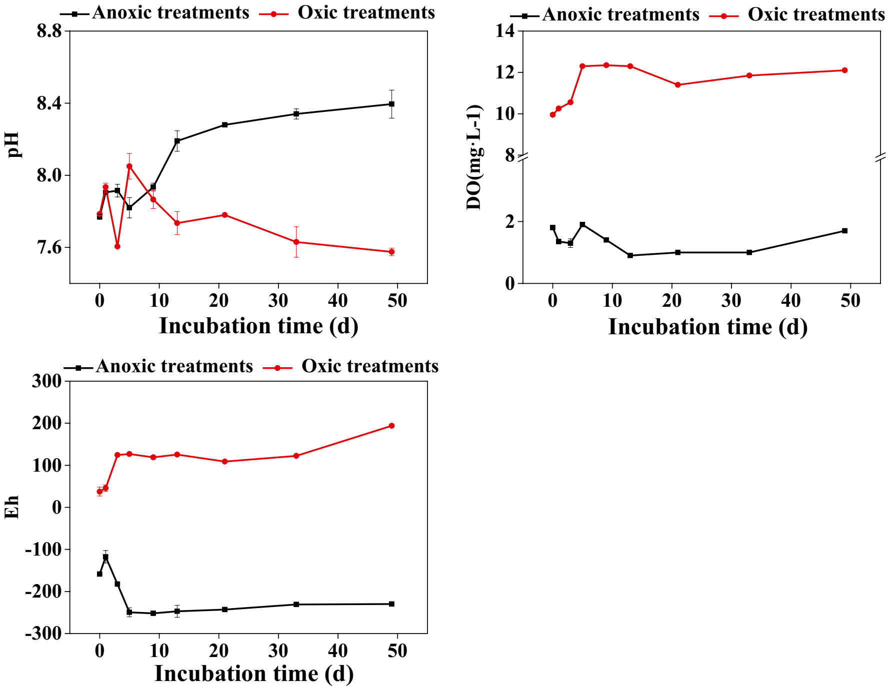

Fig. 4 Variations on pH, dissolved oxygen (DO), and redox potential (Eh) values of overlying water in oxic treatments and anoxic treatments with time (GD1 represents pre-incubation sediments)

In oxic treatments, the peak concentrations of Cu, Cd, Cr, and Pb in the overlying water reached 191.93, 0.27, 32.55, and 0.66 $\mu g \cdot L^{-1}$, respectively. However, in anoxic treatments, the maximum concentrations of Cu, Cd, Cr, and Pb in the overlying water reached 175.35, 0.09, 25.39, and 0.55 $\mu g \cdot L^{-1}$, respectively. Furthermore, the four metals showed different release trends in the incubation experiment. The concentrations of Cu and Cd in oxic treatments and anoxic treatments differed from the beginning of the experiment, and the gap widened over the course of the incubation. In oxic treatments, Cu and Cd had a high concentration at day 1 in oxic treatments, followed by a decrease and then to increase. In anoxic treatments, Cu and Cd showed an obvious increase in the first 9 days and 5 days, respectively, and then to decrease. Here, Cr and Pb presented almost identical trend of increasing initially and then decreasing in both oxic and anoxic treatments. At the end of the experiment, the concentrations of Cu and Cd in oxic treatments were significantly higher than those in anoxic treatments, while Cr and Pb showed no significant difference between the two treatments ($P < 0.05$). Moreover, the concentrations of Cu in both oxic and anoxic treatments were substantially higher than that in the class III of the Sea water quality standard (GB3097-1997) (Table S5). The concentrations of Cd and Pb were lower than the threshold values in the class I. In total, Cu was the most sensitive to changes in redox conditions.

The binding of heavy metals in sediments is mainly governed by Fe(III) oxides, and sulfides (Banks et al., 2012). The oxic environments may have promoted the release of metals by oxidation of, for example, CuS and CdS. Metal sulfide is an important sink of heavy metals in anoxic sediments (Chou et al., 2018). Calmano et al. (1993) found that the mobility of Cd and Cu increased in sediments after 35 days of aeration. Therefore, metal sulfide may be an important source of heavy metals in oxic environments. The adsorption of heavy metals by Fe(III) oxides is one of the most important geochemical processes controlling their environmental fate and mobility (Duan et al., 2021). Studies have shown that Fe(III) oxides had high adsorption capacity to heavy metal ions (Yuan et al., 2020). In this work, different dynamic concentrations of Pb and Cr may be related to strong adsorption of Fe(III) oxides. It is reported that Pb has the highest affinity for Fe(III) oxides in sediments. The removal of Pb from water and sediment by Fe (III) oxides is considered to be an important process controlling Pb fraction and geochemistry (Chakraborty et al., 2016).

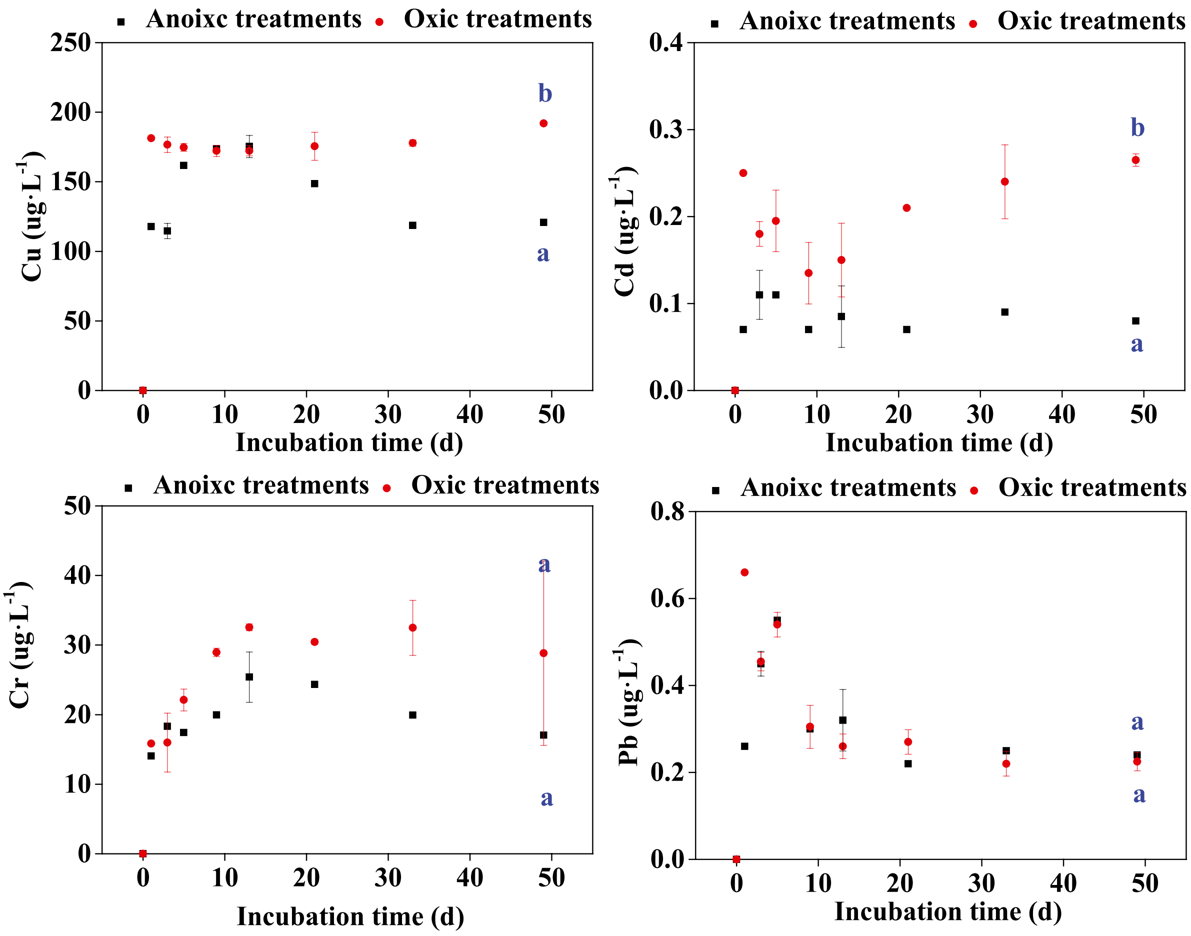

Fig. 5 Heavy metal (Cu, Cd, Cr, and Pb) concentrations in overlying water under different treatments (different letters (**a** and **b**) on the bars denote significant differences among different groups ($P<0.05$))

The release of heavy metals in anoxic treatments may be related to the reduction of Fe (III) oxides in anoxic treatments. The reducing conditions of anoxic treatments were beneficial to the reduction of species, such as Fe(III) oxides and sulfates. In the presence of organic carbon, Fe(III) is reduced mainly by dissimilated iron-reducing bacteria under anoxic environments (Zhang et al., 2020). The sediments used for incubation experiments have high OM content (9.24%), which can provide sufficient carbon source for microorganisms. Therefore, Fe(III) oxides are likely to be reduced by microorganisms in anoxic treatments, leading to desorption of Cu, Cd, Cr, and Pb. However, sulfate reduction to sulfide increased the content of sulfide in the sediments in anoxic treatments (Fig. 3). AVS are crucial for controlling the activity of divalent cationic metals (Butler, 2009; Wang et al., 2019) and may account for the decrease of heavy metal concentrations in anoxic treatments.

The exchange fluxes of Cu, Cd, Cr, and Pb over the SWI

As displayed in Table 2, from 0 to 3 days, the fluxes of Cu, Cd, Cr, and Pb were positive (from sediment to overlying water) in oxic treatments, indicating that diffusion was the dominant process during this period. From 3 to 9 days, the exchange fluxes of Cu, Cd, Cr, and Pb sharply decreased compared to the previous period (0–3 days). In this period, the exchange fluxes of Cu and Pb were negative (from overlying water to sediment), indicating that Cu and Pb were mainly adsorbed by sediments. In this case, the adsorbent was likely to be Fe(III) oxides (Drahota et al., 2021). From 9 to 21, the exchange fluxes of the Cu, Cd, and Cr were relatively small, but still presented positive values. At the end of the incubation, the exchange fluxes of Cu and Cd in oxic treatments were positive, showing that these heavy metals could still be released.

In the first period of anoxic treatments, the four heavy metals also presented positive fluxes, among which the fluxes of Cu and Cd were far less than those in oxic treatments. In next period (3–9 days), the exchange fluxes of Cu and Cr still presented desorption state. The exchange flux of Cd and Pb was negative, but the value is very close to zero, indicating that the adsorption and desorption had reached metastable equilibrium state. In the following two time periods, the exchange fluxes of Cu, Cd, Cr, and Pb metals in anoxic environments gradually approached zero, indicating that the adsorption and desorption had reached metastable equilibrium state.

Table 2 Exchange fluxes of heavy metals in μmol·m^{-2}·day^{-1} computed using metal concentrations in the overlying water (positive values were the fluxes from sediments to overlying water, negative values were the fluxes from overlying water to sediments)

	Oxic treatments	Anoxic treatments
From day 0 to day 3		
Cu	96.85	62.85
Cd	0.06	0.03
Cr	10.78	12.35
Pb	0.08	0.08
From day 3 to day 9		
Cu	−1.21	16.18
Cd	0	−0.01
Cr	4.37	0.55
Pb	−0.01	−0.01
From day 9 to day 21		
Cu	0.45	−3.44
Cd	0.02	0
Cr	0.25	0.74
Pb	0	0
From day 21 to day 49		
Cu	0.96	−1.63
Cd	0	0
Cr	−0.12	−0.53
Pb	0	0

Bioavailability of the heavy metals in the sediments

The BCR sequential extraction can generate important data for studying the bioavailability of heavy metals and is critical for revealing the migration of heavy metals in sediments (Liu et al., 2020). Heavy metals in F1, which are weakly combined with sediments, are easily released into the overlying water (Kang et al., 2019). The F4 is considered as the most stable fraction; F2 and F3 are potentially toxic fractions due to changes in redox conditions (Baran et al., 2019). In the GD1 (Fig. 6), Cu in raw sediments was dominated by F2 and F3 (37% and 36% of the total, respectively). Cd was dominated by F1 and F2 (32% and 48% of the total, respectively). Cr was primarily controlled by F4 (80% of the total). Pb was dominated by F2 (47% of the total). Totally, Cu, Cd, and Pb in the raw sediments were all presented non-residual fractions, which indicated the high mobility and ecological risk.

After the incubation, the F1 contents of Cu, Cd, and Pb decreased in oxic treatments while increased in anoxic treatments compared to GD1 (Fig. 6). However, F1 Cr increased in oxic treatments. Compared to GD1, F1 Cr increased 0.18 mg·kg^{-1}. Compared to anoxic treatments, the F2 contents in oxic treatments generally enhanced in the order: Pb (1.79 mg·kg^{-1}) > Cu (1.65 mg·kg^{-1}) > Cd (0.26 mg·kg^{-1}) > Cr (0.15 mg·kg^{-1}). Moreover, the F3 contents for Cu, Cd, Cr, and Pb in oxic treatments decreased, while the opposite phenomenon was observed in anoxic treatments. The F3 contents of Cu, Cd, Cr, and Pb decreased by 20%, 11%, 17%, and 10%, respectively, compared to the values in anoxic treatments.

The F1 fractions, consisting of exchangeable and carbonate-associated metals, are regarded as the most unstable metal fractions (Kang et al., 2019).The F1 fraction decreased in oxic treatments may be related to the decrease of pH in oxic sediments. Low pH may reduce the adsorption of heavy metals on sediments and promote the mobility of heavy metals, while high pH may promote the adsorption and precipitation of heavy metals and decrease the concentrations of heavy metals (Liu et al., 2021a, b). Therefore, Cu, Cd, and Pb in F1 fraction decreased in oxic treatments and increased in anoxic treatments.

The F2 fractions, associated with Fe/Mn oxides, are sensitive to redox variations (Qiao et al., 2020).

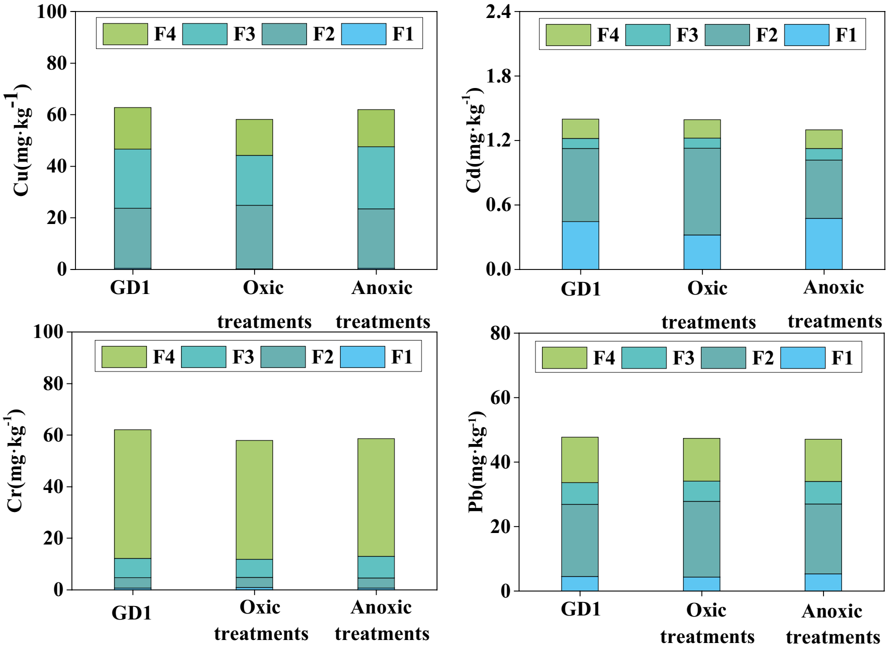

Fig. 6 The fraction of heavy metals in sediments in different treatments after incubation (GD1 represents pre-incubation sediments)

At higher levels of DO concentration, the increase of F2 fraction in sediments may be due to the formation of Fe (III) oxides with strong affinity for heavy metals. Studies have shown that dissolved heavy metal ions can combine with mineral structure during the formation of Fe (III) oxides, and then can be adsorbed to the mineral surface (Shi et al., 2021). This is also an important reason for the decrease of heavy metal concentration in oxic overlying water. However, anoxic environments promoted the reduction and dissolution of Fe (III) oxides in sediments, and these processes were also closely linked to the desorption of heavy metals bond to Fe(III) oxides (Singh et al., 2018). Anoxic conditions can induce the reduction of Fe(III) and the release of active metals bound to Fe(III) oxides, which then release into the overlying water, resulting in an increase in the concentration of heavy metals in the overlying water.

The F3 fractions refer to metals bound to OM and sulfides. Sulfide is a crucial binding component of heavy metals in sediments and plays an indispensable role in controlling the mobility of heavy metals in sediments. The AVS content was 22.70 μmol·g^{-1} in oxic treatments and 55.97 μmol·g^{-1} in anoxic treatments. The increased DO in oxic treatments made sulfides expose to a chemical oxidant and oxic microorganisms. Under the action of sulfide-oxidizing bacteria and oxygen, sulfides were oxidized to sulfates, causing the release of heavy metals associated with the sulfide. At this time, sulfide as an important source of heavy metals releases heavy metal ions into the overlying water. As the Eh decreased, sulfate reduced to sulfides. Dissolved heavy metals can be restricted by co-precipitation with sulfides (Liang et al., 2017). If there is a high concentration of Fe^{2+} in the system, the sulfide may react with it to form secondary mineral iron sulfide (FeS), which can be used as an important adsorbent of heavy metals (Xu et al., 2019). Thus, the low concentrations of Cu, Cd, Cr, and Pb in anoxic treatments were mainly caused by co-precipitation with sulfide. Additionally, the F4 fraction is associated with aluminosilicate minerals and features low fluidity and environmental risk; thus, it is considered the nonbioavailable fraction (Krausse et al., 2019; Zhao et al., 2020). Compared to that in anoxic treatments, F4 in oxic treatments underwent less change.

The RACs

As shown in Fig. 7, the RACs of Cu were below 1% in both oxic and anoxic treatments, indicating no risks to the environments. The RACs of Cr were below 10% in both oxic and anoxic treatments,

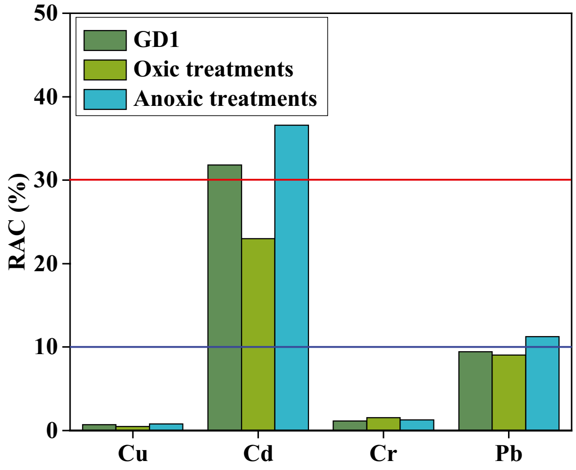

Fig. 7 The risk assessment code (RAC) of heavy metals in sediments after incubation. The blue line represents RAC = 10%, while the red one is RAC = 50% (GD1 represents pre-incubation sediments)

indicating low risks to the environments. Pb posed low risk to the environment in the raw sediment but medium risk in anoxic treatments. The RAC of Cd was more than 30% in the raw sediments and reached 36% in anoxic treatments, respectively, presenting a high risk to the aquatic environment. The calculated RACs suggested that anoxic conditions increased the potential environmental risk posed by heavy metals from sediments.

Conclusions

Oxic environments promoted the concentrations of Cu and Cd in overlying water by dissolving acid-soluble and oxidizable fraction. However, due to the strong adsorption capacity of the sulfide, the release of heavy metals under anoxic conditions was limited. The exchange flux showed that the four heavy metals gradually reached metastable equilibrium in the late anoxic environments. However, Cu still presented release trend in oxic environment. Heavy metals partially released by changes in anoxic environments were re-adsorbed and became bound to the more unstable acid-soluble fraction, which greatly enhanced the ecological risk posed by the heavy metals. Although the incubation conditions in the laboratory were different from natural conditions, this study can offer important theoretical support to predict the release behavior of heavy metals from sediments under varied DO conditions.

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Data availability The datasets used during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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