REPORTS

Remobilization of trace metals induced by microbiological activities near sediment-water interface, Aha Lake, Guiyang

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Abstract The Aha Lake, as a seasonally oxygen-absent man-made reservoir, has been polluted by acidic mining drainage and domestic sewages for a long time, with iron, manganese and sulfate excessively enriched in water and sediment. By means of microbe counting, the analysis of trace metals in pore water and electronic acceptors for organic matter decomposing, we have found that strong biogeochemical remobilization of trace metals occurred near the water-sediment interface. The microbial reduction of iron, manganese and sulfate took place in different parts throughout the sediment core with the extend of iron reduction lower than that of sulfate reduction, which happened in the surficial sediments and hampered the upward release of some trace metals to some extent. Some trace metals in pore water, due to the "dual releasing" effects caused by the reduction of Fe^{3+} and Mn^{4+} at varying depth, show a tendency of being enriched excessively in the upper 10 cm of sediment. In this study, we discussed the microbiological mechanism of trace metals enrichment in surficial sediments and the environmental condition, with an attempt to realize the unsteady mobilization of trace metals and their potential harm to overlying lake water in the Aha Lake, Guiyang.

Keywords: Aha Lake, trace metals, microbe, releasing effect.

Lake sediments, as the sink of various substances from a drainage area, especially from mining areas, accommodate some harmful heavy metals. More and more attention has been paid to the "sink/source" transformation of trace metals due to various biogeochemical processes near the sediment-water interface, for the sake of water resource management[1—4]. The distribution of different geochemical phases of trace metals in lake sediments, has been particularly emphasized in previous studies[5—7]. It has been realized that the continuous input of organic matter and the seasonal change of redox condition are the important factors affecting the geochemical cycling of trace metals in lake sediments, and the preferential reduction sequence of primary oxidants due to organic matter

degradation has been established, that is, O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2[8], which also follows the classical thermodynamics theory. But most studies are focused on marine sediments, but few on lacustrine sediments, and the microbiological process and the mechanism of trace metal cycling during early diagenesis are poorly documented[9—14].

The Aha Lake is a man-made reservoir with seasonally oxygen-absent bottom water, located in the southwest of Guiyang City. Since over 200 coal mines are scattered in the drainage area, plenty of acidic mining drainage flows into the Aha Lake directly, causing excessive enrichment of iron, manganese and sulfate in water and sediments, while domestic sewages enter the lake from the catchment area. The water column of this lake has not been obviously acidified for the lake is developed in the karst area, with pH equal to 7.28. The input of high-concentration electronic acceptors in response to organic matter degradation under anoxic condition, substantially changed the water quality and the distribution mode of trace metals in lake sediments, and organic matter degradation at the sediment-water interface is different from the situation encountered in other freshwater lakes. Since the strong acid-buffering potential of lakes in karst areas, trace metals can easily be fixed in lake sediments if there is the sole acid mining drainage pollution, but if the organic pollution is persistently introduced, the redox state in lake sediments can be changed, and furthermore trace metals can be re-mobilized, causing serious "secondary pollution", which can threaten the safety of lake water, and become a "chemical bomb" buried at the bottom of the lake. In this study, the sample localities are near the dam of Aha Lake, for there has a composite feature of coal mining drainage and domestic sewage pollution. This paper deals with the relationship between the distribution of microbes responsible for iron and manganese reduction and the trace metals in pore water, and elucidates the mechanism of trace metals enrichment in surficial pore water.

1 Sampling and experimental

(ⅰ) Sample collection. The Aha Lake, constructed in 1958 and put into operation in 1960, covers a lake area of 3.4 km^2 and a catchment area of 190 km^2, and has an altitude of 1108 m, with the water residence time of 0.44 a. The maximum water depth is 24 m, averaging 13.2 m. By means of a portable non-disturbing sediment sampler[15], sediment cores were collected at the site of lake center near the dam of Aha Lake in May 2002. Bottom water was very clear, indicating a success in sampling. After siphoning out bottom water, sediment was segmented in-situ at intervals of 1.0 cm. Pore water was collected by centrifugating the sediment at 3500 r/min under low temperature (4℃).

(ⅱ) Experimental. Pore water was divided into

three portions after 0.45 μm filtration: the first portion was used to measure SO_4^{2-} by liquid chromatography (HP1100); the second was used to measure dissolved Fe after being acidified with super pure HNO_3 by atomic absorption spectrophotometry (ASS PE5100PC); the third was used to measure Mn, Co, Ni, Pb, Mo and Sc by ICP-MS (Finnigan MAT-ELEMENT), with Rh as the internal standard, after being acidified with super pure HNO_3. Analytical error is lower than 5% for the above elements.

Microbe counting: 1.0 g sediment was dissolved in 20 mL bacteria-free water, after dilution step by step, incubating under strict anoxic condition, at 30℃. SRB (sulfate reduction bacteria) culture medium was prepared with the following ingredients: lactic acid, 2.5 mL; yeast extract, 1.0 g; DL-Cysteine, 0.6 g; Na_2SO_4, 1.0 g; NH_4Cl, 1.0 g; $CaCl_2$, 0.1 g; K_2HPO_4, 0.5 g; $(NH_4)_2SO_4$, 0.5 g; resazurin (0.1%), 1.0 mL; agar, 15.0 g, and filtrated lake water, 1000 mL. The pH value was adjusted to 7.0.

Dissimilatory Iron Reducing Bacteria (DIRB) culture medium[16,17]: $NaHCO_3$, 2.5 g; NH_4Cl, 1.5 g; KH_2PO_4, 0.6 g; KCl, 0.1 g; vitamin mixture 10.0 mL; trace element mixture 10.0 mL; sodium acetate, 1.5 g; amorphous $Fe(OH)_3$, 50.0 mmol/L; resazurin (0.1%), 1.0 mL; agar, 15.0 g, and filtrated lake water, 1000 mL. The pH was adjusted to 7.0.

2 Discussion and results

（ⅰ） Microbiological activities and reduction to electronic acceptors. According to the results of counting for DIRB and SRB in Aha Lake sediments, it was found that DIRB and SRB have different preferential growth areas, as shown in Figs. 1 and 2. The process of sulfate reduction, as is controlled by SRB distribution, has played an important role in organic matter degradation in an anoxic environment[1,18]. Fig. 1 shows that in this study, SRB have maximum activities at 2 cm below the sediment-water interface, with little activity below 6-cm depth. Sulfate concentrations in pore water tend to decrease rapidly in the top 5-cm sediment, strictly obeying the SRB distribution, which indicates that sulfate reduction occurs in the surficial sediment, as shown in Fig. 3.

Just like sulfate reduction, iron reduction is also an important factor leading to organic matter degradation in anoxic sediments as well[17,19—22]. But unlike SRB, DIRB have the strongest activity at the 10-cm depth under the water-sediment interface, with weak activity in surficial sediments, which is in concordance with the iron concentration profile in pore water (Fig. 4), that is, the stronger the DIRB activity is, the higher the dissolved iron concentrations will be. The distribution profiles of DIRB and SRB indicate that sulfate reduction is prior to iron reduction, which is different from the preferential reduction sequence in the marine anoxic environment[8]. Manganese

reduction process is relatively complex, involving inorganic and microbiological reduction. Furthermore, some metal reducing bacteria, such as some of the DIRB, can reduce Mn as well, so dissolved Mn concentration profile is usually taken to indicate Mn reducing process. Fig. 4 shows that Mn reduction is prior to sulfate and iron reduction, but has a relatively wide reducing range down to 9-cm depth.
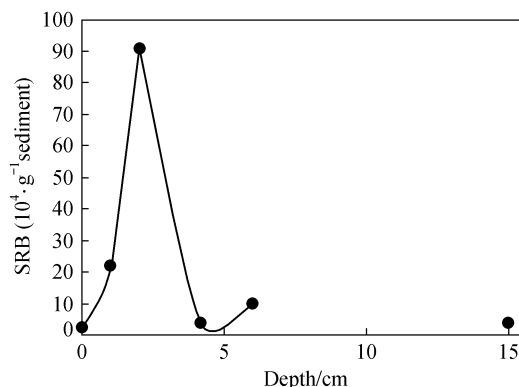

Fig. 1. Distribution of SRB near the sediment-water interface in the Aha Lake.
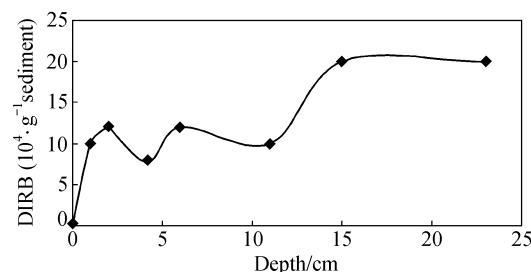

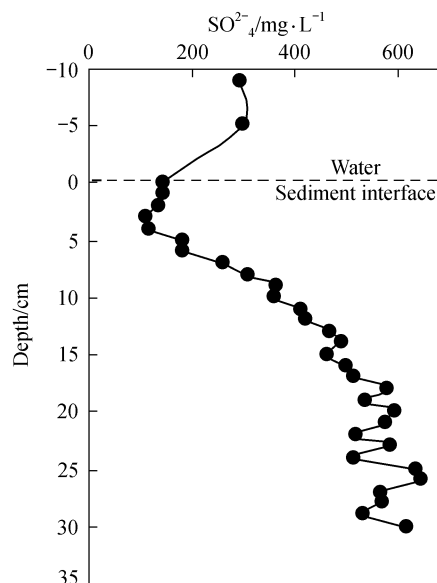Fig. 2. Distribution of DIRB near the sediment-water interface in the Aha Lake.

Fig. 3. Distribution of sulfate near the sediment-water interface in the Aha Lake.
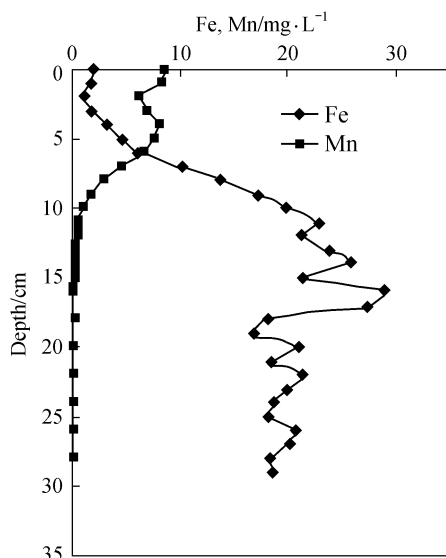
Fe, Mn/mg·L^{-1}

Fig. 4.   Distribution of Fe and Mn in pore water of sediment in the Aha Lake.

(ii) Distribution of trace metals in pore water. In natural environments, microorganisms can utilize some trace elements as life-indispensable ingredients to take part in some physiological functions in organism, which require a little amount of such trace elements, and hence would exert a negligible influence on trace element mobilization. But environmental media, in cases the materials contain trace metals, can be changed by physiological activities of microorganisms to some extent, exerting a great influence on the mobilization of some trace metals.

As shown in Fig. 5, Co, Ni, Sc, Ba, Mo and Pb in pore water tend to be enriched excessively in surficial 10-cm depth sediments, with respective concentration peaks appearing at different positions. Co and Ni, with the same distribution characteristics, show "dual peaks" at 2-cm and 4-cm depths, respectively. Mo only has a single concentration peak at 2-cm depth, while Sc has a peak at 3—4-cm. A good correlation ($r = 0.98$) exists between Ba and Mn. Dissolved Pb decreases rapidly from the sediment-water interface to 3-cm depth, and shows a concentration peak at 5-cm depth. As a whole, the trace metals listed above have the same feature, i.e. strong enrichment in surficial pore water, and at the same time, they also show different distribution characteristics controlled by their unique geochemical properties.

(iii) The release of absorbed trace metals induced by microbiological iron and manganese reduction. In most natural surface water environments, the concentrations of trace metals are restricted mainly by adsorption or co-precipitation processes[23]. Plenty of acidic mining drainage, containing Fe, Mn, SO_4^{2-} and other trace metals, from upstream, enters the Aha Lake, but the pH of

lake sediments and lake water still keeps neutral, owing to the strong acid buffering potential of lake in karst areas, and the neutralizing treatment of coal mining drainage using lime in the recent decade. Along with increasing pH, dissolved iron and manganese will become oxides or hydroxide, while trace metals are adsorbed or co-precipitated synchronously.

In the Aha Lake, when the sediment-water interface becomes anoxic, organic matter still continues to be mineralized by way of reducing other electronic acceptors, such as Fe^{3+}, Mn^{4+} and SO_4^{2-} , depending on their concentrations in the environment. From the above data, it is clear that manganese reduction restrained iron reduction in the upper part of the sediment core. DIRB activities began to increase in going downward, with decreasing Mn reducing ability, leading to the release of adsorbed trace metals on iron and manganese oxides or hydroxides, respectively[16,24], as shown in Figs. 2 and 4. Consequently, the desorbed trace metals may show "dual concentration peaks" at depth during the iron and manganese reducing process. The upper peak may be caused by manganese reducing, while the lower one by iron reducing. The released trace metals may diffuse toward overlying water column, along the concentration gradient.

(iv) Factors affecting the precipitation of trace metals. During the process of iron and manganese reducing, dissolved Mn and Fe and released trace metals may diffuse upwards, but in some cases they may be restricted by the sulfate reducing process and dissolved oxygen content. One particularity of the Aha Lake is that sulfate reduction happens in the surface layer of the sediment core, just overlapping the manganese reducing position, and higher than the iron reducing position. Part of the released Fe and trace metals diffusing from lower pore water may react with H_2S, produced by sulfate reduction near the sediment-water interface, to form sulfide precipitants (FeS, FeS_2), on which some trace metals even can be adsorbed[11]. Fe (II) diffusing into the overlying water column can be oxidized to Fe (III) rapidly, even in the low oxygen condition, and then hydrolyzed to form hydroxyl compounds, which can capture trace metals in water synchronously, and be re-precipitated on the water-sediment interface. In seasons with oxygen enrichment in lake water, redox boundary can lie just below the SWI (sediment-water interface), thus forming an adsorption layer consisting of iron and manganese oxides or hydroxides, which baffles greatly the upward-diffusion of trace metals, caused by reduction process in lower-level sediments.

(v) Mechanism of trace metal mobilization and enrichment in pore water of surface sediment. Iron and manganese oxides or hydroxides are widespread in the hypergene environment, and show strong adsorption potential of trace metals in water owing to their huge specific surface area and surfacial chemical activity.
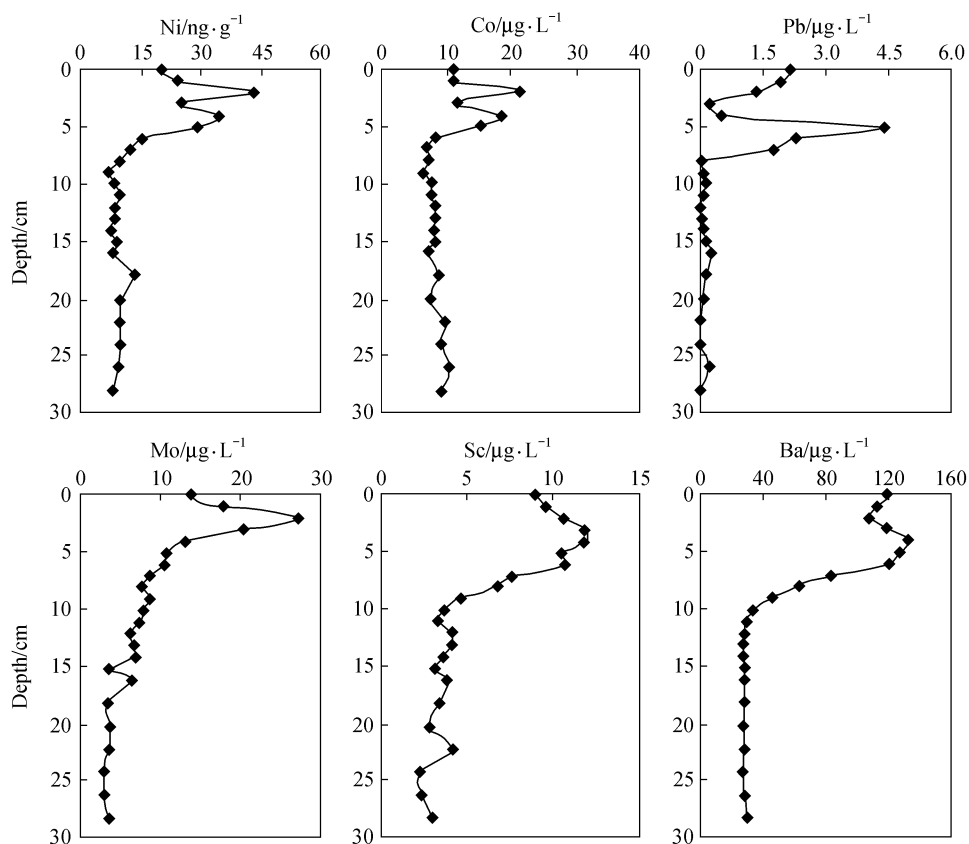
Fig. 5. The concentration profile of Co, Ni, Sc, Ba, Mo and Pb in pore water of the Aha Lake.

Organic matter degradation, which needs the participation of microbes at ambient temperature, is the most important geochemical process, and it can provide driving force for early diagenesis[27]. In 1988, two dissimilatory iron reducing bacteria (*Shewanella putrefaciens* and *Geobacter metalloreducens*) were successfully separated, and the importance of iron and other electronic acceptors in the process of microbiological anoxic respiration has been gradually realized[28].

Seasonal oxygen absence in lake water, persisting input of organic carbon, coupling with the excessive loading of iron, manganese and sulfate, provide necessary conditions for trace metal-remobilization at the sediment-water interface. (1) In an anoxic season, with the propagating of anaerobic bacteria, dissimilatory reduction is enhanced, causing the activation and mobilization of some trace metals. But as discussed above, sulfate reduction, which happened in surficial sediments, may restrict the upward-diffusion of trace metals in pore water to some extent, and iron and manganese cycling between water and sediment can capture trace metals diffusing into the overlying water column and return to the sediment-water interface. (2) In a season with oxygen enrichment in bottom water, both the growth of anaerobe and anoxic respiration in surficial sediments are restrained, and trace metals, released in response to reduction in the lower layer, are retained in the surface adsorbing layer, mainly con-

sisting of iron and manganese oxide or hydroxide. The long-term effect of seasonal oxygen-absent process in this lake is that most trace metals are enriched in surficial sediment and its pore water, with the gradual decrease of trace metals present in reducible phase of the lower-level sediments, caused by strong cycling of iron and manganese. This is why DIRB activity is stronger in the lower sediment layers, but the released trace metals are extremely low in amount. On the contrary, most trace metals are released in surface layers with weak DIRB activity. Previous studies, mainly on marine sediments, have also revealed the enrichment of trace metals in surficial sediments, and the significance of iron and manganese cycling[3,25,26,29], but the extent of enrichment is not so typical as compared with that observed in our study. The change of trace metals concentrations in pore water depends on homeostasis between releasing and precipitation processes. As discussed above, iron, manganese and sulfate reduction happen at different depths. Since iron and manganese oxides and hydroxides are good sorbents, their reduction will lead to the release of adsorbed trace metals, causing the dual peaks of trace metals in pore water. Specifically, Co and Ni have the same distribution curves, since both belong to the iron-family elements, with the similar atomic structure and geochemical behavior. The dual peaks of Co and Ni, as discussed above, are caused by iron and manganese reduction, respectively, while the upper peaks of

Co and Ni are higher than the lower ones, indicating that manganese reduction is stronger than iron reduction. Mo and Sc only have a single peak, with Mo-peak higher than Sc peak vertically, reflecting a greater influence of Mn reduction on Mo, while Fe reduction on Sc. Pb shows very obvious "dual peaks", but because of its strong chalcophile affinity, Pb can combine rapidly with H_2S produced by sulfate reduction in surface sediments, resulting in the fast decrease of Pb in the top five centimeters of pore water, where sulfate reduction proceeds intensively. The second Pb peak due to iron reduction appears at the 6-cm depth below the sediment-water interface. Ba in pore water has an excellent correlation with dissolved Mn, with r = 0.98, indicating that Mn reduction is a primary factor controlling the geochemical behavior of Ba.

According to our study, it is found that some trace metals (including some harmful heavy metals) have a tendency of being enriched in the top several centimeters of pore water in lake sediments. Since eutrophication has not happened in the Aha Lake, organic load is still light in the whole lake, and electronic acceptors (Fe^{3+}, Mn^{4+}, SO_4^{2-}) for anoxic respiration are still enough. Consequently, organic matter degradation has a limited influence on the redox state of the whole lake, and harmful metals in the lake sediments as the "secondary pollution source" are of little harmfulness temporarily. So, it is still necessary to reduce the trophic level of this lake, while restricting the inflow of acidic mining drainage.

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