Screening Effect of the Diffusive Boundary Layer in Sediments of Lake Aha in the Suburbs of Guiyang City, Guizhou Province*

WAN GUOJIANG (万国江), HUANG RONGGUI (黄荣贵), PU YONG (普 勇)
(*State Key Lab. of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang*, 550002)
AND WAN XI (万 曦)
(*Institute of Soil and Fertilizer, Chinese Academy of Agricultural Sciences, Beijing*, 100081)

Abstract: The redox cycle of iron and manganese is a major geochemical process at the boundary layers of lake sediments. Lake Aha, which lies in the suburbs of Guiyang City, Guizhou Province, China, is a medium-sized artificial reservoir with seasonally anoxic hypolimnion. Long-term sedimentary accumulation of iron and manganese resulted in their enrichment in the upper sediments. In the anoxic season, Fe^{2+} and Mn^{2+}, formed by biological oxidation, would diffuse up to overlying waters from sediments. However, the concentration of Fe^{2+} increased later and decreased earlier than that of Mn^{2+}. Generally, sulfate reduction occurred at 6 cm below the sediment-water interface. Whereas, in the anoxic season, the reduction reached upper sediments, inhibiting the release of Fe^{2+}. The Fe concentration of anoxic water is quickly decreased from high to low as a result of reduction of the sulphur system.

Key words: **Fe-Mn cycle; diffusive boundary layer; screening effect; Lake Aha; Guizhou**

Introduction

The redox cycle of iron and manganese is a major geochemical process at the boundary layers of lake sediments. The major sources of iron and manganese in the hypolimnion of seasonally anoxic lakes are the diffusive boundary layers of lake sediments. However, iron and manganese show different geochemical behaviors at the sediment boundary layers(Stumm and Morgan, 1981; Davison, 1985; Wersin et al., 1991; Yagi, 1993).

Lake Aha, which lies in the suburbs of Guiyang City, Guizhou Province, China, is a medium-sized artificial reservoir built in 1960. It is a drainage basin covering an area of 190 km^2, and its surface area is 3.4 km^2 with a mean depth of 13 m and a maximum depth of 24 m. The total capacity of this lake is about 0.445×10^9 m^3. Its mean water flux is 1.02×10^9 $m \cdot a^{-1}$, and the residence time of water is 0.44 a. Lake Aha slightly remains thermally stratified in the summer and autumn.

Exposed rocks around Lake Aha are the Permian limestones and coal layers, which are overlain by sialic or/and sifeic yellow soils. In the yellow soil the contents of iron and manganese are within the range of 4.3% – 5.6% and 0.1% – 0.14%, respectively.

Through long-term accumulation, Fe and Mn are enriched in the diffusive boundary layer with a thickness of 2 cm so that the Fe and Mn contents of sediment particles in this layer are

ISSN 1000-9426
* The project was financially supported by the National Natural Science Foundation of China(49333040).

as high as to be 12% and 1.5%, respectively. Therefore, Lake Aha is regarded as the best candidate for research on the geochemical behavior of Fe-Mn at the sediment/water interface.

Difference in Seasonal Release Between Iron and Manganese

When water in the epilimnion and hypolimnion of Lake Aha is anoxic in late summer and early autumn, iron and manganese are released to overlying water from the Fe-Mn-enriched layer, leading to an increase in Fe, Mn concentrations of the water column. However, the changing pattern is different between iron and manganese in this lake. Although the Fe, Mn concentrations show an increase mainly from July to October, the latter (Mn) appears earlier and longer than the former (Fe)(Fig. 1).

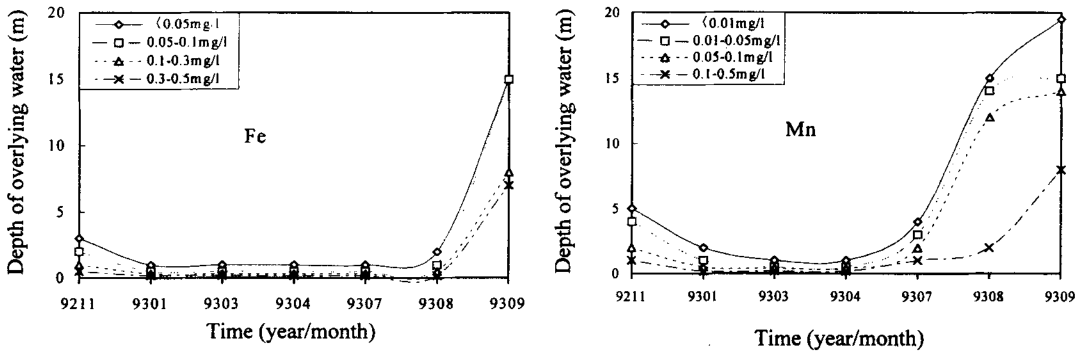

Fig. 1. Seasonal changing trend of the Fe-Mn concentrations in the water of Lake Aha.

Relationship Between Hydrochemical Conditions & Concentrations of Fe and Mn in the Anoxic Season

Seasonal variations of Fe and Mn are closely related to physico-chemical conditions in lake waters. During July to September, water temperature goes up obviously and the difference is 10℃ between the upper and lower layers (Fig.2a), pH value is obviously lower (Fig.2b), saturation of dissolved oxygen is declined to minimum (<30%) (Fig.2c), and the concentration of SO_4^{2-} is decreased more violently owing to dilution by rainwater or SO_4^{2-} reduction (Fig. 2d).

In order to ascertain the mechanism of differential release of iron and manganese from the sediments to the overlying water column, we first analyze the relationship between hydrochemical conditions and high Fe-Mn concentrations.

The relation between dissolved oxygen and Fe-Mn concentrations

From Fig.3 we can see that during anoxic seasons, higher Mn concentrations mainly appear under the condition that the saturation degree of dissolved oxygen is 20% – 60%, and that of iron is 30% – 50%. Under this condition, however, lower Fe concentrations are observed, too.

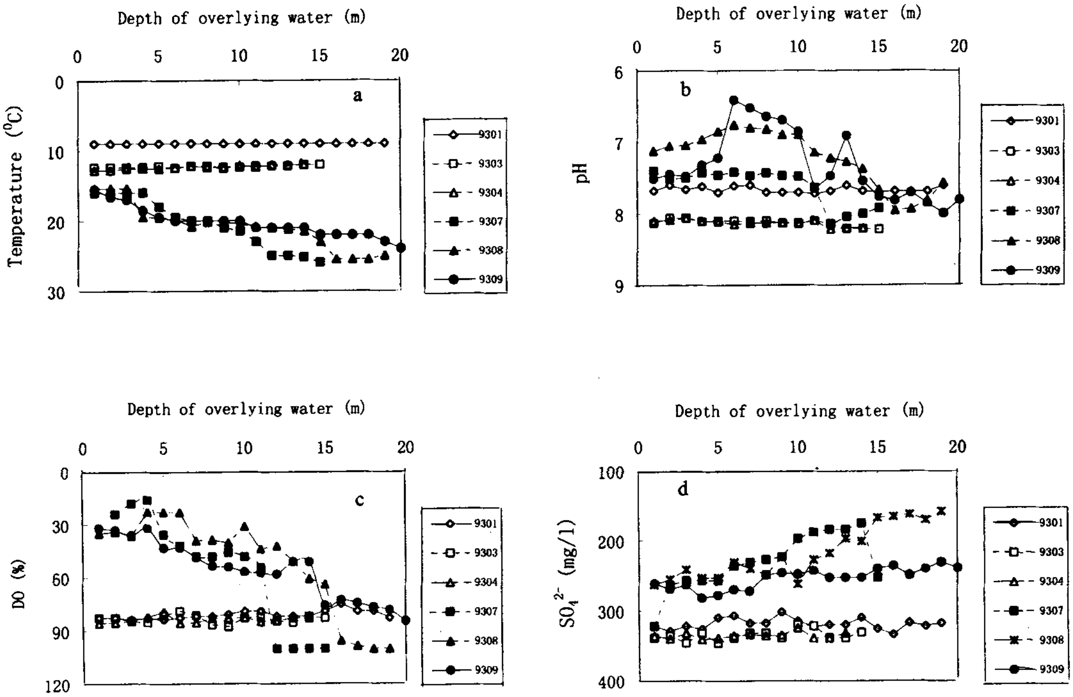

Fig. 2. Vertical variations of T, pH, dissolved oxygen and SO_4^{2-} in Lake Aha.

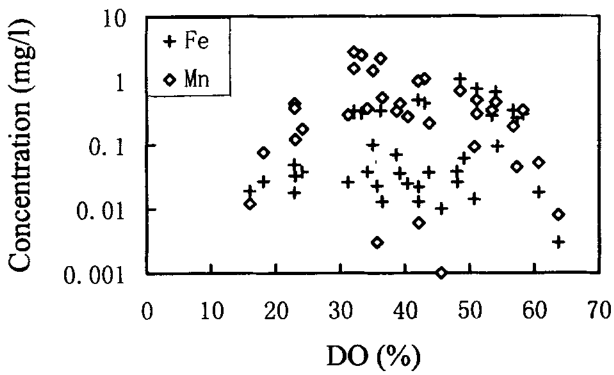

Fig. 3. The relation between dissolved oxygen & Fe-Mn concentrations.

The relation between pH and high Fe-Mn concentrations

In this lake, when the pH value of lake water is less than 7.5, higher Mn concentrations appear, but for iron, the relation between pH and Fe concentration is not so obvious (Fig. 4).

The relation between the concentrations of SO_4^{2-} and Fe-Mn

Because of the existence of coal seams in the watershed, the concentration of SO_4^{2-} is higher in the water of Lake Aha, but when the concentration of SO_4^{2-} is obviously decreased, the concentrations of Fe and Mn tend to increase in the anoxic season (Fig. 5). However, the relation between higher Fe concentration and lower SO_4^{2-} concentration is not a typical one.

In Lake Aha, when lake water in the hypolimnion is seasonally anoxic (in autumn), it is

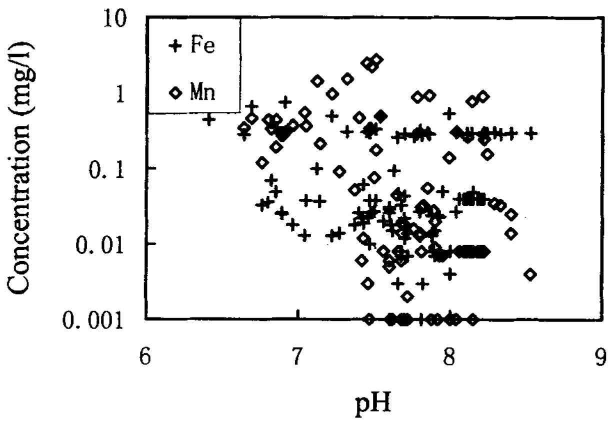

Fig. 4. The relation between pH & Fe-Mn concentrations.

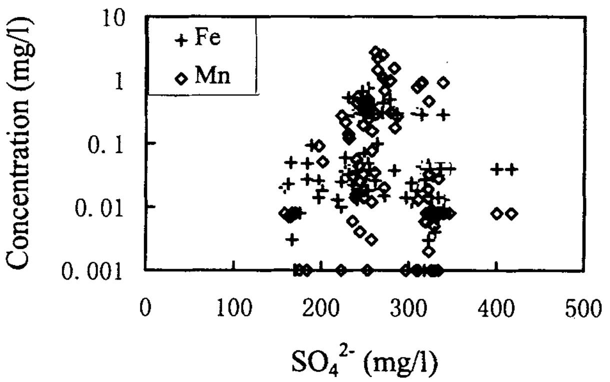

Fig. 5. The relation between SO_4^{2-} & Fe-Mn concentrations.

acidized (pH< 7.5) with SO_4^{2-} in the lake water being reduced ($S^{6+} \rightarrow S^{2-}$), leading to the rapid release of manganese at the diffusive boundary layer toward overlying water, and this part of manganese is constantly retained in the overlying anoxic water until lake water becomes oxygen-enriched (in winter). On the other hand, iron in the overlying water was released from anoxic sediments following SO_4^{2-} reduction, and partly turned back to the sediments. That is to say, the high Fe concentration of anoxic water is quickly decreased as a result of reduction of the sulphur system. The bacterial mats (*Beggiatoe* sp.) play a key role in exerting a screening effect on iron in the diffusive boundary layer of sediments (Wan Xi and Wan Guojiang, 1996; Furrer and Wehrli, 1991).

Either in sediments or sediment-water interface, particle-water distribution coefficient of Fe (K_d) in autumn is evidently lower than that in winter, indicating that Fe^{2+} diffused up to overlying waters from sediments in the anoxic season (Davison, 1993; Johnson, 1991; Chen et al., 1996). Meanwhile, the increase of K_d showed that the cycling of Fe^{2+} was screened by the diffusion boundary layer. However, the K_d of Mn in autumn decreases more actively than that in winter, but also the K_d of interface water is lower than that in the sediments, demonstrating that the release of Mn^{2+} is very violent at the sediment/water interface (Fig.6).

Screening Effect of Pore Water on the Release of Anoxic Iron

The vertical profile of SO_4^{2-} concentrations in the overlying water column at the sediment boundary is homogeneous, but the concentration of SO_4^{2-} in pore water tends to decrease rapidly with increasing depth. Especially, at the depth of 6 cm at the sediment boundary, the SO_4^{2-} concentration of pore water is less than 10 mg/L (Fig. 7). That is consistent with the variation of iron concentration of pore water.

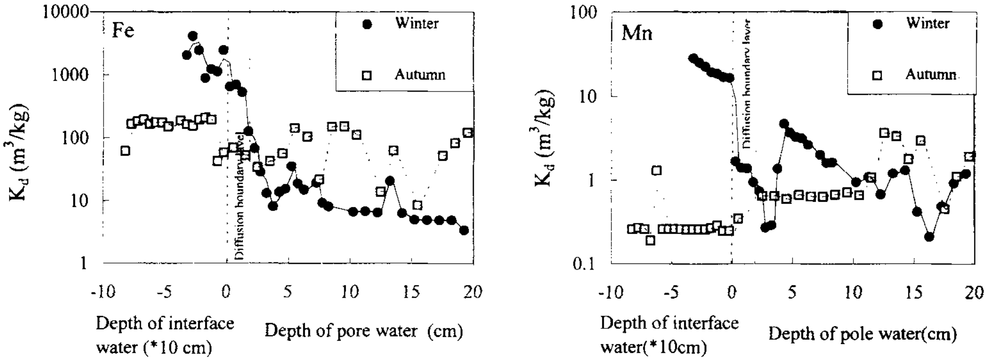

Fig. 6. Vertical variation of the particle-water distribution coefficients of Fe and Mn at the sediment/water interface of Lake Aha.

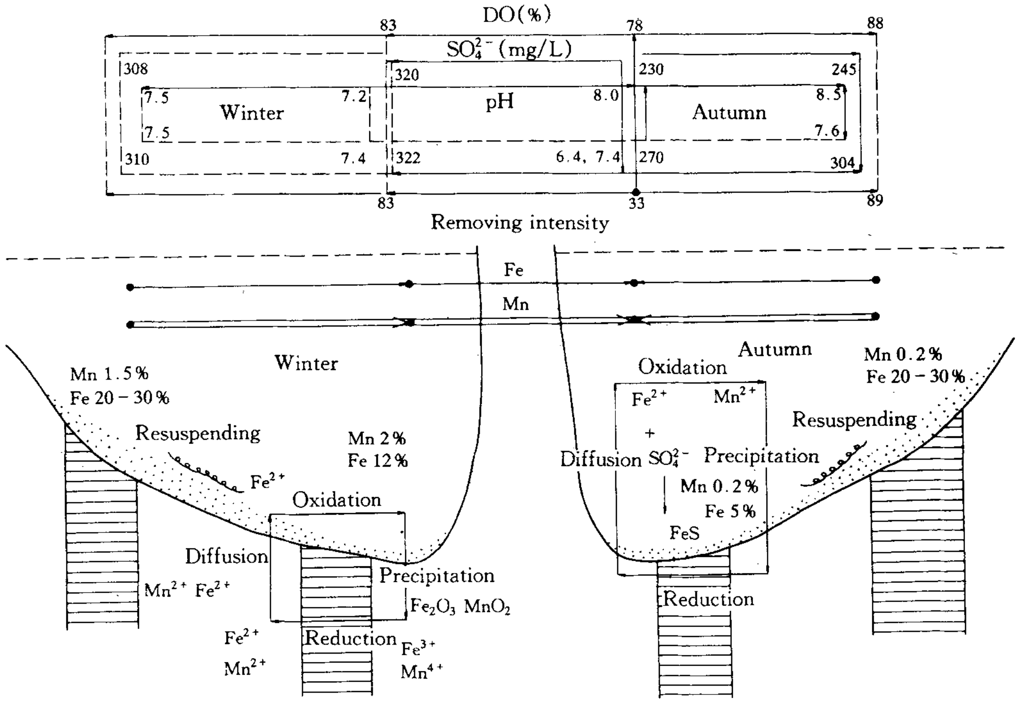

Fig. 7. Schematic depiction of the geochemical effect of the Fe-Mn cycle on the composition of water in Lake Aha.

Conclusions

1. In the water of Lake Aha, the Fe-Mn concentrations show different trends of increasing in late summer and early autumn, and the concentration of manganese varies earlier and longer than that of iron.

2. Higher manganese concentrations are closely associated with the anoxic conditions and lower pH value. However, the relation between the variation of iron concentration and the dissolved oxygen and pH value is not obvious.

3. In the anoxic season, SO_4^{2-} concentrations tend to decrease. SO_4^{2-} is reduced due to the effect of bacterial mats, and the diffusive boundary layer exerts a screening effect on the release of iron toward the overlying water column.

Acknowledgements: The authors wish to thank Mr. Zhang Jun, Zhou Shenqing, Wu Fengchang, Zhou Jingye and Mrs. Li Sunrong et al. for their help.

References

Chen Zhenlou, Pu Yong, Huang Ronggui & Wan Guojiang, 1996, The character of seasonal diffusion of Fe and Mn in the sediment-water interface in Lake Aha: Chinese Science Bulletin, v.41, n.16, p.1359 – 1363.

Davison, W., 1985, Conceptual models for transport at a redox boundary, in W. Stumm, ed., Chemical processes in lakes: New York, John Wiley & Sons, Inc., p.31 – 53.

Davison, W., 1993, Iron and manganese in lakes: Earth-Science Reviews, v.34, p.119 – 163.

Furrer, G. & B. Wehrli, 1991, Biogeochemical processes at the sediment-water interface: measurements and modeling: Applied Geochemistry, n.2, p.117 – 119.

Johnson, C, A., 1991, A mathematical model of the manganese cycle in a seasonally anoxic lakes: Limnol. Oceanogr., v.36, n.7, p.1415 – 1426.

Stumm, W. & J.J. Morgan, 1981, Aquatic Chemistry: New York, John Wiley & Sons, Inc., 2nd ed., 780p.

Stumm, W. & B. Sulzberger, 1991, The cycling of iron in natural environments: consideration based on laboratory studies of heterogeneous redox processes: Geochimica et Cosmochimica Acta, v.56, p.3233 – 3257.

Wan Xi & Wan Guojiang, 1996, Biogeochemistry of Fe and Mn in Lake Aha and their seasonal pollution, in Institute of Geochemistry, Chinese Academy of Sciences, ed., Developments in Geochemistry—Contribution to 30th International Geological Congress: Guizhou Science and Technology Publishing House, Guiyang, China, p.273 – 278.

Wersin, P., P. Hohener, R. Giovandi & W. Stumm, 1991, Early diagenetic influences on iron transformations in a freshwater lake sediment: Chemical Geology, v.90, p.233 – 252.

Yagi, A., 1993, Manganese cycle in lake Fukami-ike: Internal. Assoc. Limnol. Proceedings, v.25 (Part I): p.193 – 199.