

GEOCHEMICAL BEHAVIOR OF DISSOLVED IRON IN WATERS FROM THE AMUR RIVER, AMUR-LIMAN AND SAKHALIN BAY

**NAGAO S.¹, TERASHIMA M.², TAKATA H.¹, SEKI O.¹, KIM V. I.³, SHESTERKIN V. P.³,
LEVSHINA I. S.³ AND MAKHINOV A. N.³**

¹*Faculty of Environmental Earth Science, Hokkaido University*

²*Research Institute for Humanity and Nature*

³*Institute of Water and Ecology Problems, Far Eastern Branch of the Russian Academy of Sciences*

INTRODUCTION

To understand the input of iron from river to ocean, we need to study the geochemical behavior of iron in estuarine environments. Complex geochemical reactions occur in estuaries due to the mixing of freshwater with seawater. The distribution of iron in estuaries is well documented and the dissolved iron is found to be largely removed, the major fraction being on suspended particulate materials through colloid flocculation (Sholkovitz, 1976, Fox and Wofsy, 1983, Fox, 1988, Guo et al., 2000). It is important to study the fractionation of dissolved iron and its geochemical forms in estuaries because of estimation on flux of dissolved and particulate iron forms, and study on the transport processes and bioavailability. The purpose of this study is to elucidate the geochemical behavior of iron in the estuary of Amur River, Amur-Liman and Sakhalin Bay.

MATERIALS AND METHODS

Location is shown in Figure 1. Water samples were taken from surface and bottom layers at nine stations on the early of August in 2006. Salinity and turbidity were measured in-situ by a water checker (TOA DKK WQC-24). Dissolved iron in the water samples was measured by ICP-MS. Dissolved + acid leachable iron concentration was measured by colorimetry with 1,10-phenanthroline after the addition of HCl and the filtration. Dissolved organic carbon (DOC) concentration was determined by wet chemical method (Levshina and Karetnikova, 2008). The iron content of soil and river bottom sediment was measured by ICP-MS following total acid digestion with a mixture of HCl+HNO₃+HF.

RESULTS AND DISCUSSION

Figure 1 shows concentration of dissolved + acid leachable iron, turbidity and DOC concentration at each sampling station. The concentration of dissolved + acid leachable iron ranges from 1.78 mg/l to 2.96 mg/l at St. 1-3 in the estuary. The dissolved iron concentration filtered with GF/F filters and 0.2 µm membrane filters was 0.25-0.33 mg/l and 0.02-0.04 mg/l, respectively. Iron is dissolved as colloidal particles in freshwater environments. The dissolved + acid leachable iron rapidly decreases at St. 5 in the Amur-Liman. Above 90% of dissolved

and acid leachable iron, that is some part of suspended solids, is removed by the mixing of freshwater with seawater. The similar removal rate for iron is presented at estuarine environments (Sholkovitz et al., 1978, Kraepiel et al., 1997, Ouddane et al., 1999). The decrease in iron concentration that colloidal fraction of iron is coagulated during the mixing at the liman. The non-conservative behavior of iron has been observed at estuaries (Sholkovitz 1976, Boyle et al., 1977, Sholkovitz and Copland, 1981, Fan et al., 2008, etc.).

The turbidity, concentration of dissolved + acid leachable iron and dissolved organic carbon (DOC) as a function of salinity is presented in Figure 2. The decrease in turbidity from the freshwater to the seawater indicates a removal of suspended solids by a concave curvature of the data. On the other hand, the concentration of dissolved + acid leachable iron sharply decreases above salinity of 3.0. The DOC concentration decreases with increase in salinity linearly. Terashima and Nagao (2007) carried out laboratory mixing experiments for dissolved iron in the presence of river humic substances. They have shown the removal of dissolved iron up to 86% by the mixing, and the value agrees with the field research results at Amur-Liman. The discrepancy in removal behavior among iron, DOC and suspended solid indicates the formation of iron oxyhydroxides (Fan et al., 2008). Unfortunately, the detection limit of iron using analytical method in this study is 0.02 mg/l so that we can't elucidate the concentration of dissolved iron in Amur-Liman and Sakhalin Bay. Nakatsuka et al. (2007) have shown that the concentrations of dissolved iron in surface water at the sites close to the Amur River mouth are two orders magnitude higher than the Oyashio intermediate water. Therefore, iron in the Amur-Liman is coagulated, but some part of iron may be still dissolved in saline and seawaters.

The particulate iron is not precipitated on the surface sediments at Amur-Liman and Sakhalin Bay. The surface sediments collected by Ekman-berge bottom sampler during our research cruise are sandy and we did not recognize the presence of fine particles such as iron oxyhydroxides and clay minerals. The iron content of surface sediments in the Amur estuary is one-third lower than that of surface soil and sediments at the Lower Amur River (Table 1). The acid leachable iron was presented in the range of 6.7 to 84 $\mu\text{g/l}$ for the bottom layer at Sakhalin Bay (Nakatsuka et al., 2007). Therefore, iron precipitated from water column may be transported from Amur –Liman to Sakhalin Bay.

FUTURE STUDIES

In 2008 we will make plan for the research on the Amur estuary, Amur-Liman and Sakhalin Bay to understand behavior of coagulation and transport of iron in the mixing zone between freshwater and seawater. Three types of filters with pore size of 0.7 μm , 0.2 μm and 0.02 μm will be used to study existent forms of iron in saline and marine environments. Dissolved and colloidal organic matter may be critical intermediates in controlling the fate and transport of iron (Guo et al., 2000, Pokrovsky and Schott, 2002). We also study association of humic substances with iron in the mixing zone by field and laboratory experiments. Organic ligands such as humic substances, a major fraction of DOC in river water, play an important role of behavior of trace metal ions because of strong complexation

(Viers et al., 1997, Matsunaga et al., 1998). The geochemical forms of iron are a key parameter to understand bioavailability of iron in marine environments.

ACKNOWLEDGEMENTS

We thank Mrs. T. Tolkachova of IWEP for arrangements of our research cruise at the Amur-Liman and Sakhalin Bay.

REFERENCES

- Boyle, E. A., Edmond, J. M. and Sholkovitz, E. R. (1977) The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta*, 41, 1313-1324.
- Fan, D. J., Neuser, R. D., Sun, X. G., Yang, Z. S., Guo, Z. G. and Zhai, S. K. (2008) Authigenic iron oxide formation in the estuarine mixing zone of the Yangtze River. *Geo-Mar. Lett.*, 28, 7-14.
- Fox, L. E. (1988) The solubility of colloidal ferric hydroxide and its relevance to iron concentration in river water. *Geochim. Cosmochim. Acta*, 52, 771-777.
- Fox, L. E. and Wofsy, S. C. (1983) Kinetics of removal of iron colloids from estuaries. *Geochim. Cosmochim. Acta*, 47, 211-216.
- Guo, L., Santschi, P. H. and Warnken, K. W. (2000) Trace metal composition of colloidal organic material in marine environments. *Mar. Chem.*, 70, 257-275.
- Kraepiel, A. M., Chiffnqois, J.-F., Martin, J.-M. and Morel, F. M. M. (1997) Geochemistry of trace metals in the Gironde estuary. *Geochim. Cosmochim. Acta*, 61, 1421-1436.
- Levshina, S. I. and Karetnikova, E. (2008) Specifics of organic substance geochemical migration and phytoplankton distribution in the system Amur River-Amur Liman. Amur-Okhotsk Report Vol.5 (this volume), RHIN.
- Matsunaga, K., Nishioka, J., Kuma, K., Toya, K. and Suzuki, Y. (1998) Riverine input of bioavailable iron supporting phytoplankton growth in Kesenuma Bay. *Water Res.*, 32, 3436-3442.
- Nakatsuka, T., all members of research groups 1 and 2 (2007) How can the iron from Amur River support the primary productivity in North Pacific Ocean? Amur-Okhotsk Report Vol.4, RHIN, pp.25-36.
- Ouddane, B., Skiker, M., Fischer, J. C. and Wartel, M. (1999) Distribution of iron and manganese in the Seine river estuary: approach with experimental laboratory mixing. *J. Environ. Monit.*, 1, 489-496.
- Pokrovsky, O. and Schott, J. (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem. Geol.*, 190, 141-179.
- Sholkovitz, E. R. (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta*, 40, 831-845.
- Sholkovitz, E. M., Boyle, E. A. and Price, N. B. (1978) The removal of dissolved humic acids and iron during estuarine mixing. *Earth Planet. Sci. Lett.*, 40, 130-136.

Sholkovitz, E. R. and Copland, D. (1981) The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochim. Cosmochim. Acta*, 45, 181-189.

Terashima, M. and S. Nagao (2007) Removal and fractional characteristics of dissolved iron in estuarine mixing zone. *Amur-Okhotsk Report Vol.4, RHIN*, pp.69-74.

Viers, J., Dupre, B., Polve, M., Schott, J., Dandurand, J. and Braun J. J. (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): comparison between organic-poor and organic-rich waters. *Chem. Geol.*, 140, 181-206.

Table 1.

Fe content in surface samples from soils and river bottom sediments in the Lower Amur River and its estuary.

| Sample | Area | No of sample | Fe content (%) | |
|-----------------------|------------------|--------------|----------------|---------|
| | | | Range | Average |
| Soil | Lower Amur River | 18 | 2.94-6.54 | 4.7±1.2 |
| River bottom sediment | Lower Amur River | 16 | 3.91-6.79 | 5.7±0.8 |
| | Estuary | 1 | 1.68 | 1.68 |

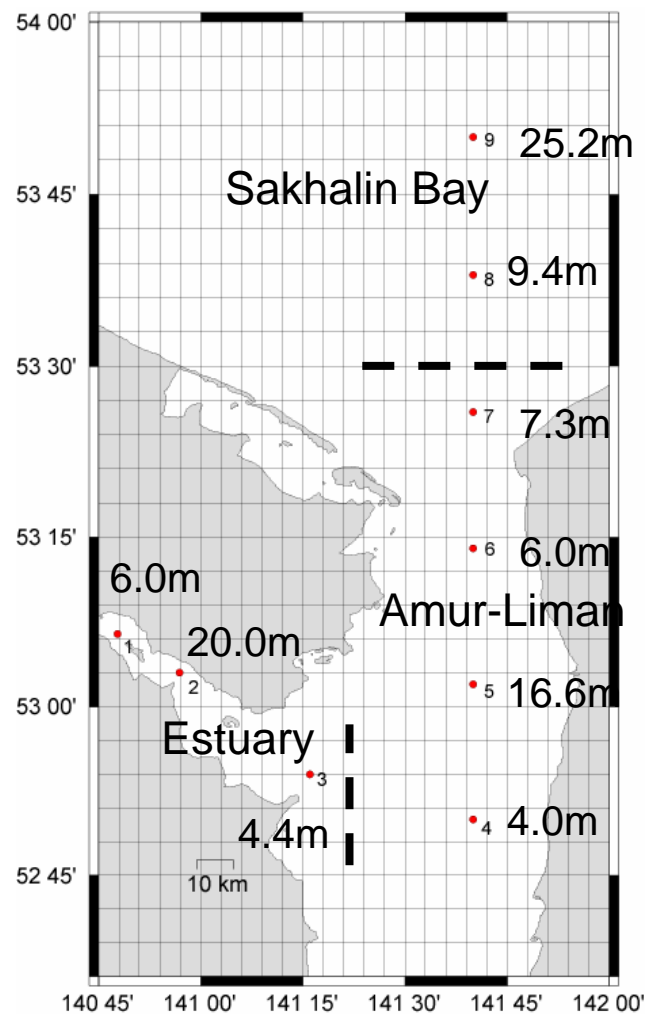


Figure 1 Sampling stations in estuary of the Amur River; Amur-Liman and Sakhalin Bay. Water depth in each station indicates in this figure.

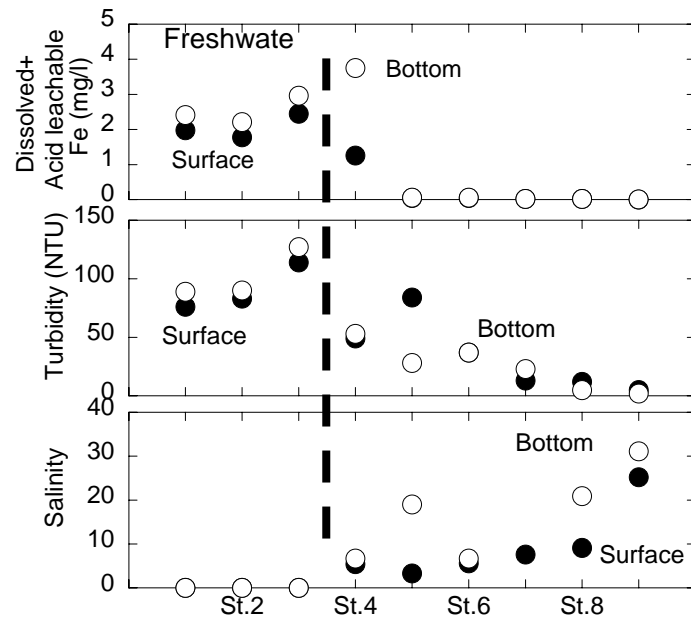


Figure 2 Turbidity, concentration of dissolved + leachable iron and salinity in estuary of the Amur River (St.1-3), Amur-Liman (St.4-7) and Sakhalin Bay (St.8-9).

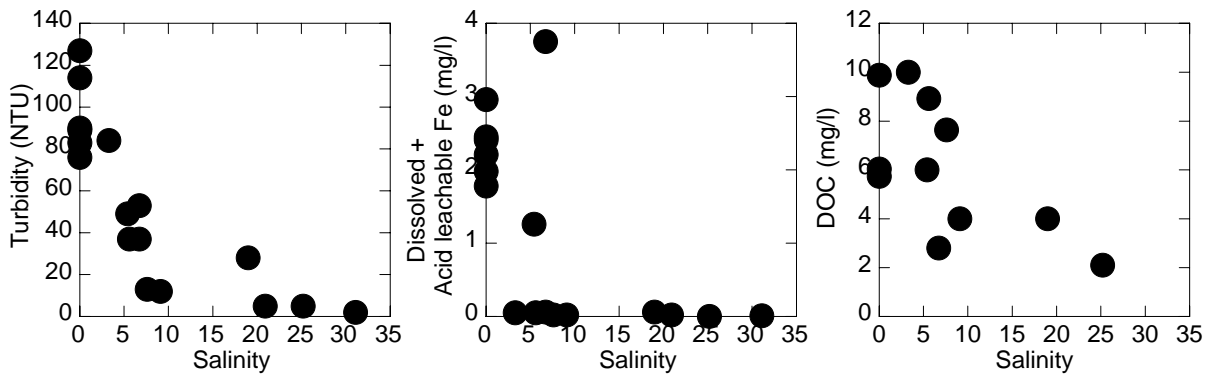


Figure 3 Turbidity, concentrations of dissolved + leachable iron and dissolved organic carbon (DOC) as a function of salinity.