

## — GROUP 3 REPORT —

**BIOGEOCHEMICAL BEHAVIOR OF IRON IN THE LOWER AMUR RIVER AND AMUR-LIMAN**

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**1. INTRODUCTION**

Iron is an essential nutrient known to limit primary productivity in HNLC regions of the oceans (Martin et al., 1994; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004). Recently many reports have been suggested that organically-bound iron, fulvic acid-iron, is supplied from forest and wetlands, and may contribute to maintain the growth of phytoplankton in the coastal region (Matsunaga et al., 1998; Krachler et al., 2005). Key element supporting the biomass production in the Sea of Okhotsk, therefore, is considered to be iron, especially “dissolved iron” from the Amur River.

The Amur River system is originated from the Argun and Shilkan Rivers, and one of largest rivers in eastern Asia. The Amur River Basin in north boundary coincides with mountain ridge and in southern border pass across low flood plain. The watershed is 2.05x10<sup>6</sup> km<sup>2</sup> and consists of 54% for forest area and 20% for agricultural land on the basis of the map with “Modern Land-use in Amur River Watershed” (Ganzey et al., 2007). The area is disturbed currently by various anthropogenic and natural impacts. Land-use change in the Amur River drainage might have caused significant change in the flux of dissolved iron. For better understanding the effects of land-use changes on transport of iron, effective approach is to study relationship between variations in riverine iron concentration and watershed environments with land-use in the Amur River Basin.

Research Group 3 of the Amur-Okhotsk Project has two main objectives: 1) estimation on iron flux from the Amur River to the Sea of Okhotsk, and 2) study on biogeochemical behavior of iron in the Amur River system. We made research plan to understand the source area of iron, its export processes, and migration behavior of iron throughout the Amur River and Amur-Liman as follows:

- a) Spatial variations of iron concentration in the Amur River system in a year
- b) Monthly water sampling at three monitoring stations (Khabarovsk, Bogorodskoe, and Nikolaevsk-na-Amure) along the Amur River;
- c) Research cruise for the lower Amur River from Khabarovsk to Nikolaevsk-na-Amure;
- d) Research expedition at the estuary of Amur River, Amur Liman and Sakhalin Bay.

## 2. MATERIALS AND METHODS

### 2.1. Sampling

Location of field survey is shown in Figure 1. This land-use map was referred from a paper by Yermoshin et al. (2007). Water samples from the lower Amur River were taken from surface and bottom layers at 10-13 stations during research cruise on August 16-24th in 2005 and on August 6-15th in 2007. We also carried out research expedition for the estuary, Amur Liman and Sakhalin Bay on August in 2006 and 2008. Salinity, pH, conductivity and turbidity were measured *in-situ* by a water checker (TOA DKK WQC-24). Monitoring survey was performed at Khabarovsk, Bogorodskoe, and Nikolaevsk-na-Amure once a month during 2006 to 2008. The water samples were filtered with Nucleopore filters and acidified to  $\text{pH} < 2$  with HCl for analyses of trace elements. The water samples collected during the research expedition in 2005 were filtered with Whatman GF/F glass fiber filters for the trace metal analyses due to high turbidity. Dissolved organic carbon (DOC) and spectroscopic analyses were used for water samples filtered with GF/F filters.

### 2.2. Analytical methods

Dissolved iron concentration was measured for the river water samples using ICP-MS. Dissolved + acid leachable iron concentration was measured for the water samples from the river estuary, Amur Liman and Sakhalin Bay by colorimetry with 1.10 phenanthroline after the addition of HCl and the filtration. The iron content of riverine suspended solid, soil and river bottom sediment was measured by ICP-MS following total acid digestion with a mixture of  $\text{HCl} + \text{HNO}_3 + \text{HF}$ .

DOC concentration was determined for the river waters by wet chemical method (Levshina and Karetnikova, 2008). Three dimensional excitation emission matrix (3-D EEM) spectra of water samples were measured by fluorescence spectrophotometry according to the method of Nagao et al. (2003). Relative fluorescence intensity (RFI) of samples was expressed in terms of quinine sulfate unit (QSU).

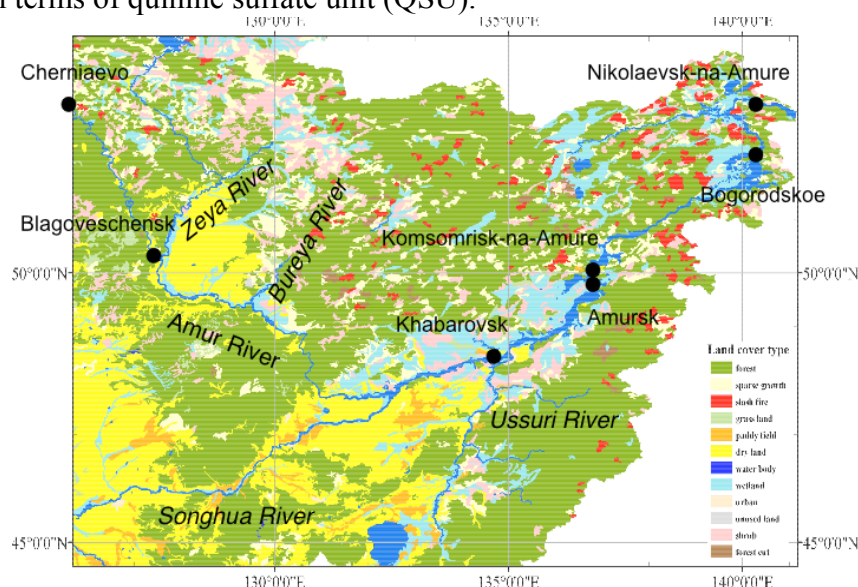


Figure 1 Sampling location of the Amur River

### 3. RESULTS AND DISCUSSION

#### 3.1. Spatial variations in iron concentration in the Amur River system

Nagao et al (2007a) summarized the variations in dissolved iron concentration in waters from the upper, middle and lower Amur River in 2002. The dissolved iron concentration was almost constant,  $0.11 \pm 0.13$  mg/l at Cherniaevo in the upper Amur and  $0.41 \pm 0.09$  mg/l at Blagoveschensk in the middle Amur. On the other hand, the iron concentration at Khabarovsk had variation ranging from 0.38 mg/l to 1.12 mg/l and showed a maximum in summer season. The similar variation was found at Amursk, Komsomrisk-na-Amure, and Nikolaevsk-na-Amure in the lower Amur River, though the maximum value was lower than the Khabarovsk site. The tributaries located in wetland around Khabarovsk also had high iron concentration in summer. These results indicate that wetland around Khabarovsk is major sources of iron in the lower Amur River waters.

#### 3.2. Temporal and downward variations of iron concentration in the Amur River

Water samples were collected during the research cruise of R/V *Ladoga* on August in 2005 and 2007 under collaboration with the Institute of Water and Ecology Problems (IWEP). Nagao et al. (2007a) have shown that dissolved iron concentration in the Amur River waters from Khabarovsk to Nikolaevsk-na-Amure together with the results of the middle Amur River, Songhua River, Ussuri Rive in Sanjiang Plain on July-August in 2005. In the Ussuri River, dissolved iron concentration increased from 0.17 mg/l at the upstream to 0.44 mg/l at the downstream. The Songhua River had high iron concentration from 0.68 mg/l to 0.73 mg/l. However, water samples in lower part of the middle Amur had iron concentration of 0.27-0.33 mg/l. On the other hand the iron concentration ranged from 0.55 mg/l to 0.70 mg/l at the lower Amur River. Maximum iron concentration was found at the sampling points located in the wetland area around Khabarovsk, Malmyzh and Sofiiskoe. The tributary waters collected from wetland extended around rivers indicate 2-3 times higher than the Amur River waters. The results from river expedition coincide with the spatial variations for iron.

There is a good positive correlation between iron and DOC concentration from these data set. The relationship has been reported for the rivers flowing through wetland (e.g., Tani et al., 2001; Shibata et al., 2004; Heikkinen, 2006). The brownish river waters in wetlands indicate higher percentage of humic substances having high affinity for multivalent ions (Aiken et al., 1985). Therefore, these results from the Amur River suggest that major part of dissolved iron is present as organic complexes. The similar variation trend for DOC and iron was also observed during the research expedition on August in 2007.

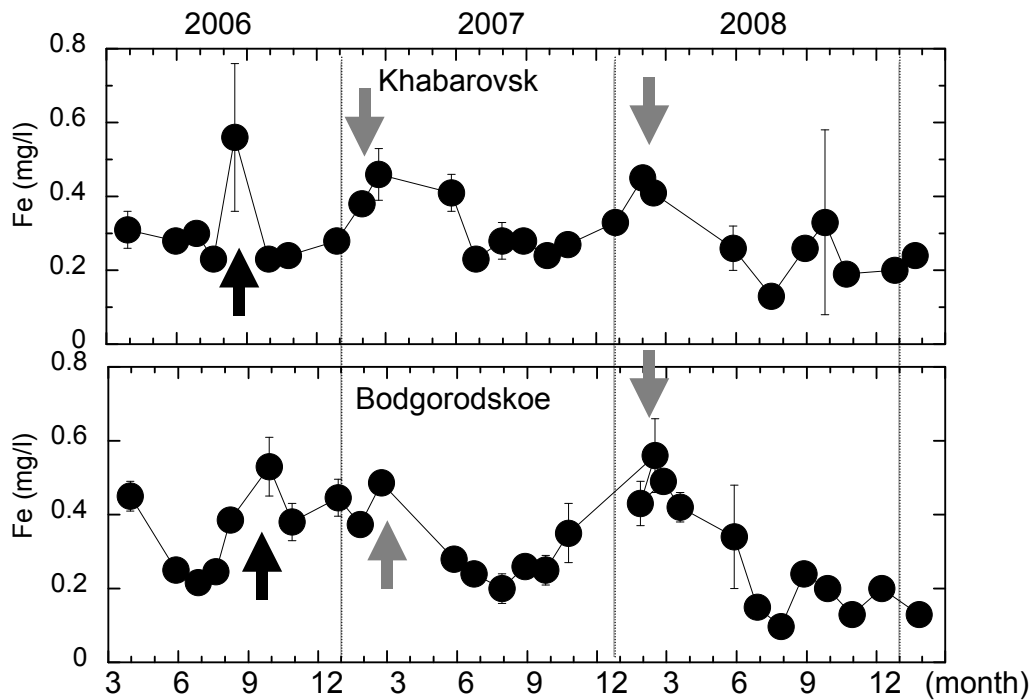


Figure 2 Variations in dissolved iron concentration at Khabarovsk and Bodgorodskoe in 2006-2008.

Figure 2 shows temporal variations of dissolved iron in the Amur River waters at the monitoring stations during 2006-2008. Averaged value of dissolved iron is  $0.30 \pm 0.10$  mg/l for the Khabarovsk and  $0.31 \pm 0.13$  mg/l for he Bogorodskoe, and two orders magnitude higher than that of world rivers (Dai and Martin, 1995). Higher concentrations of iron have been observed in many boreal rivers with drainage from peatlands. As shown in Figure 2, peaks of dissolved iron were found in summer and winter season before snowmelt due to different mechanisms. In the view point of iron export, we focus on the summer peak because of high water discharge. Maximum iron concentration in 2006 apparently relates to high water level of the Amur River at Khabarovsk point reported by Makhinov et al. (2007) and Kim et al. (2008). The change in water level of rivers is directly related with the groundwater level and biogeochemical conditions of wetlands. Therefore, the water level is one of important factors controlling dissolved iron concentration in the lower Amur River.

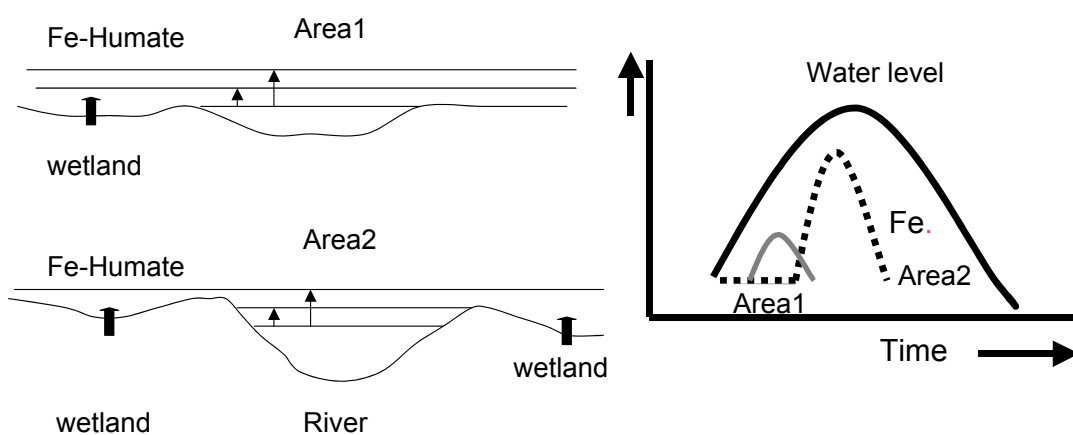


Figure 3 Schematic illustration of supply mechanism of dissolved iron from watershed to river.

Counter plots for fulvic-like materials have been reported for the middle and lower Amur River during the river expedition in 2005 and 2007 by Nagao et al. (2009). The water samples from the middle river exhibited a broad maximum at Ex. 318-323 nm/ Em. 410-430 nm. On the other hand, the lower Amur River waters, downstream below Khabarovsk, had two broad maxima at Ex. 313-318 nm/ Em. 427-433 nm and Ex. 338-356 nm/ Em. 465-480 nm. Two fluorescent peaks have been reported for the Suwannee River fulvic acid (Nagao et al., 2003), which is located in the Okefenokee Swamp, and for the brownish river waters through wetland (Kumegawa, 2007; Nagao et al., 2007b). Non-colored river waters with the DOC concentration less than 2 mg/l have a broad maximum at shorter wavelengths of excitation and emission (Suzuki et al., 1997, Nagao et al., 2003). Therefore, wetland origin fulvic-like materials are present in the lower Amur River waters. Humic substances including fulvic acid occupy more than 35% of DOC in river waters (DOC 5mg/l<) running through wetlands (Aiken et al., 1985; Miles et al., 1996; Sharp et al., 2006) and high complexation for iron (Pettersson and Bishop, 1996; Setiawan et al., 2002).

Figure 3 shows schematic illustration on supply of iron from watershed to river. When the water level rise up over river bank due to rainfall event in summer season, flooding water spills out to the wetlands. Type of wetland and its geomorphological features are related to the release of iron. From our monitoring study in 2006, dissolved iron may be released from wetlands as humate complexes. Dissolved iron supplied from wetlands depends on the geomorphology and water level of the Amur River because of changing DOC concentration, microbial activities and redox conditions for wetlands (Olivie-Lauquet et al., 2001; Grybos et al., 2007).

### **3.3. Estimation of iron flux at Khabarovsk**

Time series of dissolved trace elements in rivers are important for flux calculation and for understanding the mechanisms controlling the concentrations of these elements. Monthly monitoring survey has been conducted at Khabarovsk by the Hydromet from 1960 to present. Nagao et al. (2007a) estimated annual iron flux on the basis of data set every five years from 1960 to 2000 and 2002. The iron concentration ranged from 0.04 mg/l to 1.28 mg/l. There was a maximum in summer in 1975, 1980, 1995, and 2002. Flux of dissolved iron at Khabarovsk site was estimated using water discharge weighted mean value of dissolved iron from 1960 to 2002. The dissolved iron flux increases with increasing time from 1960 to 1975, and then has some variation ranging from  $0.56 \times 10^{11}$  g/yr to  $1.57 \times 10^{11}$  g. Onishi et al. (2008) have shown that the averaged flux is  $1.1 \pm 0.7 \times 10^{11}$  g/yr and is about one-tenth of the global riverine flux (Raiswell, 2006). The iron flux in summer (July-September) is  $50 \pm 13\%$  of the annual flux and is important for the export of iron from the Amur River Basin (Nagao et al., 2007a). This suggests important role of wetlands as iron source of the Amur River Basin.

### **3.4. Fate of iron in the Amur Liman and Estuary environments**

Our research group focuses on geochemical behavior of iron at estuary, which is mixing zone between freshwater and seawater, to understand physico-chemical forms of iron from the Amur River through the Amur Liman to the Sea of Okhotsk. Nagao et al. (2008)

have shown the concentration of dissolved + acid leachable iron, turbidity and DOC concentration at nine sampling station from the estuary to Sakhalin Bay. The concentration of dissolved + acid leachable iron ranged from 1.78 mg/l to 2.96 mg/l in the estuary, and rapidly decreases at the Amur Liman. Above 90% of dissolved and acid leachable iron, that is some part of suspended solids, was 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).

Terashima and Nagao (2007) reported the behavior of iron in the estuarine environments using laboratory experiments with mixing between freshwater and artificial seawater. They showed that iron was rapidly removed from the sample solution at salinity of 5‰. From salinity of 12-33‰, 90% and 43% of iron were precipitated in the presence of humic and fulvic acids, respectively. Similar results have been reported by Sholkovitz (1976), Fox and Wofy (1983), and Guo et al. (2000). The removal rate of iron is different from the results of research expedition. This may be contributed by the interaction of suspended particles.

Figure 4 shows schematic illustration on the export mechanism of iron from river through estuary to Sakhalin Bay. When dissolved iron transport to the estuary environments, iron coagulates and precipitated to the bottom sediments due to the mixing between fresh river water and seawater. The surface sediments collected by Ekman-grab sampler during the research cruise in 2006 and 2008 are sandy at the Amur Liman and Sakhalin Bay. We did not recognize the presence of fine particles such as iron oxyhydroxides and clay minerals. Averaged iron content at the area is  $1.4 \pm 0.6\%$  and one-fourth of the river bottom sediments. From the field survey, analytical results and laboratory mixing experiments, we conclude that riverine dissolved iron mainly export from estuary to the Sea of Okhotsk as particulate forms. Particulate iron supplies to the Okhotsk intermediate water, which is the source water for ventilation of northwestern North Pacific. However, Nakatsuka et al. (2007) have shown that the concentrations of dissolved iron in surface water at the sites close to the Amur River mouth ( $5-20 \mu\text{g/l}$ ) are two orders magnitude higher than the Oyashio intermediate water. Therefore, major part of iron in the Amur Liman is coagulated, but small part of iron may be still dissolved in saline and seawaters as iron-humate complexes.

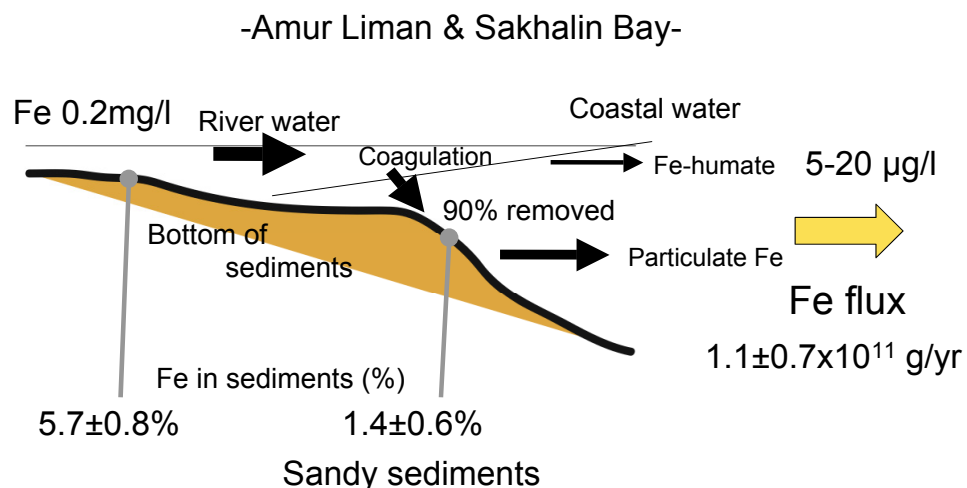


Figure 4 Fate of dissolved iron in the Amur River water at the estuarine environments.

#### 4. SUMMARY

Sub-group 3 has been carried out the research expeditions at the lower Amur River, its estuary, Amur Liman and Sakhalin Bay to understand biogeochemical behavior of iron in the Amur River system. We also performed monitoring survey at Khabarovsk, Bodogorotkoe, Nikolaevsk-na-Amure during 2006 to 2008. From these field observations and laboratory experiments, we got following results:

- 1) Dissolved iron flux from the Amur River to the Sea of Okhotsk is estimated as  $1.1 \pm 0.7 \times 10^{11}$  g/yr.
- 2) Major sources of iron in the lower Amur River waters is wetlands around Khabarovsk and Malmyzh-Sofiiskoe. Dissolved iron concentration shows maximum in summer and water level is main factor controlling dissolved iron concentration in the river waters.
- 3) More than 90% of dissolved iron is removed from waters as particulate forms but still high concentration (5-20 µg/l) at the Amur Liman. The export of iron from the Amur Liman to the Sea of Okhotsk may be two pathways. The dissolved iron transports to surface layer in the Sea of Okhotsk and particulate forms may be transported to the Okhotsk intermediate layer.

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