# TRANSPORT OF BIOGEOCHEMICAL MATERIALS FROM THE AMUR River to The Sea of Okhotsk

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## **ROLE OF IRON FOR PRIMARY PRODUCTION**

The importance of the role of iron as a limiting micronutrient for primary production in the world ocean has become increasingly clear following large-scale in-situ iron fertilization experiments in HNLC regions. Dissolved iron (III) has been found to be >99% complexed by strong organic ligands in seawater (Gledhill and van den Berg, 1994; van den Berg, 1995; Rue and Bruland, 1995; Wu and Luther, 1995; Kuma et al., 1998; Powell and Donat, 2001). The presence of strong organic complexation has a significant effect on the speciation and solubility of iron in seawater (Ussher et al., 2004).

Humic substances are naturally occurring, biogenic, heterogeneous organic substances that can be characterized as being yellow to black in color, of high molecular weight, and refractory (Aiken et al., 1985). These substances have a great ability to form complexes with trace metals, and thereby act as carrier influencing the mobility and distribution in the water of the metals (Stevenson and Fitch, 1986; Weber, 1988). Humic substances, which are supplied by riverine input, contribute to iron complexation and keep iron in a soluble form at neutral pH and high salinity environments in estuarine system (Hering and Morel, 1988). It has been demonstrated that iron-humate complexes stimulate the growth of coastal marine phytoplankton in laboratory cultures (Graneli and Moreira, 1990; Carlsson and Granet, 1993; Matsunaga et al., 1998) and contribute to the phytoplankton bloom in marine coastal waters (Glover, 1978). Therefore, the concentration and forms of dissolved iron has an important role in the limitation of the production of phytoplankton in estuary, costal sea and pelagic ocean.

#### TRANSPORTATION OF IRON FROM RIVER TO OCEAN

Figure 1 shows the possible sources of iron to the Amur River. The sources of iron to the river water may be considered to be forest soils, and groundwaters in the middle of Amur, and bogs and swamps in the middle and lower Amur area. Schesterkin (2004) reported that averaged iron concentration was about 0.2 mg/l and 0.7mg/l for the Amur River water at Blagoveshchensk and Khavarovsk, respectively. Therefore, the main sources of iron in the Amur River water may be considered to be supplied from the Middle of Amur. The iron concentration was 2.57-4.84 mg/l for the Sungary junction, 1-54 mg/l for the groundwaters in the Middle of Amur and ~25mg/l for the bogs and swamps in the Middle and Lower Amur. The study on the distribution and dissolved forms of iron in the Middle and Lower Amur is

important to understand sources and transport of iron from watershed to the river.

Iron is transported to the ocean via three pathways: riverine input, atmospheric deposition, and processes occurring on the sea floor. Rivers and land run-off are estimated to supply approximately half of the surface global iron input to the ocean. In our preliminary research, we estimated the flux of dissolved iron from the Amur River to the Sea of Okhotsk as about  $2.0 \times 10^{10}$  g/yr on the basis of the reported values in other Siberian rivers (Nakatsuka, per. com.). These values are obviously higher than the estimated flux of aerosol iron from atmosphere. Therefore, dissolved iron from the Amur River is considered to be one of key elements supporting the biomass production in the Sea of Okhotsk. However, these estimates are based on tentative observation of water chemistry in the estuarine area and do not cover the seasonal and/ or inter-annual variation of the flux.

The distribution of iron in estuaries is well documented and the dissolved iron is removed by mixing with seawater due to the neutralization, and the major fraction being on suspended particulate matter through colloidal flocculation (Scholkovitz et al., 1978, Scholkovitz and Copland, 1981). Estuarine mixing reduces the global dissolved iron flux to the ocean by about 70-95% because of the scavenging of iron (Chester, 2000). Schematic illustration is presented in Fig. 2. The geochemical behavior of iron in the Amur-Liman and Sakhalin Bay is important to estimate the iron flux from the Amur River to the Sea of Okhotsk. Powell and Finelli (2003) have shown that iron is transported a great distance from the Mississippi River due to the complexation with organic ligands and is available for biological utilization in the coastal zone. To estimate future change in the iron flux, we have to clarify the variability of iron flux and its mechanisms.

### SAMPLING PLAN FOR THE AMUR-OKHOTSK PROJECT

In this sub-theme (group 3), we make a following research plan to understand migration behavior of iron throughout the Amur River and Amur-Liman.

1) Seasonal water sampling at monitoring stations in the Amur River system.

We will understand the special and temporal variations in iron concentration in river waters from the Amur River system. We will compare the variation pattern in iron concentration with watershed environments of the river system.

2) Continuous water sampling at several fixed station along the Amur River.

We will cover the seasonal and inter-annual variations for chemical components including dissolved and suspended iron and dissolved organic matter.

3) The research cruise throughout the Amur River.

To understand the source area of iron dissolved in the Amur River waters, the one-dimensional distributions across the many tributaries will be investigated by this cruise.

4) The research cruise at the Amur Liman and Sakharin Bay.

We will focus on the relationship between salinity and iron concentrations in dissolved and suspended forms, emphasizing changes in the molecular and mineralogical characteristics of iron-containing matter, and its relationship to dissolved organic molecules (humic substances).

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Fig.1 Schematic illustration of sources of iron in the Amur River system. The iron concentration was taken from Schesterkin (2004)



Fig.2 Schematic illustration of geochemical behavior of iron in estuarine area.