MIGRATION BEHAVIOR OF FE IN THE AMUR RIVER BASIN

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1. STUDY ITEMS OF RESEARCH GROUP-3

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). The key element supporting the biomass production in the Sea of Okhotsk is considered to be iron, especially “dissolved iron” from the Amur River. The Amur River drainage was historically developed after the end of 19^{th} century in the Russian Part. Accelerated human impacts became more obvious after the middle of 20^{th} century in Russian and Chinese side of the Amur River (Zhang et al., 2004, 2005, Kakizawa et al., 2005). The area is being disturbed currently by various anthropogenic and natural impacts. Land-use change in the Amur River drainage might have caused significant changes in the flux of dissolved iron. We will understand the relationship between watershed environments and land-use in the Amur River basin and present ecosystem in the Sea of Okhotsk. One of goal of the project is to elucidate the mechanism how the dissolved iron and fulvic acids are formed and transported to the ocean by the Amur River, and how the flux changes will affect the phytoplankton production in the Sea of Okhotsk.

In this sub-theme (Research Group 3), we make a research plan to understand migration behavior of iron throughout the Amur River and Amur-Liman as follows:

1) Seasonal water sampling at monitoring stations along the Amur River;
2) The research cruise throughout the Amur River;
3) The research cruise at the estuary of Amur River, Amur Liman and Sakhalin Bay.

2. TRANSPORT OF DISSOLVED IRON IN RIVER WATERS FROM THE AMUR RIVER SYSTEM

2.1 Spatial and temporal variations of iron concentration in the Amur River system

Figure 1 shows dissolved iron concentration in the waters from Amur River together with water discharge at Khabarovsk in 2002. The iron concentration was almost constant at Cherniaevo (0.11±0.13 mg/l) in the upper Amur and at Blagoveschensk (0.41±0.09 mg/l) in the middle Amur. On the other hand, the iron concentration at Khabarovsk had large variation ranging from 0.38 mg/l to 1.12 mg/l. There were three peaks before increasing water discharge. 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

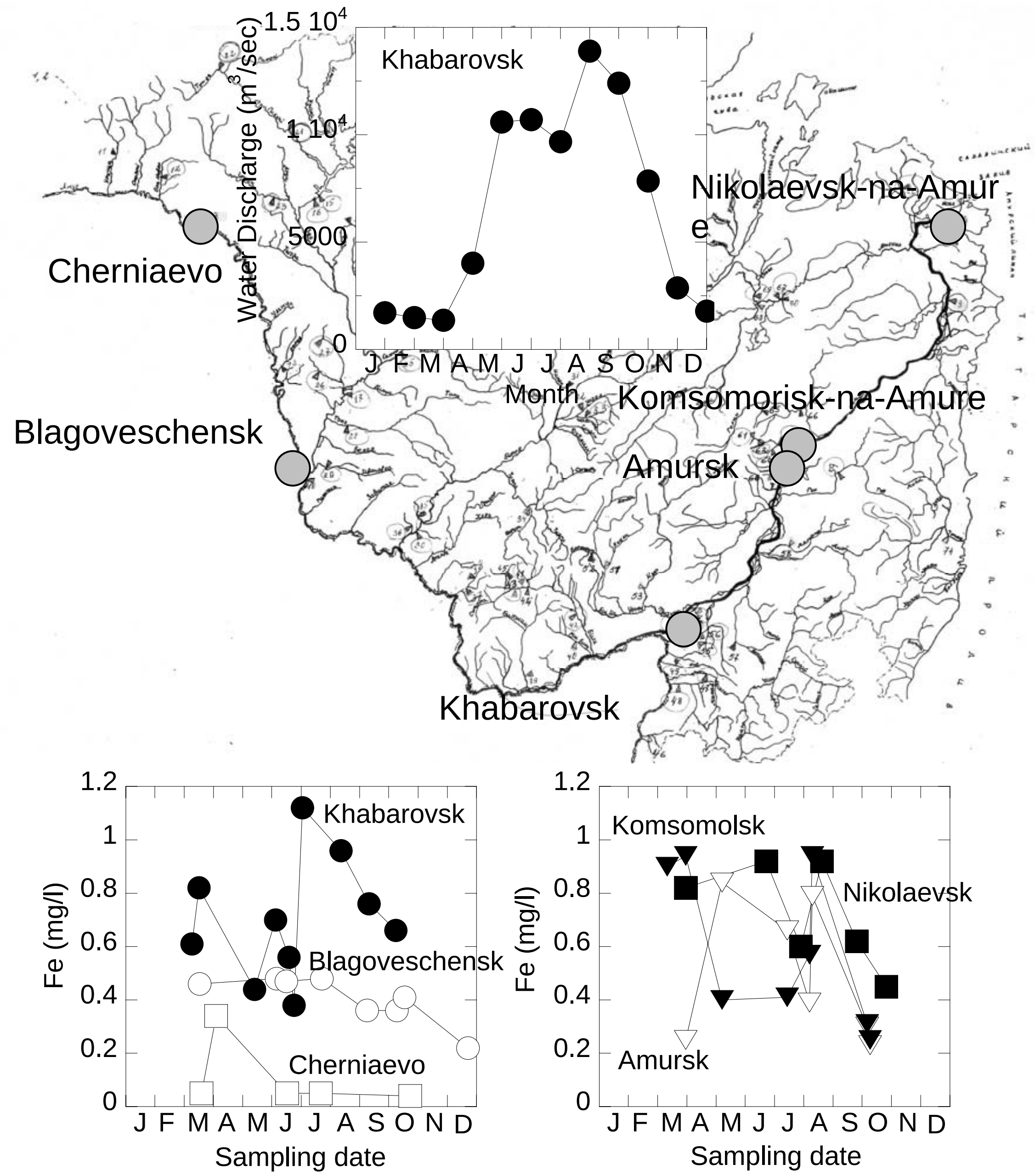

Fig.1 Monitoring observation points in the Amur River, water discharge and dissolved iron concentration in river waters in 2002. The water discharge is monthly mean value.

the Khabarovsk site.

Figure 2 shows dissolved iron concentration in river waters from main tributaries of the Amur River in 2002. The Zeya River, a major tributary of the Amur River, had the variation patterns as follows: 1) maximum concentration in July at St. 45 and, 2) in spring at St.15 and St.17, 3) almost constant at other stations. The iron concentration of Bureya River ranged from 0.13 mg/l to 0.73 mg/l. In the small rivers at St. 32-St. 35 in wetland near Khabarovsk, maximum of dissolved iron concentration was found in March and July. This is similar variation pattern with the Khabarovsk site. These results suggest that wetland near Khabarovsk may be one of important source area for dissolved iron in river waters from the

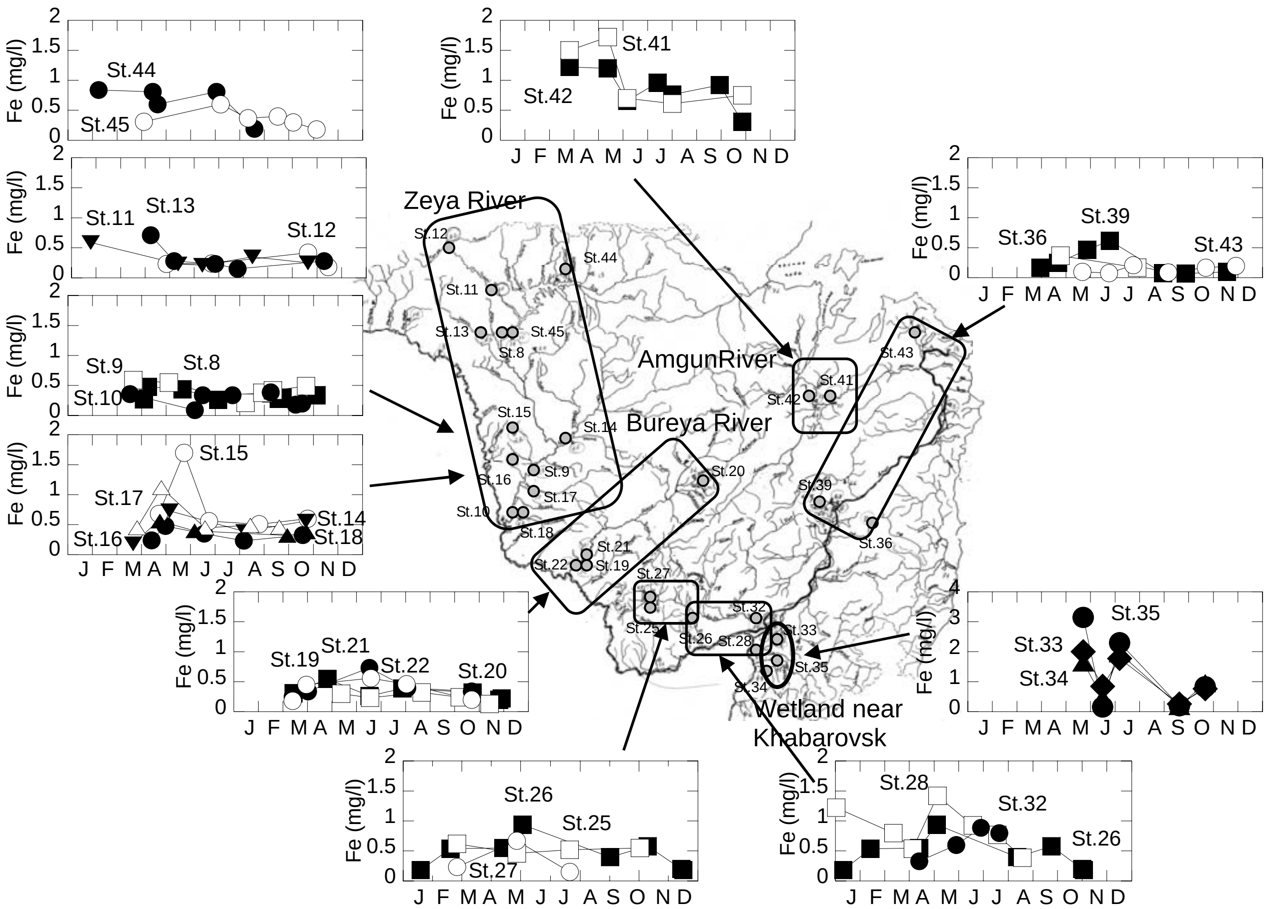

Fig.2 Dissolved iron concentration in river waters from the Amur River system in 2002.

lower Amur.

2.2 Dissolved iron concentration of the lower Amur River

Figure 3 shows sampling points at the research cruise of Lower Amur River in August 16-24. Water samples were collected during cruise of R/V *Radoga* in collaboration with the IWEP. We performed research and sampling at the Amur River, its tributaries and surrounding wetland. From August 8 to 11, our Chinese collaborators collected river water samples from the Amur River, Songhua River, Ussuri River and their tributaries in Sanjiang Plain. They also collected agricultural drainage and groundwater samples. The water samples were filtered with Whatman GF/F glass fiber filters and acidified to pH<2 with HCl for analyses of trace elements. Dissolved iron was determined by inductively coupled plasma atomic emission spectroscopy.

The lower panel of Fig. 3 shows pH and dissolved iron concentration in river waters collected at the research cruises. The Amur River water samples in lower part of the middle Amur had iron concentration of 0.33 mg/l at St.21 and 0.27 mg/l at St.14. In the Ussuri River, not shown in figure, dissolved iron concentration increased from 0.17 mg/l at the upstream to 0.44 mg/l at the downstream. On the other hand, the Songhua River had high iron concentration from 0.68 mg/l to 0.73 mg/l. As shown in Fig. 3, the iron concentration ranged from 0.55 mg/l to 0.70 mg/l at the lower Amur River. It appears that the iron concentration increases from 0.27 mg/l at St.14 to 0.68 mg/l at St.G. The maximum concentration was found

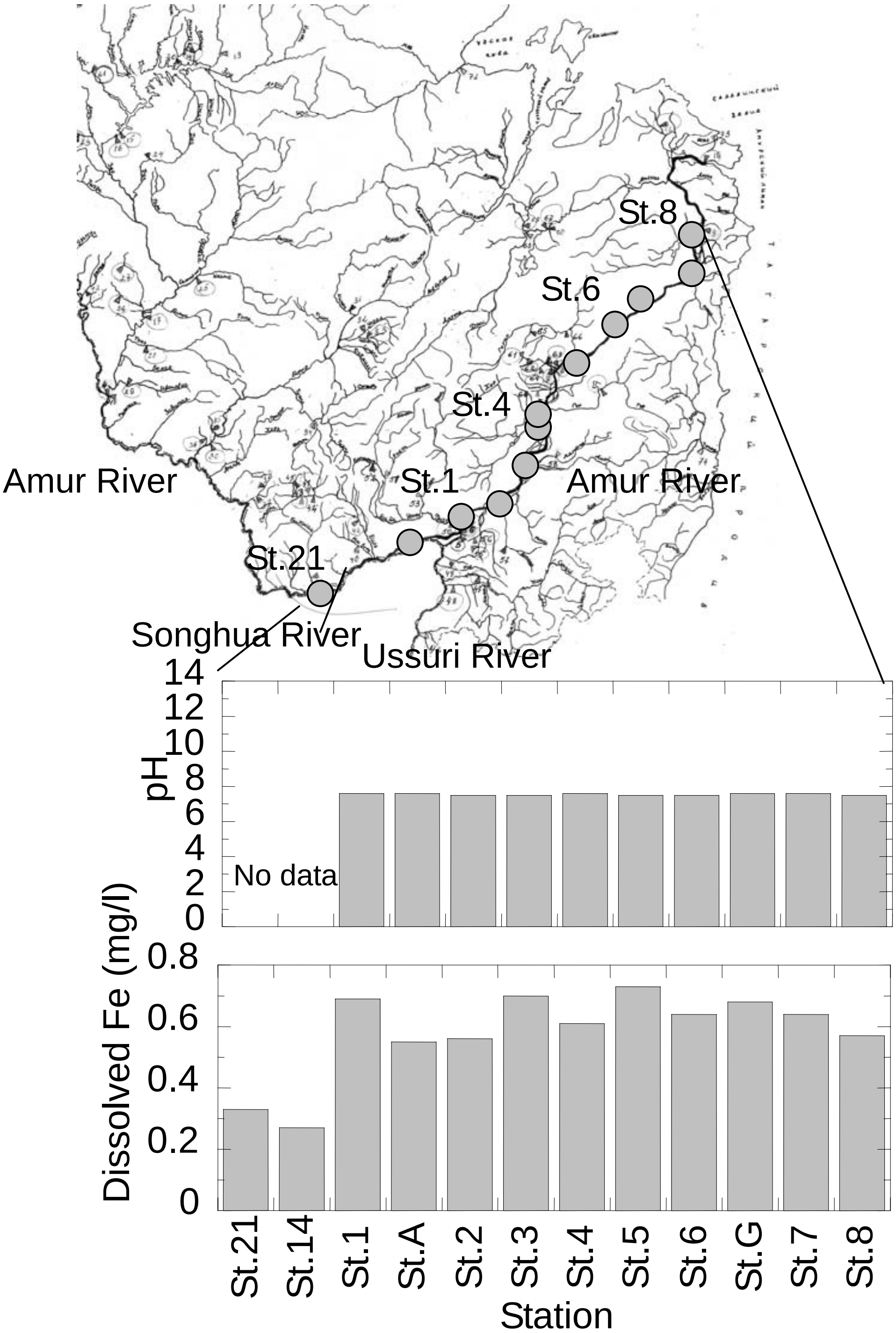

Fig.3 Variations in pH anddissolved iron concentration in river waters from the middle and lower Amur River in August, 2005. Closed circles indicate sampling stations in the Amur River.

Table 1 Iron concentration of the Amur River waters and iron flux during the research cruise in August, 2005.

Station	Water discharge ($x10^3 m^3$/sec)	Fe conc. (mg/l)	Fe flux ($x10^8$g/day)
St.1	11.0	0.57	5.41
St.4	12.0	0.61	6.32
St.6	15.5	0.64	8.57
St.8	17.4	0.57	8.57

at the sampling points of St.1, St. 3 and St.5. These sampling points are placed in the wetland area. The river waters collected from wetland extended around rivers indicate 2-3 times higher than the Amur River waters. Therefore, these results indicate the supply of dissolved iron from wetland area.

Flux of dissolved iron at each sampling point in the Amur River was estimated by averaged iron concentration from cross-section observation and water discharge at each sampling date. The results are shown in Table 1. The iron flux increased from $5.41x10^8$g/ day at St.1 to $8.57x10^8$g/day from St.6 to St.8. The difference in iron flux at St. 1 and St.4 suggests the supply of iron from watershed to river waters in the lower Amur River, and it apparently keeps a steady state condition for the supply and removal of dissolved iron in the watershed area at St. 6 and St.8. The differences in the iron flux between sampling stations is estimated and shown in Fig. 4. The iron flux at St.14 was estimated on the basis of the assumption for water discharge of $11.0x10^3$ m^3/sec measured at St. 1. The amount of iron supplied from watershed is $2.56x10^8$ g/day near Khabarovsk, “Area B”, $0.91x10^8$ g/day at “Area C” and $2.25x10^8$ g/day at “Area D”. The watershed area including wetland near Khabarovsk and Nitzhnetambovskoe is important as sources of dissolved iron in the Amur River. However, the upper and middle of Amur River with larger watershed area also has the contribution of supply of dissolved iron because of the iron flux of $2.86x10^8$ g/day. This value is three to four order magnitude higher than the lower Mississipi River reported by Shiller (1997).

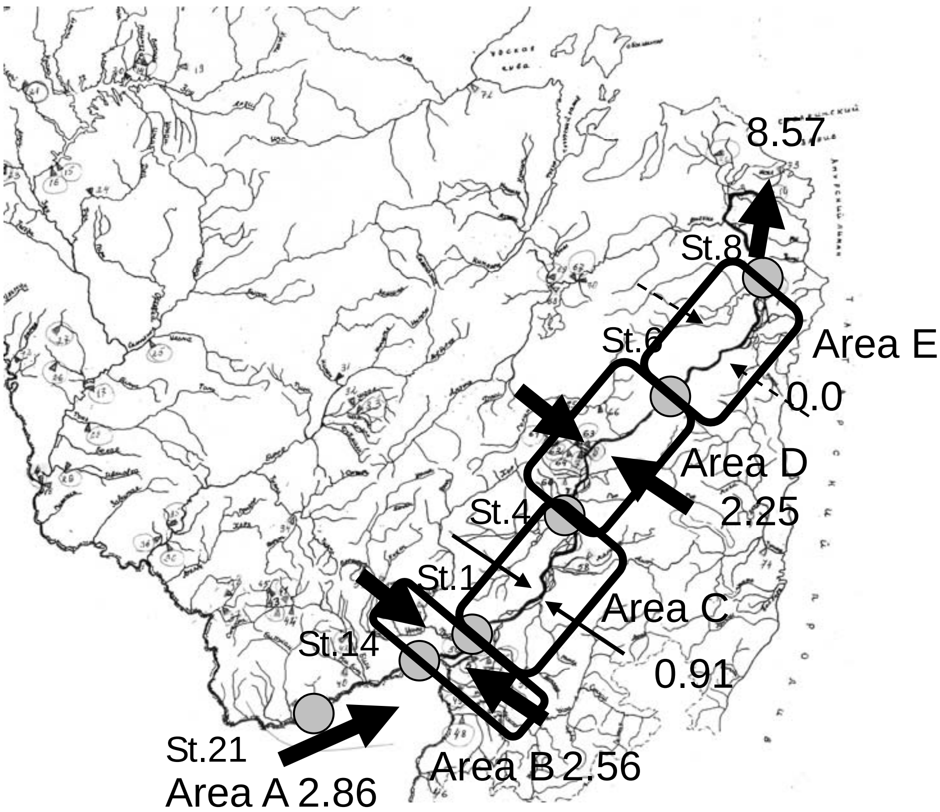

Fig.4 Flux of dissolved iron from watersheds to river waters in the Amur River during the research cruise in August, 2005.The unit is $x10^8$g/day. In this study, we describe each area to “Area A” to ”Area E”.Area E is apparently no iron supply from watersheds to river.

Figure 5 shows relationship between dissolved organic carbon (DOC) and dissolved iron concentrations in the lower Amur River. There is a positive correlation between iron and DOC concentrations. These results indicate that major part of iron is dissolved as organic complexes. Figure 6 shows iron concentration versus DOC concentration in river waters from tributaries of the Amur River in Sanjiang Plain together with the results for drainage and groundwater samples. There is no correlation with iron and DOC concentrations for the river water samples because of different watershed environments at four rivers (Usuri River, Songhua River, Yalu River, and Nangjing River). The iron and DOC concentrations for drainage and groundwater samples are higher than the Amur River and shows positive correlations.

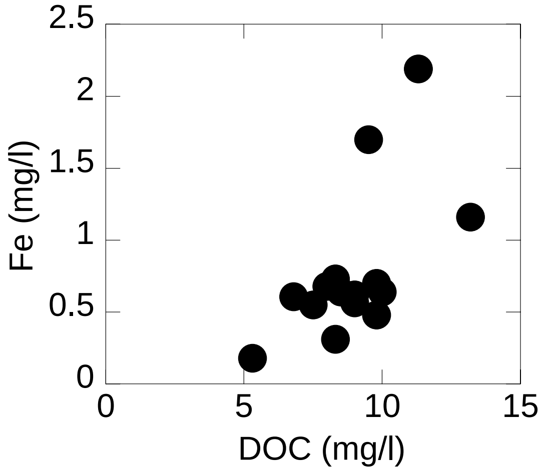

Fig.5 Variations in concentrations of dissolved iron and dissolved organic carbon (DOC) in river waters from the lower Amur River during the river research cruise from Khabarovsk to Nikolaevsk-na-Amure in August, 2005.

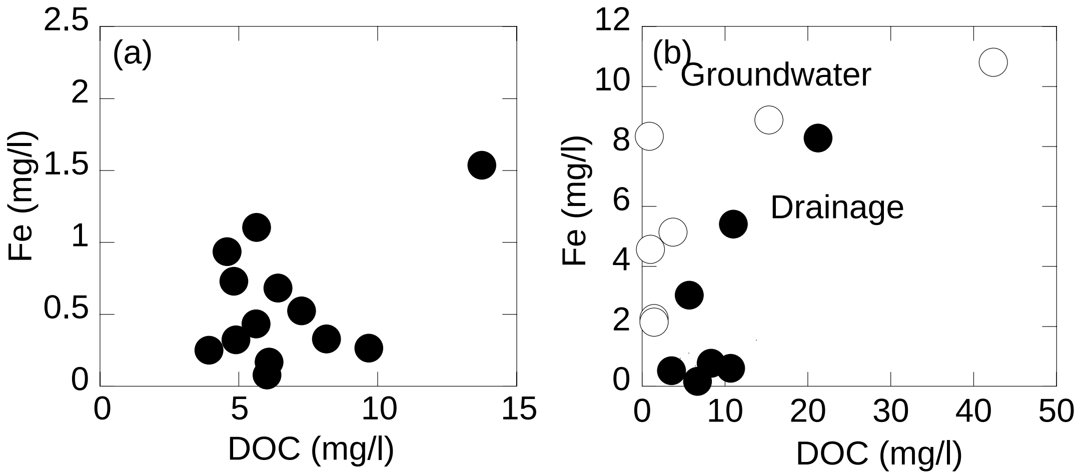

Fig.6 Variations in concentrations of dissolved iron and DOC in river waters from the tributaries of Amur River (a), and in drainage and groundwaters (b) in Sanjiang Plain in August 2005.

2.3 Temporal variations in dissolved iron concentration and its flux at Khabarovsk from 1960 to 2000

Time series of dissolved trace elements in rivers are important for flux calculation and for understanding the mechanisms controlling the concentrations of these elements in rivers. Monthly water samplings at the Khabarovsk monitoring site were conducted by the Hydromet from 1960 to 2002. Figure 7 shows time series results of iron determined in these samples. 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. These results are shown in Table 2 and Fig. 8. The dissolved iron flux increases with increasing time from 1960 to 1975, and then has some variations ranging from $0.56x10^{11}$g/yr to $1.57x10^{11}$g/yr. The iron flux can be divided into three groups as follows:

1) 1960, 1965, 1980, 1990 average annual Fe flux $0.62\pm0.08x10^{11}$g/yr;
2) 1970, 1985, 2000 average annual Fe flux $1.1\pm0.1x10^{11}$g/yr;
3) 1975, 1995, 2002 : average annual Fe flux $1.5\pm0.04x10^{11}$g/yr;

As shown in Fig.8, there is no relationship between annual water discharge and iron flux.

3. BEHAVIOR OF IRON IN ESTUARINE ENVIRONMENTS

Estuarine mixing reduces the dissolved iron flux to the ocean by 70-95% because of the scavenging of iron (Chester, 2000). It has been demonstrated that iron-humate complexes stimulate the growth coastal marine phytoplankton in laboratory cultures and contribute to the phytoplankton bloom in marine coastal waters (Graneli and Moreira, 1990, Carlsson and Granet, 1993, Matsunaga et al., 1998). 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.

3.1 Research cruise at the estuary, Amur-Liman and Sakhalin Bay

The research cruise was conducted in August 16-24, 2006. The sampling stations are shown in Fig. 9. Water samples from estuary of the Amur River were taken at three stations (St.1-3) by a speed boat. Water samples were also collected at four stations (St.4-St.7) from the Amur-Liman and at two stations (Stns. 8 and 9) in Sakhalin Bay during cruises of research vessel of Russian Navy in collaboration with the IWEP. These samples were filtered with Whatman GF/F filters for DOC analyses and 0.22 µm cartridge filter for trace element analyses. The fundamental analyses such as DOC, trace elements, nutrients etc. will be finished at the end of March in 2007.

3.2 Study on coagulation of iron in laboratory experiment

3.3 Association forms of iron in the river and estuarine environments

The results of above research items are present by Terashima and Nagao in this report.

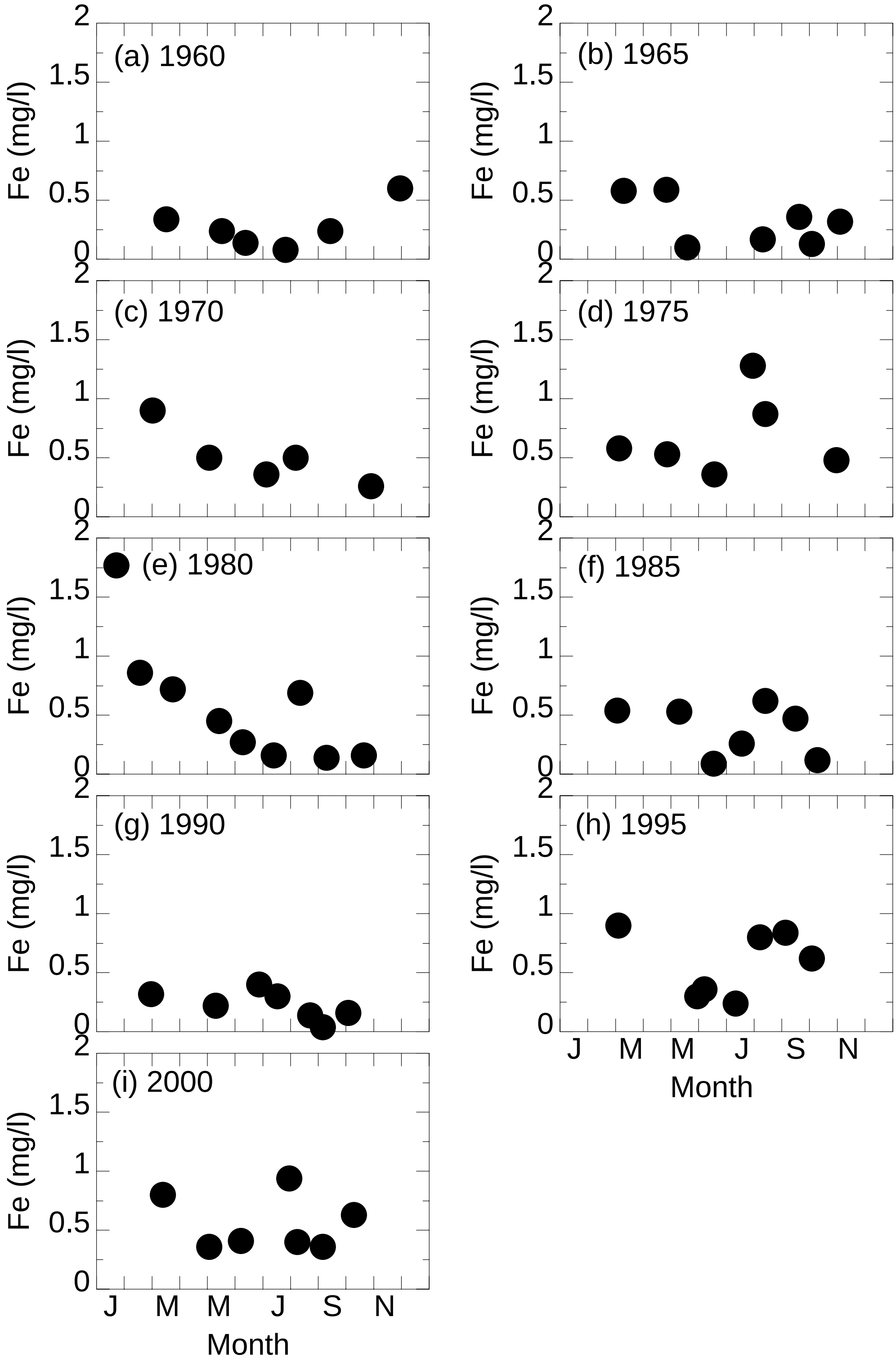

Fig.7 Dissolved iron concentration in the Amur River waters from 1960 to 2000. The water samples were collected at monitoring station near Khabarovsk.

Table 2 Iron flux at Khabarovsk monitoring station from 1960 to 2002.

Year	Water discharge ($x10^{11}m^3$/year)	Mean Fe conc.* (mg/l)	Fe flux ($x10^{11}$g/year)
1960	3.92	0.17	0.67
1965	2.47	0.23	0.56
1970	2.43	0.42	1.00
1975	1.96	0.76	1.50
1980	2.04	0.34	0.70
1985	3.17	0.38	1.21
1990	2.84	0.19	0.54
1995	2.76	0.55	1.51
2000	2.16	0.48	1.04
2002	2.07	0.76	1.57

*Water discharge weighted mean value.

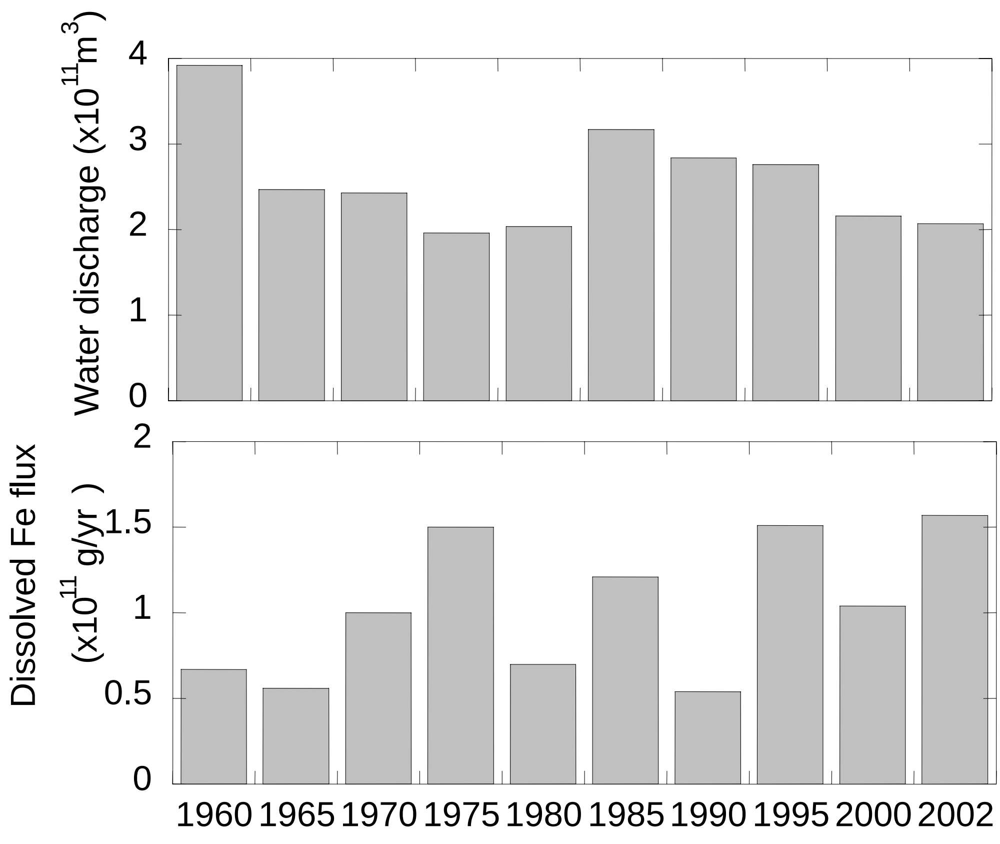

Fig.8 Annual water discharge and dissolved iron flux of the Amur River at Khabarovsk station.

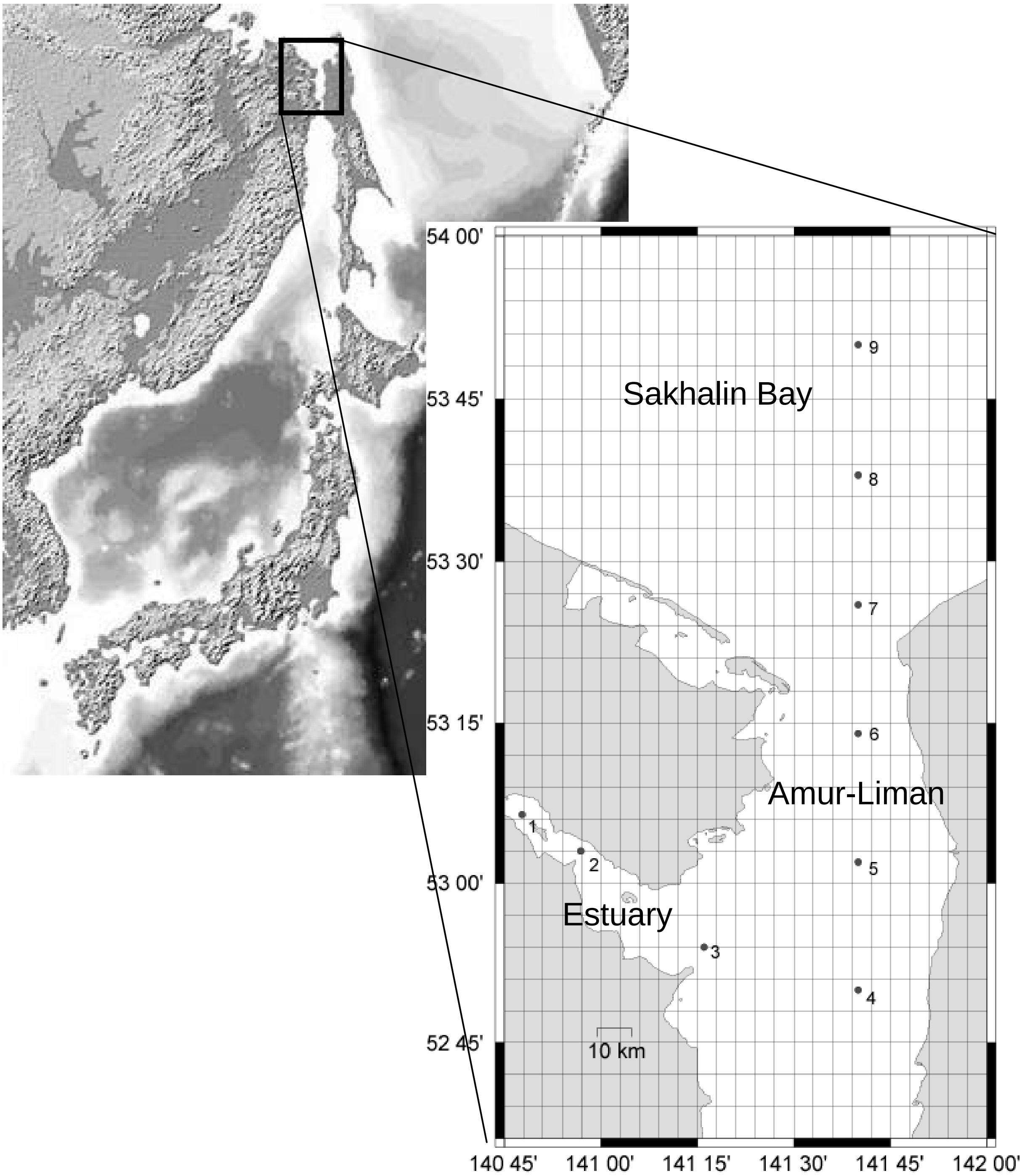

Fig.9 Sampling stations in estuary of the Amur River, Amur-Liman and Sakhalin Bay during the research cruise in August 2006.

4. FUTURE RESEARCH PLAN

We have plans for research cruises throughout the lower Amur River, its estuary and Amur-Liman, Sakhalin Bay at higher water discharge conditions in summer in 2007. We set up same sampling stations to compare the results with previous data in 2005 to understand transport behavior of iron in the Amur River system. We also continue to perform monitoring study at Khabarovsk and Bogorodtskoe, and will add the monitoring stations at estuary of the Amur River.

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