PROCESSES OF IRON TRANSPORT FROM TERRESTRIAL ECOSYSTEM TO RIVER:
PRELIMINARY ANALYSIS OF SPATIAL AND TEMPORAL PATTERNS OF IRON CONCENTRATIONS IN AMUR RIVER

SHIBATA HIDEAKI
Field Science Center for Northern Biosphere, Hokkaido University

INTRODUCTION

Although iron has been thought of as an important micro nutrient for ocean biological productivity (Ducklow *et al.* 2003), the sources and processes of iron in terrestrial ecosystems to rivers and oceans have not been well characterized. Analyses of biogeochemical processes of iron including the hydrological aspects from terrestrial ecosystems to rivers are very important to understand the fate of dissolved iron in the ground and water (Shibata *et al.* 2004). One of the major possible sources of mobile (dissolved) iron is soil and bedrock. Chemical and physical properties of soil and bedrock vary with several environmental factors. Topography, in watersheds, is one of the important drivers that creates soil moisture gradients along slopes. The result is different types of soil and vegetation depending on the soil moisture regime. For example in boreal regions, Spodsols and Cambisols are generally distributed in mountainous areas while Histosol and Fluvisol are distributed in the lowland and/or riparian area. These spatial distributions of soil and the related environmental characteristics are very important to understand the source of iron from soil because (i) chelating reactions of iron and dissolved organic carbon in the aerobic soil and (ii) mobilization of iron by the reduction processes in anaerobic soil are possible mechanisms that release iron from the solid to the liquid phase. Concentrations and fluxes of mobilized iron are transformed from the soil to rivers along varying groundwater flowpaths. Based on the above mentioned processes, iron concentrations in rivers largely fluctuate temporally and spatially in natural ecosystems.

In this paper, I analyzed spatial and temporal patterns of dissolved iron concentration in river water to examine the general pattern of iron dynamics from terrestrial to river ecosystems. This study was conducted as a preliminary survey for the integrated research project, 'Amur-Okhotsuk Project' that focused on the role of the iron supply, from the Amur River, on the biological productivity in the north Pacific ocean (Narita *et al.* 2004). This project also emphasizes human impacts (forest fire, timber production and land-use/cover change) on the iron dynamics between atmosphere-land-ocean continuums. The monthly water chemistry data from the Amur River were provided by the Hydrometeorological Office in Khabarovsk, Russia and were utilized in this analysis. The monthly river quality data were collected approximately monthly in 2002 although some months have no data in some sites especially during winter.

SPATIAL PATTERN OF IRON CONCENTRATION IN AMUR RIVER

Based on the monthly iron concentration data from Amur River in 2002 (Figure 1), the spatial pattern of the annual mean iron concentration from the main channel of Amur River is illustrated in Figure 2. All river iron concentration data in this paper is presented as dissolved total iron in water. Since each observation site for the main channel had 1-3 collections sites, respectively, there are 14 total sites for the main channel represented in Figure 2. Annual iron concentration increased from the uppermost site to Khabarovsk and was relatively stable from Khabarovsk to the lower part of Amur River (Figure 2). The annual-mean iron concentration of all sites was 0.56 ($\pm$0.17SD) mg L^{-1}. Four large tributary rivers were located from the uppermost site to Khabarovsk; Bureya, Zeya, Sungary (Songhua-Jyang) and Ussuri Rivers, implying that these tributaries supplied significant amount of iron to the main channel. Annual-mean discharge that was calculated from monthly mean discharge in Bureya and Ussuri River was 610 and 1590 m^3 s^{-1}, respectively, corresponded to 11 and 30 % of the annual-mean discharge (5310 m^3 s^{-1}) at the main channel in Khabarovsk, respectively. The relatively constant concentration of iron in stream water in the lower part of the Amur River might suggest that there is a relatively uniform supply of iron from the surrounding terrestrial ecosystems. Discharging groundwater through the large riparian wetland, located in the lower Amur, could be one of the possible sources of iron as well as abundant amounts of organic carbon to the main channel.

Figure 3 shows the spatial pattern of chloride (Cl$^-$) concentration in river water at the main channel of Amur River. Cl$^-$ concentrations in some sites were not observed in this dataset. Cl$^-$ concentration decreased with increasing iron concentration from the uppermost site to Khabarovsk (Figure 2 and 3). The contribution of tributary water affected the overall longitudinal spatial pattern of solute concentrations in the main channel. For example the Ussuri tributary contributed to the higher iron and lower chloride, in the upper reaches of the main channel (Figure 4). Furthermore, higher iron concentration found in the Ussuri River than in the main channel suggested the important role of this tributary as a supplier of iron (Figure 4).The difference in iron and Cl$^-$ concentration among each tributary river was most likely a function of varying water flow-paths, residence time and/or different source of Cl$^-$ from soil and bedrock. Comparison of solute chemistry in soil water, groundwater and river water would be useful to address more detailed mechanisms and to understand the source of this variation.

Data for the Sungary River (Songhua-Jyang), one of the largest tributaries that flows from China, were not available. Since the natural and human induced environments in Sungary (Songhua-Jyang) catchment are quite different from those in Russian catchments, integrated comparisons would be necessary to understand the role of tributaries in affecting solute concentrations in the main channel.

TEMPORAL PATTERN OF IRON CONETRATION IN AMUR RIVER

Seasonal fluctuation of monthly-mean discharge of the main channel at Khabarovsk (Figure 5) indicated that the highest discharge occurred from April to October in this basin. Figure 6 shows seasonal fluctuation in the monthly-mean concentration of iron and chloride in the main channel (average values are calculated using monthly mean data for each site in Figure 2 and 3). Iron concentration in the main channel tended to increase in April and August. According to correlation analysis between monthly-mean solute concentration (iron and chloride) and discharge (Figure 7 and 8), the relationship from March to April was quite different from those during other months for both iron and chloride. Note that discharge data at Khabarovsk were utilized as a representative for discharge in these analyses because discharge data in other sites were not available. There were significant relationships between iron (positive) and chloride (negative) with water discharge when the data from March and April were excluded (Figure 7 and 8). Similarly, there was a significant negative seasonal relationship between iron and chloride concentration (Figure 9) except for March and April. These results suggested that the seasonal fluctuation of iron and chloride exports to the river is strongly influenced by the seasonal hydrological pattern from the terrestrial ecosystem to the river. In general, chloride has been used as an inert and conservative tracer to understand solute transport by groundwater flowpaths to the river. The relationship between iron and chloride, therefore, suggests that chloride would be a useful signature to understand iron cycling and movement along hydrologic flowpaths. The different tendencies from March and April were found for both iron and chloride in the correlation analyses (Figure 7, 8 and 9). During March to April, ice breaking and higher discharge due to snowmelt are distinctive hydrological events in this region, implying that these different hydrological regimes could create different pattern of iron and chloride export to the river compared to that observed during other periods.

FUTURE DIRECTIONS

The series of analyses in this paper provided general information regarding the spatial and temporal pattern of the iron concentration in the Amur River from the middle to the lower basin. Although some important results were indicated, more intensive and integrated research would be necessary for a better understanding. An analysis to quantify the contribution of the Sungary (Songhua-Jyang) tributary from China as an iron-supplier to the Amur River would be especially critical to understand the iron dynamics in the Amur basin. In addition, human impacts including forest fire, timber production and land-use change on iron biogeochemistry (Harden *et al.* 2004; Palviainen *et al.* 2004; Shibata *et al.* 2003) are important to understanding longer temporal patterns and future predictions of iron supply from terrestrial to ocean ecosystems (Narita *et al.* 2004). Cross-site analysis including biogeochemical and hydrological monitoring in some watersheds would be a strong research tool to address the above-mentioned uncertainties and related research questions.

REFERENCES

Ducklow, H.W., Oliver, J.L. and Smith Jr. W.O. (2003) The role of iron as a limiting nutrient for marine plankton processes, In 'Interaction of the major biogeochemical cycles (Melillo, J.M., Field, C.B. and Moldan, B. Eds.)', Island Press, 295-310, Washington.

Harden, J.W., Neff, J.C., Sandberg, D.V., Turetsky, M.R., Ottmar, R., Gleixner, G., Fries.T.L. and Maines, K.L. (2004) Chemistry of burning the forest floor during the FROSTFIRE experimental burn, interior Alaska,1999. *Global Biogeochemical Cycles* **18**, GB3014, doi:10.1029/2003GB002194

Narita, H., Shiraiwa, T. and Nakatsuka, T. (2004) Human activities in northeastern Asia and their impact to the biological productivities in north Pacific ocean, In, 'Report on Amur-Okhotsk Project: Proceedings of the Kyoto Workshop 2004', Reseach Institute for Humanity and Nature, 1-24, Kyoto.

Palviainen, M., Finer, L., Kurka, A-M., Mannerkoski, H., Piirainen, S. and Starr, M. (2004) Release of potassium, calcium, iron and aluminum from Norway spruce, Scot pine and silver birch logging residues. *Plant and Soil* **259**: 123-136.

Shibata. H., Petrone, K.C., Hinzman, L.D. and Boone, R.D. (2003) The effect of fire on dissolved organic carbon and inorganic solutes in spruce forest in the permafrost region of interior Alaska. *Soil Sci. Plant Nutr.* **49**: 25-29.

Shibata, H., Konohira, E., Satoh, F. and Sasa, K. (2004) Export of dissolved iron and the related solutes from terrestrial to stream ecosystems in northern part of Hokkaido, northern Japan. In, 'Report on Amur-Okhotsk Project: Proceedings of the Kyoto Workshop 2004', Reseach Institute for Humanity and Nature, 87-92, Kyoto.
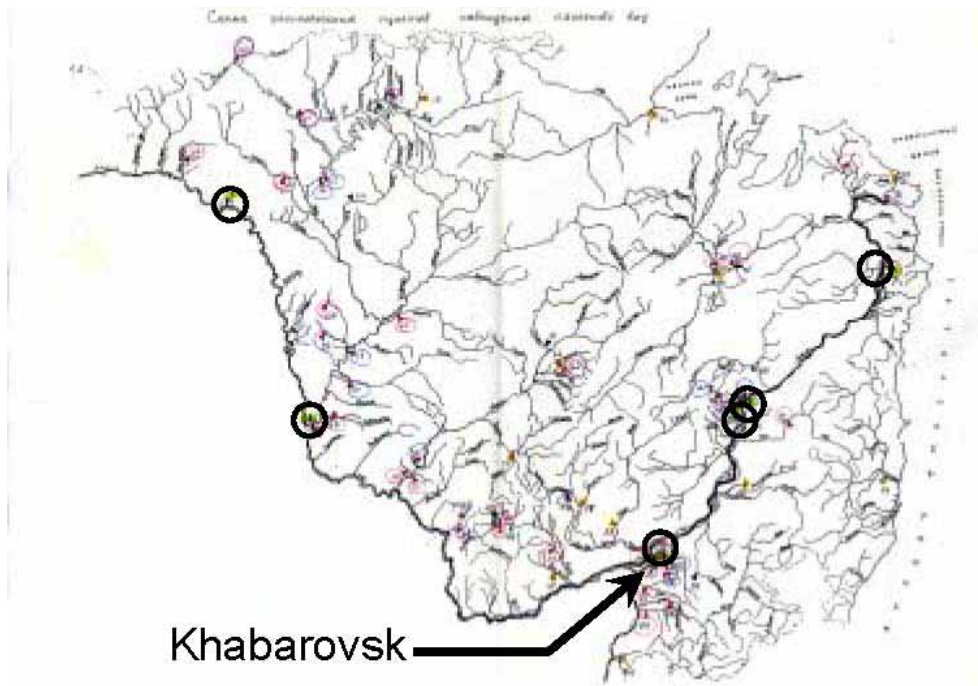
Figure 1. Location of observation sites at the tributaries and main channel of the middle to lower Amur River (provided by Hydrometeorological Office in Khabarovsk, Russia). Open circles show observation sites for the main channel of Amur River.
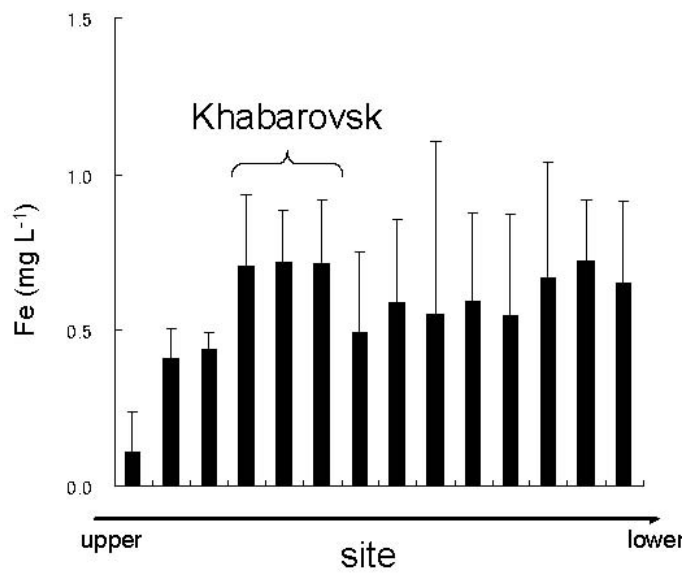

Figure 2. Spatial pattern of annual-mean concentration of iron (Fe) in river water at the main channel of Amur river. Each bar represents the standard deviation for each site.
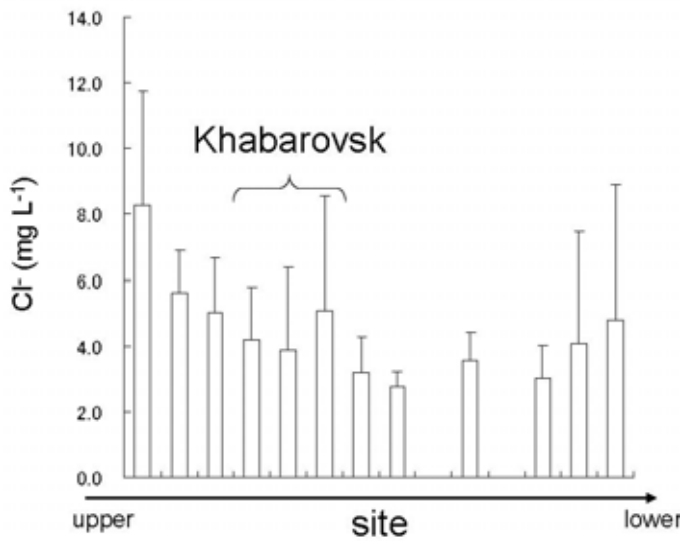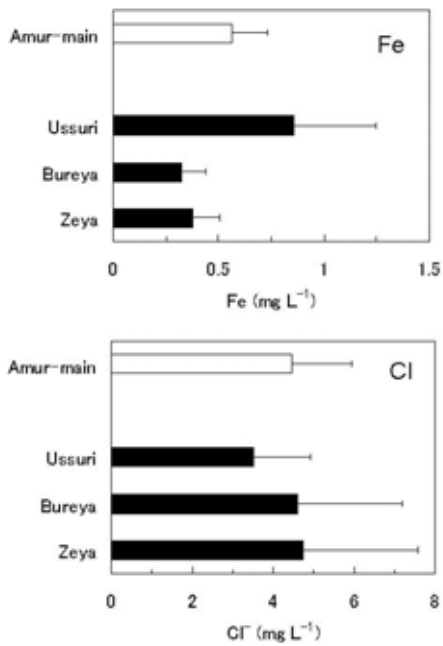
Figure 3. Spatial pattern of annual-mean ionic concentration of chloride (Cl⁻) in river water at the main channel of Amur river. Each bar represents the standard deviation for each site.

Figure 4. Annual-mean concentration in the main channel (Amur-main) and three large tributary rivers in the middle Amur basin. Each bar represents the standard deviation for each site.
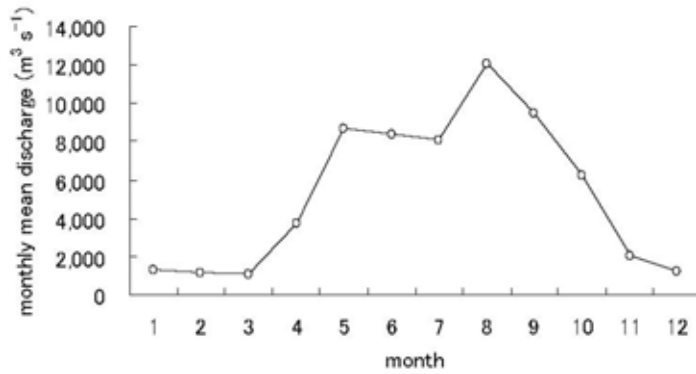
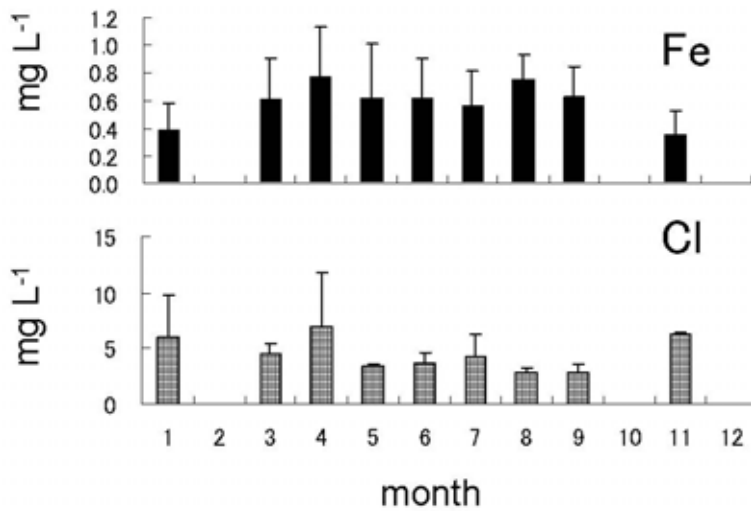*Figure 5. Monthly-mean discharge in the main channel of Amur River at Khabarovsk city in 2002.*

Figure 6. Monthly-mean concentration of iron (Fe, upper graph, n=14) and chloride (Cl, lower graph, n=12) in the main channel of Amur River in 2002. Each bar represents the standard deviation for each site.
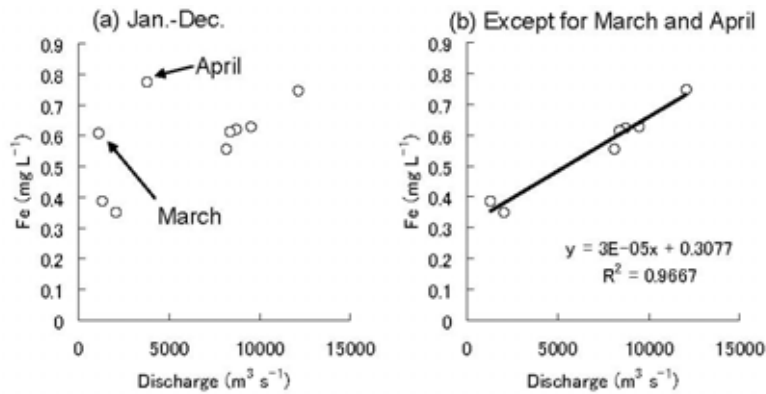
Figure 7. Relationship between monthly-mean iron (Fe) concentration and discharge (at Khabarovsk) in the main channel of Amur River in 2002. (a) All monthly data from January to December), (b) Analysis except for March and April.
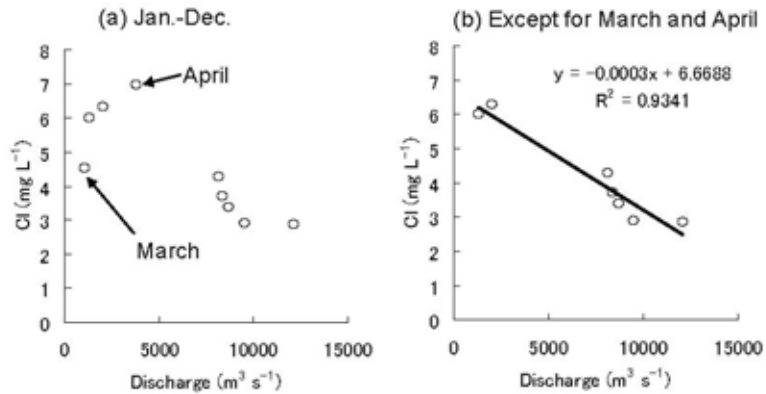

Figure 8. Relationship between monthly-mean chloride (Cl) concentration and discharge (at Khabarovsk) in the main channel of Amur River in 2002. (a) All monthly data from January to December), (b) Analysis except for March and April.
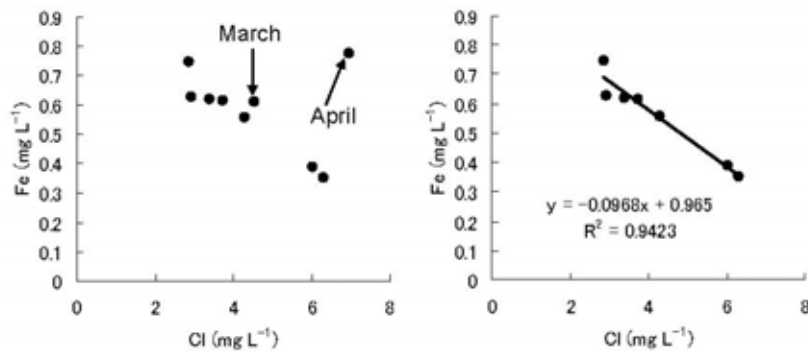

Figure 9. Relationship between monthly-mean iron (Fe) and chloride (Cl) concentration in the main channel of Amur River in 2002. (a) All monthly data from January to December), (b) Analysis except for March and April.