— GROUP 4 REPORT —

IRON DYNAMICS IN TERRESTRIAL ECOSYSTEMS IN THE AMUR RIVER BASIN

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ABSTRACT

Our focus is to understand the spatial and temporal patterns and processes of biogeochemical iron transport from terrestrial ecosystem to river with special attention to the human impacts such as forest fire, land-use change and agricultural activities. Field monitoring of iron dynamics including stream water, soil water, and groundwater has been conducted from the upstream to downstream basin of Amur river in northeastern China and far-eastern Russia under tight collaboration with Chinese and Russian scientists and institutes. We found that the major source of dissolved iron from terrestrial system to river was mainly natural wetland which largely covered near the middle to lower region of Amur river basin. In upstream forested basin, dissolved iron in soil was mainly transported with dissolved organic carbon (DOC) rather than the forms of Fe(II) and Fe(III). The swamp forest and riparian zone near the stream channel was the important source area of iron due to the wet and anaerobic conditions which increase the DOC concentration and dissolved iron in soil and groundwater. The forest fire, one of the major human disturbances in the upstream mountain, changes the quantity and qualities of the organic matter in the surface soil, resulting to the decrease of the iron transport from the burned forest to the stream. The downstream areas with gentle topography are largely covered by natural wetland especially surrounding the middle and lower part of Amur river. The spatial distribution of iron concentration in stream water indicated that the stream water at the lower elevation and the gentle watershed contained much higher iron concentrations than the upper and steep basin. DOC was the important carrier of dissolved iron in soil water and stream water in these lower wetland as well as in the upstream region. The land-use change from wetland to farmland (paddy field and cropland) caused significant changes in soil chemistry, redox potential (Eh) and soil water quality. The drainage during the crop production system increase the Eh (indicating changes from anaerobic to aerobic condition in soil), resulting the decrease of dissolved iron in soil water due to the land-use change. The development of the irrigation system has significantly decreased the groundwater table over the last several decades, possibly contributing to the decrease in iron concentration in river water in the Sanjiang plain. The irrigation of

groundwater with high dissolved iron resulted in the accumulation of amorphous iron oxides in the surface soil of the paddy filed, which was retained and not mobile from the soil. Our results indicated that the natural anaerobic environment in wetland is important for iron mobilization from terrestrial system to Amur river and that the human impact such as forest fire and land reclamation tended to make these irons immobile through mainly oxidation in the ground surface.

1. INTRODUCTION

Iron has been recognized as important limiting nutrient for ocean productivities in North Pacific Ocean during last decades (Martin et al. 1994; Boyd et al. 2000) and the high concentration of iron in the Sea of Okhotsk has sustained their high productivities (Nakatsuka et al. this issue). Therefore, the primal question of this Amur-Okhotsk project is “How dissolved iron is transported from the Amur River basin to the Sea of Okhotsk and Oyashio region?” To address this question, our research group (Group 4) focused on the terrestrial systems and their role as an iron supplier to Amur River. The iron is a major element in the lithosphere as well as oxygen, silicon and aluminum, but is insoluble and immobile in most aerobic conditions. Thus, anaerobic and reductive environments (low redox potential) are very important to make the stable iron dissoluble and mobile in soil and water (e.g. Achtnich et al. 1995; Roden and Wetzel 2002; Gutknecht et al. 2006). In the mobilization of the iron, dissolved organic carbon (DOC) is also important as a carrier of iron through the formation of the complex (e.g. Dillon and Molot 1997). Therefore, wet and DOC-rich environments such as swamp forest, riparian zone, natural wetland and paddy fields are expected to be a possible “hot spot” to produce dissolved iron in terrestrial systems (Kawaguchi et al. 1994; Kortelainen et al. 2006). In this project, our group also focused on the forest fire and land reclamation for agriculture as major changes of land-cover and land-use in this region (Sukhinin et al. 2004; Wu et al. 2003) because they are likely to have significant impacts on the iron transport from the terrestrial systems to river water. The forest fire alters the quantity and quality of soil organic matter (SOM) in forest floor. The changes of SOM by fire would affect the iron dynamics in the basin because the DOC is an important iron carries in soil (Shibata et al. 2003; Prokushkin and Tokareva 2007; Petrone et al 2007). Agriculture in lowland often needs to develop the drainage and irrigation system for food productions. The change in the hydrological regimes due to reclamation would largely alter the soil redox

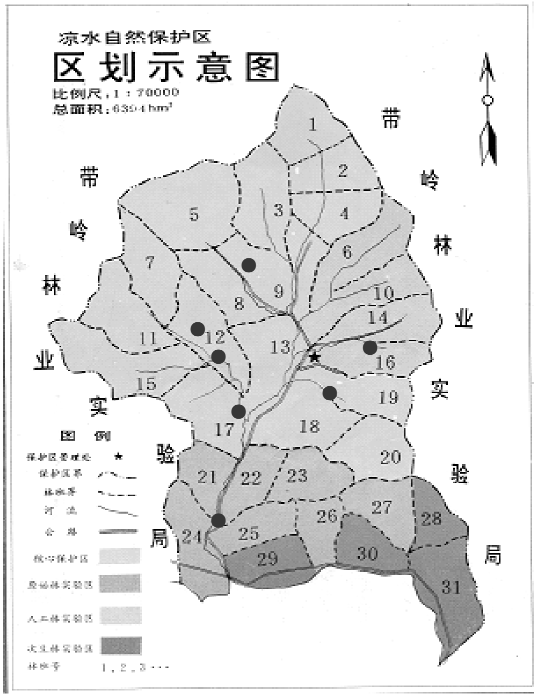

Figure 1. Study sites in Liangshui experimental station. Closed circles show sampling location for stream water

potential, which is a crucial soil parameter for the iron mobilizations. In northeastern China, rainfall amount is not sufficient to attain high yield in paddy rice production. Therefore, the groundwater has been utilized intensively for the irrigation. This anthropogenic hydrological change would also affect the iron dynamics. Based on the background and hypothesis, we set the following research goals: (i) Determination of concentration and flux of dissolved iron in terrestrial ecosystems with different land-cover in Amur river basin, (ii) Identification of the major source of dissolved iron in Amur river, and (iii) Clarification of the impacts of forest fire and land use changes for agriculture on the dissolved iron dynamics in Amur river basin.

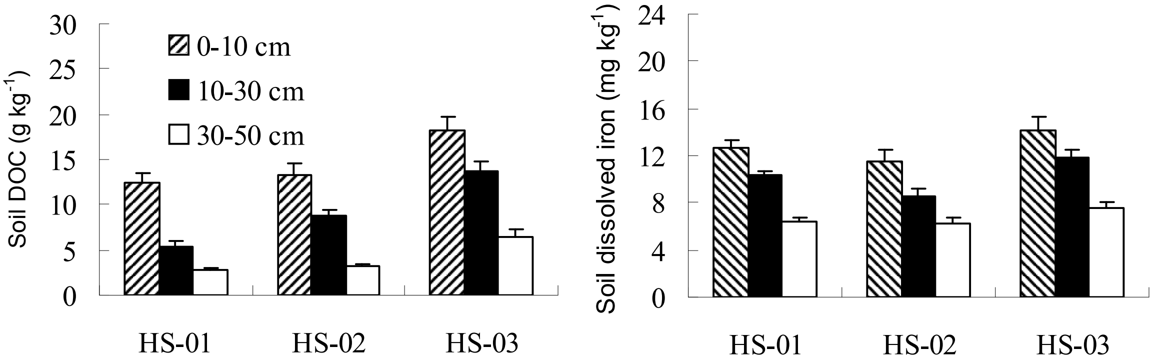

Figure 2. Contents of the dissolved organic carbon (DOC) and dissolved iron in soil with different depth at the Hanyue experimental sites. The DOC and dissolved iron was measured for the extracts of soil using ultra pure water (soil:water =1:5). See Xu et al. (in this issue) for details

2. IRON IN STREAM WATER FROM FORESTS AND THE IMPACT OF FOREST FIRE

In the upstream basin of the Amur River, forest is common land-cover both in northeastern China and far eastern Russia. We established the monitoring sites of forested basins at Liangshui (47°11' N, 128°53' E), Hanyue (47°15' N, 128°50' E) and Songling (50º54' N, 124º27' E), located in the northeastern China. Liangshui and Hanyue sites belong to the Xiaoxing'an Mountains, which native vegetation is typically warm-temperate mixed forest of *Pinus koraiensis* and deciduous broadleaved species (Fig. 1). In the soil system, the surface soil has higher content of both organic carbon and dissolved iron than the deeper soil (Fig. 2). It was indicated that the primary productions of organic matter and iron uptake by vegetation was primal pathway to accumulate both elements in the soil surface.

Figure 3 indicated that the riparian wet zone delivered the higher iron and dissolved

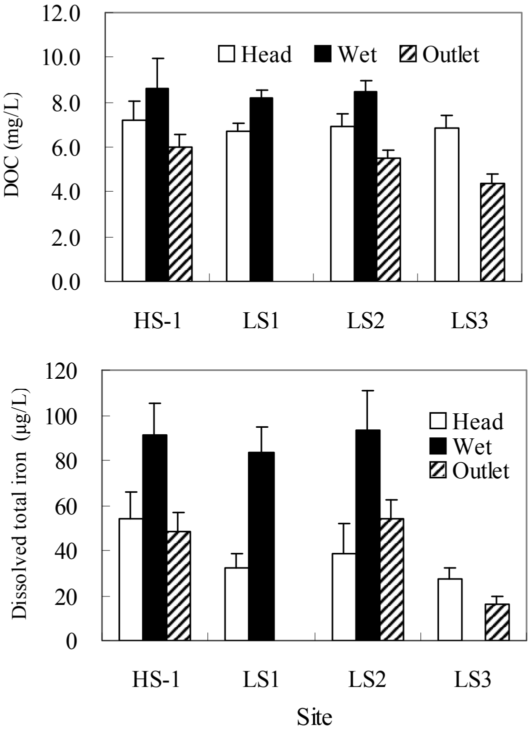

Figure 3. Concentrations of dissolved organic carbon and dissolved iron in stream water at different location including headwater (Head), riparian (Wet) and outlet (Outlet) of upstream forested basin in China. See Xu et al. (in this issue) for details.

organic carbon in stream water at the forested basin. The anaerobic condition with shallow groundwater near the stream channel enable the accumulation of organic matters in soil and enhances the reductive condition (low redox potential) in soil. Under the reductive condition, it has been known that the DOC and iron was easily dissolved compared to the aerobic condition (Roden and Wetzel 2002).

The formation of the DOC and dissolved iron complex was important processes for the iron transport from soil to stream. There was significant positive relationship between DOC and dissolved iron concentration in stream water collected at the Liangshui and Hanyue experimental sites in northeastern China (Fig. 4). The dissolved iron in surface soil collected different sites had significant positive relationship with the dissolved iron concentration in stream water (Xu et al. this issue), indicating that the surface soil was important iron source with DOC to the stream water.

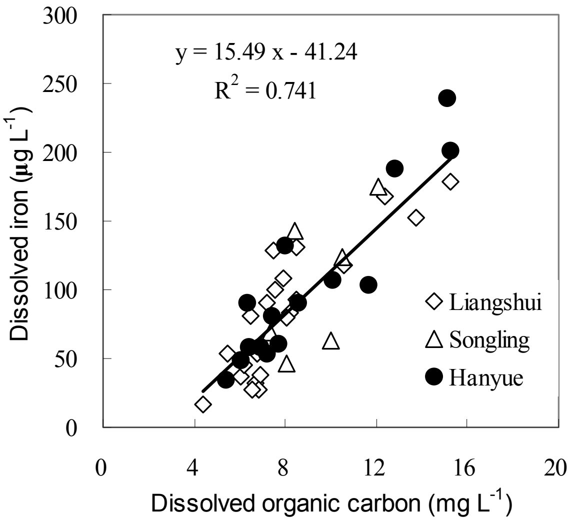

Figure 4. Relationship between dissolved organic carbon and dissolved total iron in stream water collected at upstream forested basin (Fig. 1) in northeastern China. See Xu et al. (this issue) for details

Shamov et al. (this issue) investigated dissolved iron dynamics in upstream forested basin in Russia. They especially emphasized that hydrological processes including the fluctuation of groundwater level were quite important to explain the seasonality of the dissolved iron concentration in stream water and the quantification of the iron fluxes from the watershed to the river (See details in Shamov et al. this issue).

Forest fire is major disturbances factor of the upstream forested basin both in northeastern China and far east Russia. Xu et al. (this issue) found the decrease of the dissolved iron concentration in stream water at the burned forest compared to the unburned control site (Figure 5) in the Xiaoxing'an Mountains, China. The stream water collected in the intensively burned forests at the upstream of Anyui River basin, Russia also showed lower concentration of dissolve d iron (0.07±0.02 SD mg L^{-1}) compared to the other site. The fire reduce the soil organic matter and create the charcoal in the soil surface, altering the physical and chemical properties of soil organic carbon such as moisture, water permeability, pH, solubility and absorption capacity of heavy metals and so

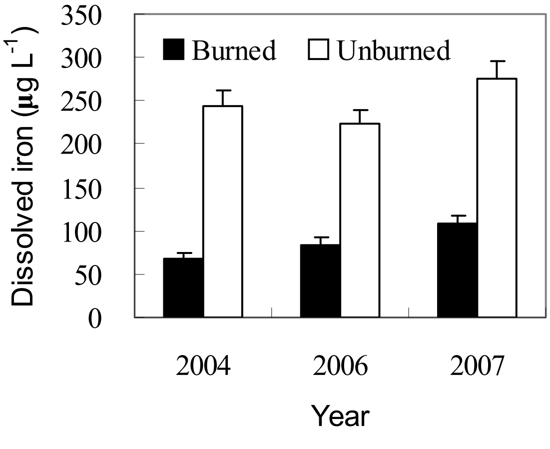

Figure 5. Comparison of dissolved iron concentration in stream water at burned and unburned forest basins of the Songling site. The forest fire at the burned basin occurred in 2004.

on (Shibata et al. 2003; Gonzalez-Perez et al. 2004; Certini 2005). Our results suggested that the change of the mobility and solubility of DOC reduced the mobility of dissolved iron from soil to stream water. The fire intensity and types (i.e. surface fire, canopy fire and so on) would provide different physico-chemical properties of the soil surface after the fire. For example, (i) the change of the albedo due to the black carbon and charcoal may increase air temperature, (ii) the absence of the vegetation after the catastrophic and intensive fire would increase the soil moisture due to the decrease of the evapo-transpiration, and (iii) the changes of the hydrological flow-pass due to the change of the water permeability by fire would alter the water and iron flow in the soil. Although these uncertainties still remained, our research data strongly suggested that the forest fire in the upstream region decrease the concentration and flux of dissolved iron from terrestrial system to the river water.

3. IRON IN STREAM WATER FROM WETLAND

Wetlands are the most possible candidate of dissolved iron source because water-logged conditions promote anaerobic condition by a limited diffusive supply of oxygen from the atmosphere, where microbial reduction of iron produces soluble Fe^{2+} and more stable organic-iron complex associated with humic substances. To make clear the processes to produce dissolved iron with a reference to hydro-topographical and ecological situations in the Amur Basin, stream water chemistry was intensively studied in a natural watershed (Gassi Lake basin, Russia) as a model field, which apparently has a set of ecological and landscape structure common to other branch watersheds in the Amur Basin (Fig. 6). The results indicated a systematic change in concentrations of dissolved iron, showing a remarkable increase in lower altitudes of watershed (Fig. 7). Elevated concentrations of dissolved iron were also observed in the soil water from lower reaches, corroborating that dissolved iron in streams originated from the soil in their watershed. The slope in lower reaches of watershed is getting more gentle and could be almost minimal from a geomorphological reason as generally seen in river courses. Thus, the striking dependency of dissolved iron concentration on their elevations suggests that topographical gradient of land surface is a determinative factor to control dissolved iron concentration in discharge water. The flatness should be a fundamental variable to control dissolved Fe concentration by retarding water drainage from the land to develop wetlands.

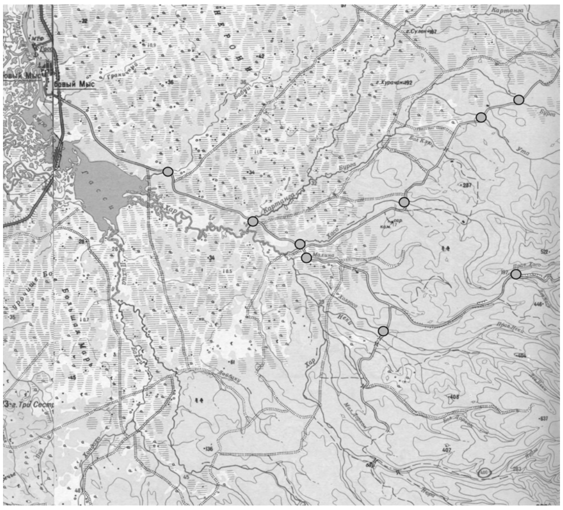

Figure 6. Study sites in Lake Gassi basin, Russia. Circles denotes the locations of stream water sampling. Lake Gassi (the upper right in the map) lies downstream of this watershed and is directly connected to the Amur River. Wetlands are distributed in the lower reaches.

Water chemistry was surveyed for rivers, agricultural canals, ground waters, and the surface water of wetlands and paddy fields in Sanjiang plain from May to October in 2005-2008. Dissolved Fe concentration observed for a number of rivers and agricultural canal waters without frozen periods averaged around 1 mg Fe L^{-1}, with a considerable variation according to the condition of their watersheds. Dissolved iron concentration in marshy rivers ranged 0.430- 4.874 mg L^{-1} with an average of 1.40 mg L^{-1}, which was relatively higher than that in Amur River (0.020-0.880 mg L^{-1}), Songhua River (0.050-1.010 mg L^{-1}), and Ussuri River (0.128-0.980 mg L^{-1}) (Fig. 9). Marsh and marshy rivers appear to currently act as a source of dissolved iron from Sanjiang plain for the main rivers. DOC concentration was also higher in marshy rivers (11.4 mg L^{-1}) than the above main rivers (8.64 mg L^{-1}). Considerable year-to-year variation in dissolved iron concentration was found in these main rivers and marshy rivers (Fig. 9), but its cause remained obscure.

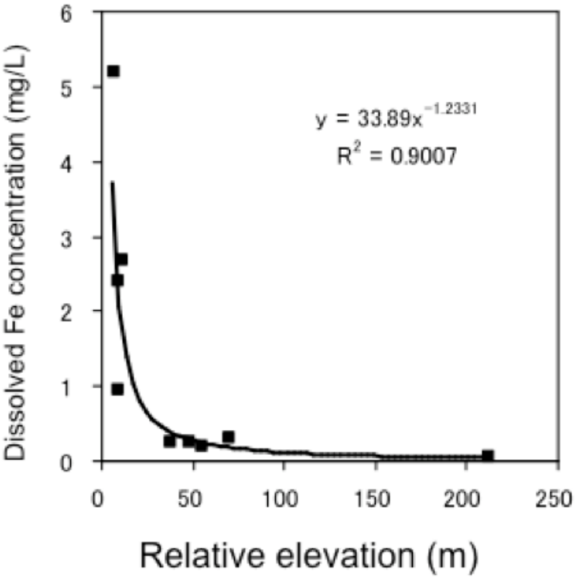

Figure 7. Dissolved iron concentration in stream water as a function of relative elevation of the sampling point in the Lake Gassi basin, Russia.

Relative proportion of iron forms in water was studied using a cross-flow device with ultrafiltration method, which separates into four fractions: high-molecular-weight iron (HMW;0.7~0.05μm),medium-molecular-weight iron(MMW;0.05~0.01μm),and low-molecular-weight iron (LMW; <0.01 μm), and acid soluble suspended iron. LMW iron fraction includes ferrous ion (Fe^{2+}) and complexed iron (organic iron). LMW iron was the major fraction of dissolved iron both in wetland and marshy streams, and 71% of LMW iron was in organic form in wetland. 73%-82% of dissolved iron was in the form of complexed iron in rivers. In contrast, ferrous iron accounted for 80.5% of dissolved iron in groundwater.

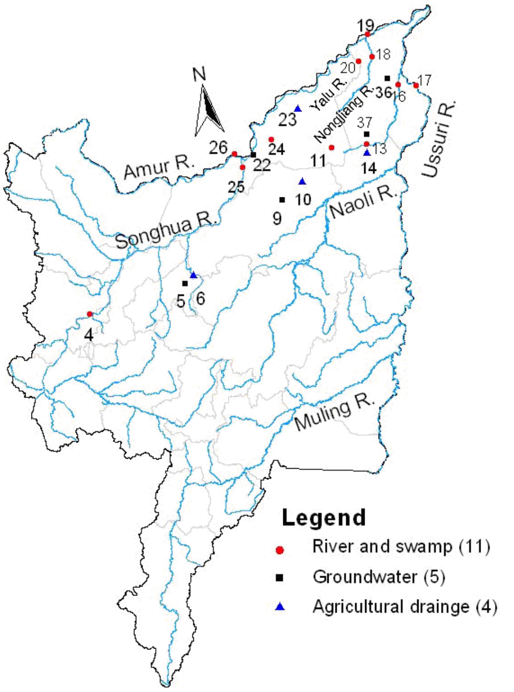

Figure 8. Sampling sites for river water, marsh water, ground water and agricultural canal water in Sanjiang plain, China

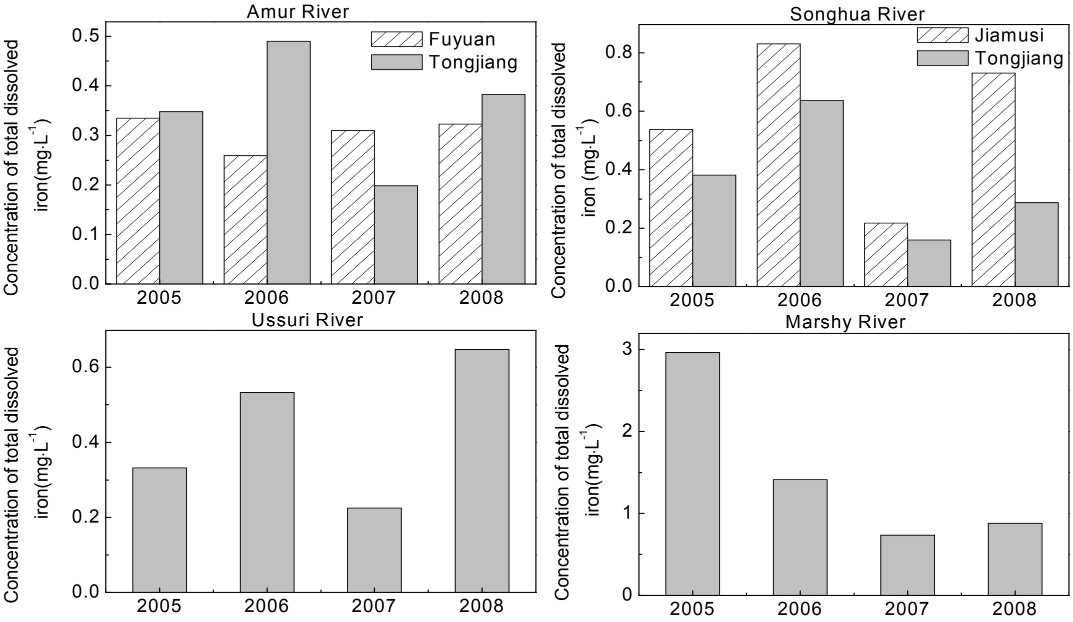

Figure 9. Year-to-year variation of averaged total dissolved iron concentration in main rivers and marshy rivers in Sanjiang Plain

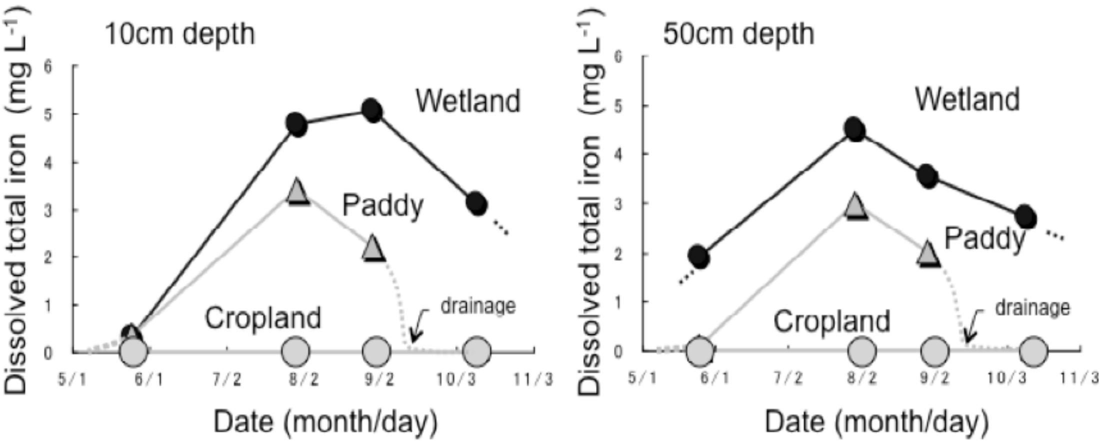

Figure 10. Seasonal change of dissolved iron concentration in soil solution at three land-use types in Sanjiang Plain

4. IMPACT OF LAND-USE CHANGES ON DISSOLVED IRON IN STREAM WATER

It is an issue of great importance to understand the impact of land use change on dissolved iron discharge, which has been largely expanded in Sanjiang plain in these fifty years (Liu, 2000; Li et al., 2002). Behavior of dissolved iron was studied for the surface water and the soil interstitial water in experimental plots of upland fields and paddy fields in Sanjiang plain, which were converted from natural wetlands several decades ago (Fig. 10). Soil in the upland fields proved to hold oxidized conditions throughout a year, indicating the absence of dissolved iron discharge. Paddy fields had lower dissolved iron concentrations in both surface and soil interstitial waters throughout a year and a shorter period of reductive condition due to agricultural water managements (Fig. 10). But importantly, the controlled water drainage and negligible water penetration into soil is considered to largely lower the strength of Fe discharge.

Paddy fields in Sanjiang plain are irrigated with ground water in most cases. Containing strikingly high concentration of dissolved Fe (largely in a form of Fe^{2+}), these ground waters could be a candidate of additional Fe source. Chemical analysis of iron forms in soil, however, illustrated that the contents of amorphous Fe was significantly larger in paddy fields than in upland fields especially for cultivated horizons (Fig. 11) (Chi et al, this issue). Amorphous Fe is a typical iron fraction secondarily formed, and accordingly, the difference in amorphous Fe contents (20 cm in depth) between paddy fields and upland fields, 1.17 - 2.25 g Fe kg^{-1}, can be expected to derived from the irrigation of groundwater at least partly. Assuming that 12 mg/L as the dissolved iron concentration in groundwater used for irrigation (Yan, unpublished), 697 mm as the total amount of irrigation water in a year (Yan, unpublished), 20 years as the duration of paddy field cultivation, and 0.5 Mg m^{-3} as the soil bulk density, Fe supply from groundwater is estimated to be equivalent to 1.7 g Fe kg^{-1} when Fe is retained in the cultivated horizons of 0 - 20 cm depth. Thus, elevated contents of amorphous iron oxides observed in the upper soil layer in paddy fields could adequately account for the calculated total amount of Fe supplied from the irrigation of ground water since the commencement of rice paddy in Sanjiang plain. It is reasonable to assume that amorphous Fe would be simply accumulated under such a condition as paddy fields. This evidence suggests an almost complete retention of Fe added by ground water. In combination with the controlled water discharge as above, it can be concluded that ground water irrigation would contributed little to iron discharge. Thus, the intensity of iron export is likely to be greatly reduced in paddy field in comparison with natural wetlands.

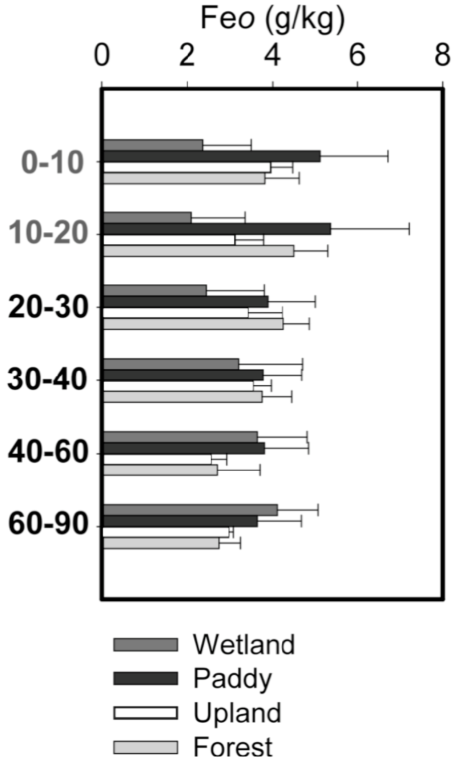

Figure 11. Difference in amorphous Fe (Feo) content in the soil profile among different land cover types

Ground water table was surveyed using wells newly constructed in Sanjiang plain to know the current hydrological situation under the ground. Even a mid-level terrace site with relatively higher elevation than surrouding areas had a ground water level as shallow as 1.0 m, where a reclamation (water drainage) has started comparatively recently (around the year of 2004; Yan, pers. comm.). In view of presence of peat layer observed in most terrains (Yamagata et al., 2007) in combination with the above evidence, it is reasonable to presume that most of the area in Sanjiang plain was covered with wetlands in pristine age (before starting land use change) except for hilly areas. However, the ground water table at other locations was found to be greatly decreased down to the levels almost equivalent to river water surface nearby, to which ground water is expected to flow away eventually (Fig. 12). It appears that reclamation conducted over most area of Sanjiang plain has greatly lowered ground water tables to alter the ground from water-saturated to unsaturated and drier condition, which has probably caused a significant reduction in soluble iron export to downstream rivers.

On the basis of sporadic historical data from hydrological department in combination with the results during this project, it was found that dissolved Fe^{2+} + Fe^{3+} concentration in a marshy river (Naoli R.) running through Sanjiang plain shows a consistent decreasing trend from 1960’s to present; the present concentration level seems to be several-fold lower than that 40 years ago (Fig. 13) (Yan et al., this issue). In this Naoli River basin, wetland area is reported to have decreased by 87% during a period of 1985-2000 (Liu, 2005). The results suggest that the discharge of dissolved iron is certainly under a way to decline due to the loss of natural wetlands and the shift to drier condition in Sanjiang plain.

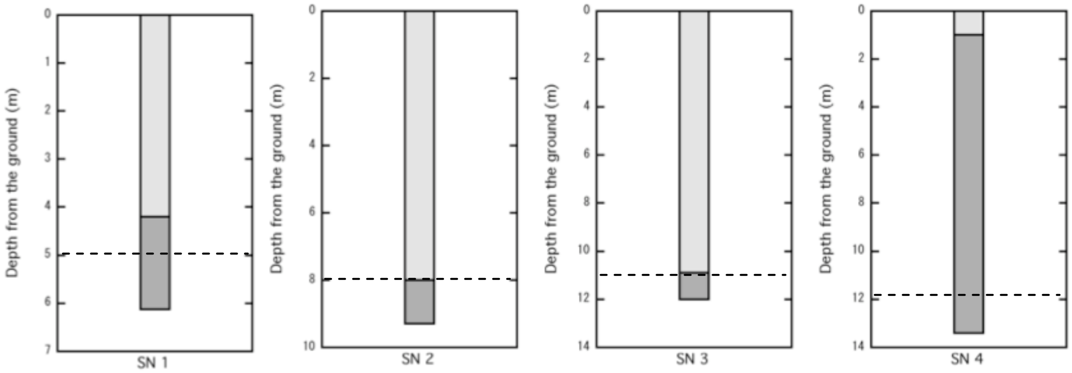

Figure 12. Ground water table observed from wells constructed at several locations in Sanjiang plain in 2009. The dark part, the bottom of whole bar and dotted lines denote ground water, the bottom of well and the surface water level of the rivers nearby each location, respectively.

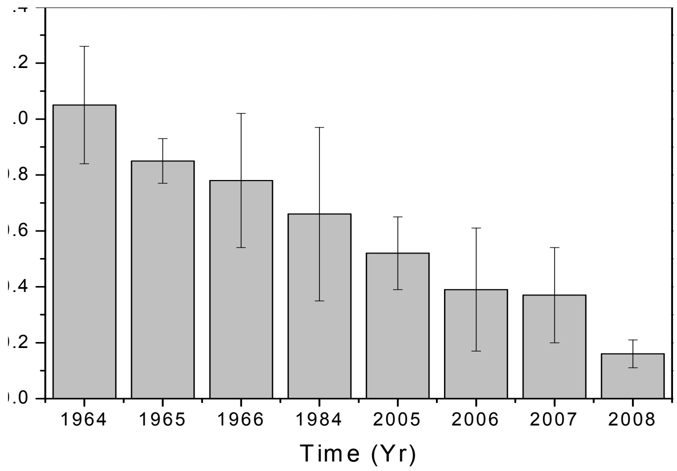

Figure 13. The change in ferrous and ferric iron concentration in a marshy river (Naoli River) in Sanjiang plain from 1960’s to present

5. FUTURE RESEARCH NEEDS

As we described above, our studies provided the strong evidences that natural wetland was important iron source to the Amur river and human impacts including forest fire and land-use changes for agriculture are reducing the concentration and flux of dissolved iron from terrestrial system to the Amur River. However, some of the unsolved questions are still remained as follows. The peat fire on the surface of wetland commonly occurred in dry season just after the soil thaw at middle part of Amur river (e.g. near Khabarovsk). Since the wetland is important iron sources, the combustion of the standing vegetation and provisioning of the black carbon and charcoal would cause some impact of iron transport from peat surface to river water. The further study on the impact of peat fire on the iron dynamics would be needed.

It is expected that the global warming will change the freezing regimes in the ground of Amur River basin. The decrease of the freezing as a result of warming would alter the hydrological processes and the associated redox conditions in wetland because the presence of freezing layer (even seasonally) may contribute to create anaerobic condition in soil due to its low permeability. The understanding how global warming will affect the iron dynamics through the change in anaerobic conditions and peat accumulation would deserve future investigation. Climate change does not always gradually fluctuate, but can be abrupt and extreme. The rare, but catastrophic climate event such as extreme storms has a potential to cause large and irreversible shifts of iron dynamics and fluxes associated both with natural and anthropogenic systems as described in this chapter. The understandings and the prediction of these changes under the abrupt and catastrophic events would be important in the next step.

The further economic development especially in China would cause different regime shift of land-use and land-cover changes such as more urbanization and industrialization. The impact of these changes on the iron dynamics would be also future research theme.

6. CONCLUSION

The principal factor that controls dissolved Fe discharge from the land surface is likely to be the topographical gradient in both basin scale and a watershed scale. Gentle or almost minimal slope is developed in lower reaches such as riparian zone and lowland wetlands, which retards water drainage from the land to create anaerobic condition in soil, promoting Fe reduction and peat accumulation on occasion. Such area could act as a dissolved Fe source at an intensity of 1 mg L^{-1} or more without frozen periods, for which dissolved humic substances usually play a role as an important carrier. Land use change due to reclamation has widely altered the condition of water saturation under ground in Sanjiang plain, currently leading to decreased intensities of dissolved iron export from that area. A large amount of dissolved iron is supplied from ground water through the irrigation to paddy fields, but could contribute little to the iron discharge to downstream because of its efficient retention after a rapid oxidation to insoluble iron oxides.

REFERENCES

Achtnich, C., Bak, F. and Conrad, R. (1995) Competition for electron donors among nitrate reducers, ferric iron reducers, sulfate reducers, and methanogens in anoxic paddy soil. *Biology and Fertility of Soils* **19**: 65-72

Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R. and 27 others (2000) A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* **407**: 695-702.

Certini, G. (2005) Effects of fire on properties of forest soils: a review. *Oecologia* **143**: 1-10.

Dillon, P.J. and Molot, L.A. (1997) Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resources Research* **33**: 2591-2600.

Gonzalez-Perez, J.A., Gonzalez-Vila, F.J., Almendros, G. and Knicker, H. (2004) The effect of fire on soil organic matter - a review. *Environ. Int.* **30**: 855-870.

Gutknecht, J., Goodman, R. and Balser, T. (2006) Linking soil process and microbial ecology in freshwater wetland ecosystems. *Plant and Soil* **289**: 17-34.

Kawaguchi, T., Wahl, M.H., Aelion, C.M. and McKellar, H.N. (1994) Organically-bound ferrous iron (org-Fe(II)) as an indicator of ecosystem health - a comparison of suburbanized and forested streams in the southeastern US. *J. Environ. Sci. Health* **29**: 1761-1776.

Kortelainen, P., Mattsson, T., Finér, L., Ahtiainen, M., Saukkonen, S. and Sallantaus, T. (2006) Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. *Aquatic Sciences - Research Across Boundaries 68*: 453-468

Li, Y., Zhang, Y. Z. and Zhang S. W. (2002) The landscape pattern and ecological effect of marsh changes in the Sanjiang Plain. *Scientia Geographica Sinica* **22**(6): 677-682. (in Chinese)

Liu, H. Y. and Li, Z. F. (2005) Hydrological regime changing process and analysis of its influencing factors in a typical wetland watershed of the Sanjiang Plain. *Journal of Natural Resources* **20**(4):493 -501. (in Chinese)

Liu, X. T. and Ma, X. H. (2000) Effect of large scale reclamation on natural environment and regional ecoenvironmental protection in the Sanjiang Plain. *Scienta Geographic Sinica* **20**(1):14-19. (in Chinese)

Martin, J.H., Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M. and 39 others (1994) Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* **371**: 123-129.

Petrone, K.C., Hinzman, L.D., Shibata, H., Jones, J.B. and Boone, R.D. (2007) The influence of fire and permafrost on sub-arctic stream chemistry during storms. *Hydrological Processes* **21**: 423-434.

Prokushkin, A.S. and Tokareva, I.V. (2007) The influence of heating on organic matter of forest litters and soils under experimental conditions. *Eurasian Soil Science* **40**: 628-635.

Roden, E.E. and Wetzel, R.G. (2002) Kinetics of microbial Fe(III) oxide reduction in freshwater wetland sediments. *Limnol. Oceanogr.* **47**:198–211.

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 Science and Plant Nutrition* **49**: 25-29.

Sukhinin, A.I., French, N.H.F., Kasischke, E.S., Hewson, J.H., Soja, A.J. and 8 others (2004) AVHRR-based mapping of fires in Russia: New products for fire management and carbon cycle studies. *Remote Sensing of Environment* **93**: 546-564.

Wu, H. Guo, Z. and Huipeng, C. (2003) Land use induced changes of organic carbon storage in soils of China. *Global Change Biology* **9**: 305-315.