EFFECT OF LUCC ON CONCENTRATION OF IRON IN AQUATIC SYSTEMS AND FLUX OF VARIOUS FORMS IRON IN MAIN RIVERS IN SANJIANG PLAIN

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INTRODUCTION

Iron in river waters is one of most primary sources for ocean iron. Wetland and groundwater are important source of dissolved iron due to the reduced condition. Now，Land use and land cover change has changed environment of wetland and groundwater greatly. So, LUCC plays an important role in affecting the concentration of iron in river waters in the Sanjiang Plain. With the rapid development of drainage channel system and reclamation of marshes to upland and paddy land in the past 50 years, cultivated land area has been increasing to 5.24Mha in the year of 2000 from about 0.79Mha in the year of 1949. Accordingly, the wetland area was decreased to 0.84Mha in the year of 2000 from 5.35Mha in the year of 1949 (Liu, *et al.*,2000; Li, *et al.*,2002). The change of marsh land was showed in Fig.1.The rapid expansion of agriculture over the past 50 years has radically changed LUCC. This conversion of natural vegetation to managed agricultural systems has not only reduced biodiversity and impacted regional climates, but also altered biogeochemical cycle. In particular, LUCC and the expansion of modern agricultural practices has significantly increased leaching of chemicals to the surface waters, that will lead to the degradation of aquatic ecosystems worldwide (Matson *et al*., 1997; Carpenter *et al*., 1998). Therefore, the Sanjiang Plain has become a representative region in China and East Asia to understand the influence of LUCC both in degree and extent on dynamics of transport mechanism and biogeochemical cycle of iron and other elements.

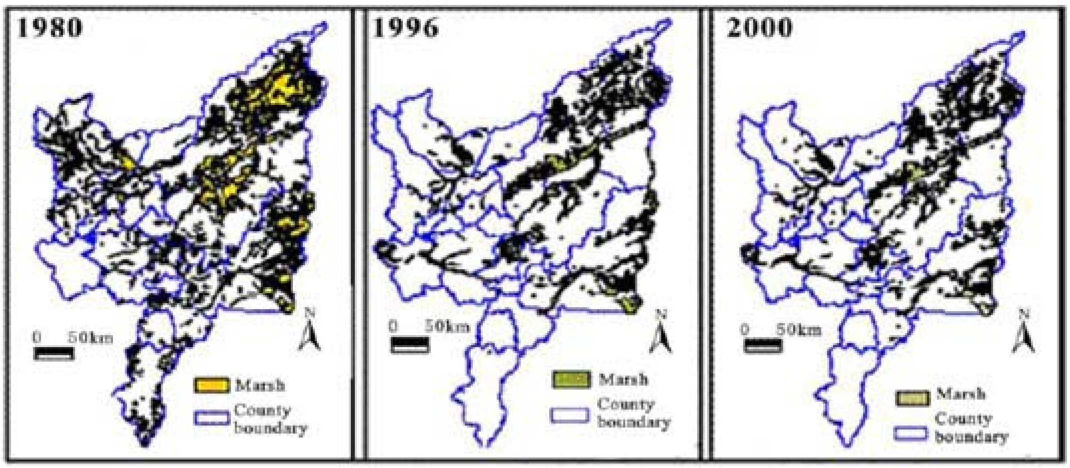

Fig. 1 Change of marshy wetland in Sanjiang Plain

Iron is an essential micronutrient for almost all organisms. In cells, iron can exist in more than one oxidation state, and catalysis of redox reactions and electron transport are two major functions of iron containing enzymes. Iron is present in the active centers of cytochromes and iron-sulfur proteins, e.g., ferrodoxin, which are important components of the photosynthetic and respiratory electron transport chain (Butler, 1998; Falkowski, 1997; Sunda, 1991). Iron has been proposed to co-limit phytoplankton growth in several marine environments (Mills, *et al*., 2004; Morel and Price, 2003; Schulz *et al*., 2004).

Iron may exist in surface and subsurface waters as simple hydrated ions and inorganic and organic complexes of low molecular weight. The speciation of iron in natural water, and their overall concentration, significantly affects water quality and bioavailability. The environmental importance physicochemical status of iron in aquatic ecosystem has been widely studied because of its importance in the prediction of transport, bioavailability and the fate of iron. Knowledge about the chemical speciation of Fe (see Fig.2) in natural water is important in interpreting biological and geochemical cycling in aquatic ecosystem. Binding iron in complexes with inorganic, and particularly with naturally occurring organic substances, are often regarded as main existing forms in ocean.

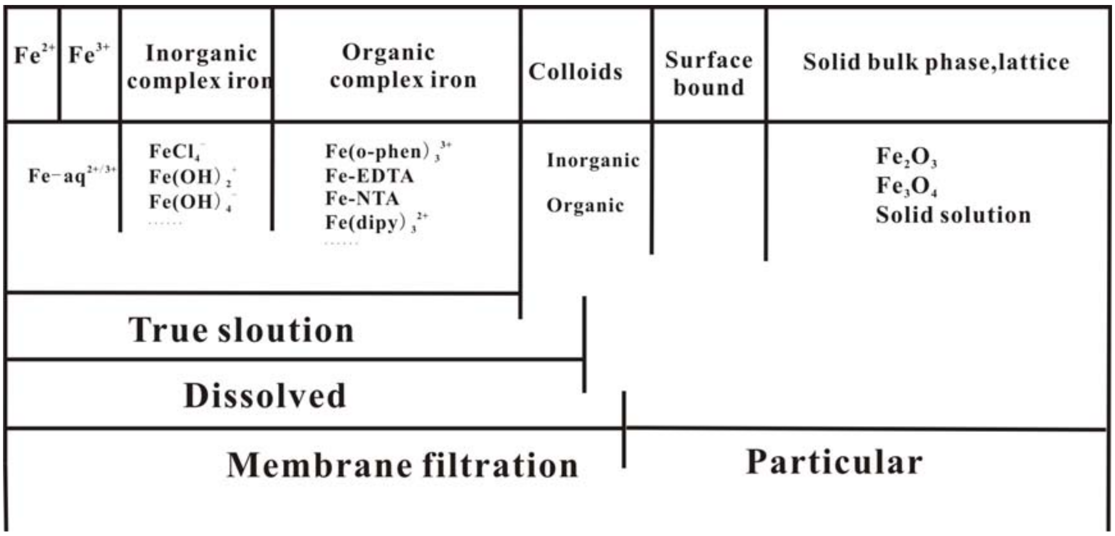

Fig.2 Forms of Fe species in natural water (Werner Stumm and James Morgan, 1996)

A limited number of papers investigates the spatial distribution of the concentration of free ion forms of iron (Fe^{2+} and Fe^{3+}) in surface and groundwater in Sanjiang Plain (Pan Y.P., *et al*., 2007). Moreover, the forms of iron transport and concentration fluctuation with LUCC in Sanjiang Plain are still poorly documented. The aim of research in the year of 2007 is to gain additional insights into iron speciation, and effect of LUCC on concentration of iron in aquatic systems and flux of various forms of iron in main rivers to the Okhotsk Sea.

MATERIAL AND METHOD

2.1 Study Sites

Sanjiang Plain was one of the largest marshy distribution regions in the Amur Basin. There are three main river systems, including Amur River, Ussuri River and Songhua River.

This region, because of its available accessibility and the presence of agricultural and industrial activity, can be considered as an environment disturbed by human activities. The velocity of river flow was higher in summer than spring and autumn, so as the flux. River water was frozen in early November and melted in late April. During frozen period, the ice layer thickness was about 50 cm to 100 cm, and the velocity of flow was slow in main rivers such as Amur River, Ussuri River and Songhua River. For the small rivers, such as Yalu River, Bielahong River, Naoli River and Nongjiang River, frozen layer is closed to river bed owing to small flow during winter. It is interesting to note that the main rivers were turbid in summer and autumn, and the color was brown in small rivers flowing through marsh owing to the high concentration of DOC from wetland.

With reclaiming intensively of marshes over the past 50 years, the much ditch systems were built in order to discharge standing water in wetland and farm land. But now, they were used as a channel to output the overflow from paddy field in the growing season. Through the rice-growing season from May (seeding) to September (harvesting), the shortage of rainfall usually occurred and is unfavorable for the rice production. As a result, the use of groundwater for irrigation is an important and common ways in the Sanjiang Plain, resulting in the decrease of the groundwater level.

2.2 Sampling and Analyses

Water samples were collected from rivers, agricultural drainages and wells in July 2007, August 2007, and October 2007, respectively. The sampling schedules were depicted in Tab.1 and the sampling sites were showed in Fig.3.

Table 1 Sample numbers in 2007 in Sanjiang Plain

No	mm/ dd / yy	Groundwater	River water	Agricultural drainage	Total samples number
1	July 23-26,2007	7	11	2	20
2	August 27-30,2007	5	11	4	20
3	October 13-16，2007	4	10	2	16
Sub-total		16	32	8	56

River and drainage samples were collected with a polymerized sampler at 50cm depth below the water surface. Wells for irrigation or pumping water were chosen as groundwater sampling site.

Water samples were collected using a special column sampler (Teflon). After collection, water samples was immediately stored in a portable refrigerator (0~4℃) until further treatment (filtration, acidification and measurement).

Chemical analysis of the samples was carried out at the laboratory of Northeast Institute of Geography and Agricultural Ecology, CAS within one week after the collection. The measurement methods of all items are listed in Tab.2.

Table 2 Measurement method and analyzer

Items	Method	Analyzer	Remark
NH_4^+,NO_3^-,NO_2^-,PO_4^{3-}	Colorimetry	SKALAR-SAN++ Model Continuous Flow Analyzer (Holland)	In lab
K, Na, Ca, Mg, Total dissolved Fe and Mn	AAS	GBC 906 Atom Absorption Spectrophotometer(Australia)	In lab
SiO_2	Colorimetry		In lab
DOC	Oxidative Combustion-infrared Analysis	SHIMADZU TOC-V_{CPH} Model Analyzer(Japan)	In lab
IC	Low Temperature and Acidification Combustion-infrared Analysis		
Fe^{2+}	Ferrozine Absorption Spectrophotometer Method (ferrozine mono-sodium salt, pH=4.6, wavelength =562nm)	Fe^{2+} Analyzer(China)	Field*
Fe^{3+}	Ferrozine + Ascorbic Acid; Absorption Spectrophotometer Method (Ascorbic acid can reduce ferric to ferrous.)		
Complex iron	Estimated from the difference between total dissolved iron and free iron.		
Acid soluble iron	Add 0.5mL of conc. HCl per 50mL of water samples, then filtrate with Whatman GF/F glass fibers, finally use AAS method to analyze conc. of iron (Acid soluble iron)	AAS	In lab
Acid soluble particulate iron	The difference between acid soluble iron and total dissolved iron.		
HCO_3^-	Titration（pH = 4.4 at end point）		Field*
pH, EC, WT, SAL (Salinity), TURB(turbidity)	Electrode Method	HORIBA U-10 (Japan)	In situ

*Measured within 12 hours. The laboratory is attached to Northeast Institute of Geography and Agricultural Ecology, CAS.

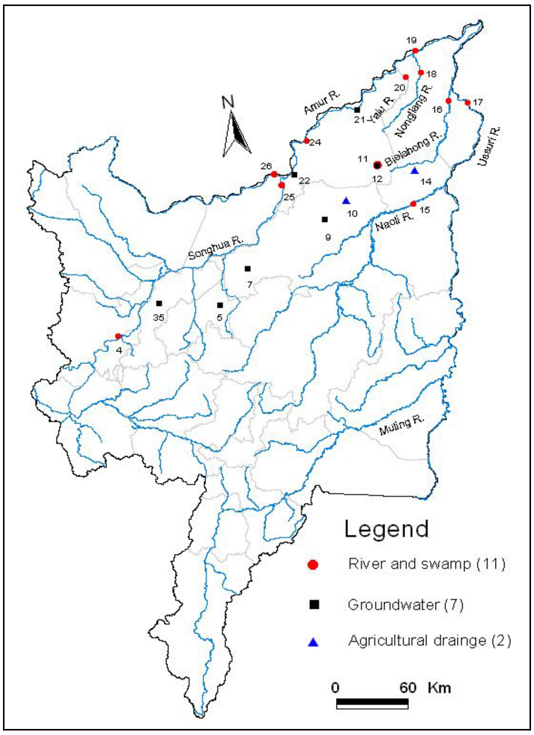

Fig.3 Sampling Location in 2007 in the Sanjiang Plain

RESULTS AND DISCUSSION

3.1 Effect of LUCC on Various Concentration of Free Iron Ion in River Waters

Taking Naoli River as an example, the drainage and use of marshes for agricultural fields in the Naoli River watershed occurred in past 50 years with intensive population growth, resulting in the decrease percentage of wetland up to 87% from 1985 to 2000 (Liu, 2005). During this period, the concentration of free iron was decreased sharply with wetland reclamation (Fig 4). This phenomenon was also observed in other river waters in the Sanjiang Plain. Hence LUCC is one of the major factors influencing the concentration of total dissolved free iron.

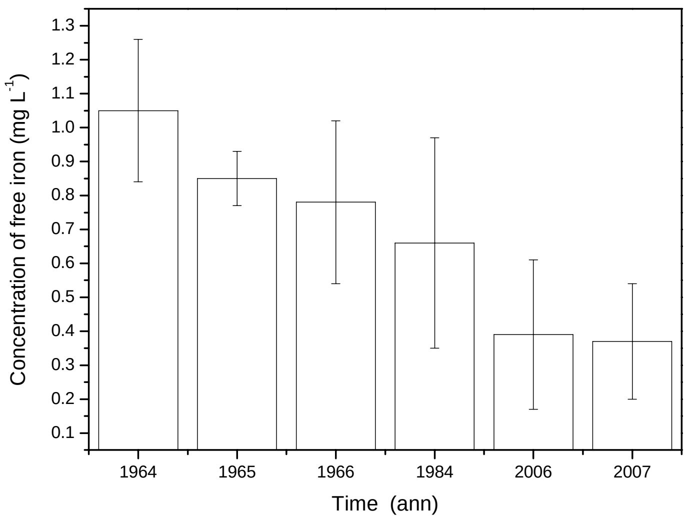

Fig.4 The concentration of iron at different time in Naoli River (hydrology document of Amur watershed, 1960-1985)

The mechanism of effect of LUCC on biogeochemical process of iron is still unclear due to lacking historical data, and should be studied in further. However, various concentration of iron can proceed through the following possible pathway: (1) the main source of iron is wetland, because of cultivation, output of iron from wetland decreases accordingly. (2) wetland soil is in anaerobic condition and Fe^{3+} transforms to Fe^{2+} with the action of iron bacteria. Furthermore, water-solubility of ferrous compound is higher than ferric compound's. Cultivation changes the environmental condition, which make a mass of production of Fe^{3+}. Some part of Fe^{3+} separate from water in the form of deposition. (3) In addition, some other factors, e.g. rainfall, contamination and so on, may be also the controlling factor. Hitherto, we lack a clear picture of the relative importance of above pathways in the mechanism of iron with Land-Use/Cover Change in freshwater systems.

Although something may be unclear, the fact is that a sharply reduction of free iron in river waters have influenced seriously ecosystem of Okhotsk Sea.

3.2 Concentrations of Free Iron, Complex and Suspend Forms of Iron in River Waters

Complexed iron was estimated from the difference between total dissolved iron and free iron. In river waters, the dissolved compounds are the main forms in which iron exist. Iron migrates mainly in ferric ion and complexed iron forms (Fig.5). Differences in the speciation of iron are related with internal process in river waters and chemical properties of iron.

Due to the aerobic environment/condition in the river, the concentration of ferric ion is higher than ferrous ion. Iron in suspended particles is less typical because the turbidity of the river waters is low. Average concentrations of suspended substance were 0.13mg L^{-1}. Maximum concentration of acid soluble particulate iron, 0.62mg L^{-1} was observed in the first usual discharge period (July).

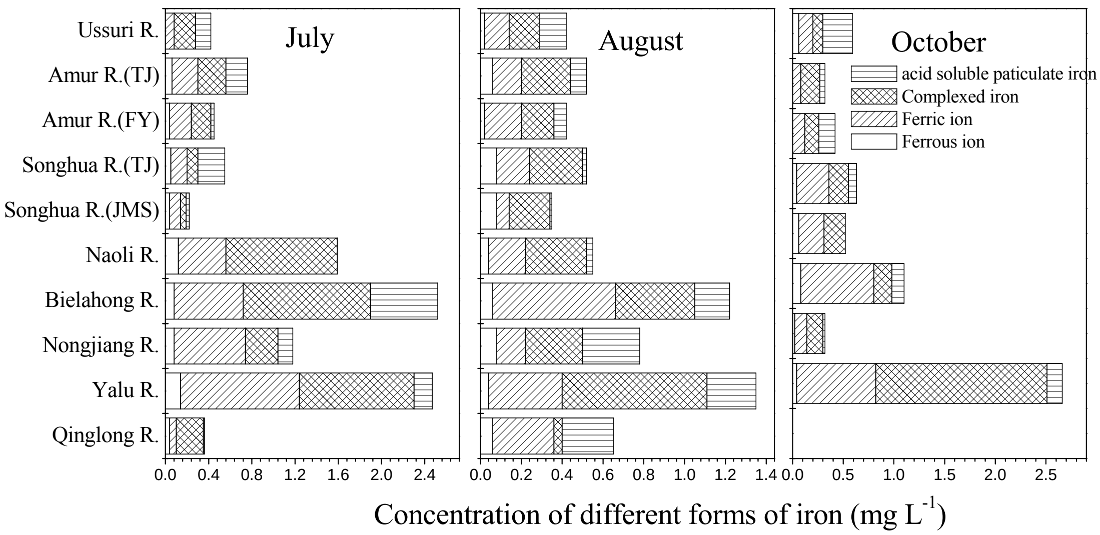

Fig.5 Concentration of different forms of iron at different time

In flood period (August) and the second usual discharge period (October), the concentration of acid soluble particulate iron decreased to 0.28~0.01 and 0.29~0.01mg L^{-1} respectively. The mean concentration of free iron including ferric and ferrous ion was 0.35mg L^{-1}.Maximum concentration (1.24mg L^{-1}) was found in July. In August and October, the concentration of free iron decreased to 0.66~0.14 and 0.82~0.08 mg L^{-1} respectively. At the same time, higher concentration of complex iron was observed in the river which derives form the marsh including Yalu R., Bielahong R., Nongjiang R., Naoli R. and Qinglong R., because high concentrations of DOM in river waters were causing active complexation, a process that can dominate the fate of iron. According to this, two parts of the river can be divided: one part is the main river including Songhua R., Amur R. and Ussuri R which represent the typical freshwater river; the other part is marshy river.

However, none of the four kinds of iron (Fe^{2+}、Fe^{3+}、complex iron、acid soluble particulate iron) concentrations correlate with significantly DOC. The nature of DOM in estuarine and seawater is complex, but is thought to include humic acids, fulvic acids, glycollic acid, peptides, proteins, amino acids, lipids and polysaccharides. In coastal waters and estuaries, DOM may also include anthropogenic chelating ligands such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetate (NTA), phosphonates, citric acid, tartaric acid and surfactants from anthropogenic sources. Indeed, organic compounds with an extremely high selectivity and affinity for iron maintain 99% in organically complexed dissolved form (Nolting *et al*., 1998; Völker and Wolf-Gladrow, 1999; Hutchins *et al*., 1999), but not all of the organic matters are complexed with iron. In other words, DOC can not reflect the real concentration of organic matters binding with iron, but only can reflect the whole trend.

Our three times investigations demonstrated that most dissolved iron in river waters was present as ferric ion and complex compound and this two fractions of dissolved iron account for 73%~82% of total concentration of iron.

3.3 Influence of Agriculture Drainage on the Fate of Iron in River Waters

There are so many irrigation channels in the Sanjiang Plain which discharge into the main rivers or marshy river finally, affecting biogeochemical process of iron. The influence of agricultural drainage can be showed in Table 3, as compared to July and October.

The concentrations of four species of iron show differences at different time with the marshy river concentrations of iron being higher and more variable than the main river concentrations (Tab.3).

Table 3 Difference in iron concentrations between main rivers and marshy rivers

item	main rivers [a]			marshy rivers [b]		
	July	August	October	July	August	October
Fe^{2+} (mg L^{-1})	0.04	0.05	0.03	0.09	0.06	0.05
Fe^{3+} (mg L^{-1})	0.15	0.13	0.17	0.58	0.32	0.47
Cmplexed iron (mg L^{-1})	0.20	0.15	0.19	0.76	0.35	0.56
Acid soluble particulate iron (mg L^{-1})	0.13	0.06	0.12	0.15	0.19	0.07

[a] Main rivers represent typical big river derived from freshwater source, including Songhua R., Amur R. and Ussuri R

[b] Marshy rivers represent small branch river derived from marshy wetland, including Yalu R., Bielahong R., Nongjiang R., Naoli R. and Qinglong R.

In cultivation periods (August), the concentrations of ferric ion and complex iron were lower, and the variation trend of acid soluble particulate iron concentrations in the main river was not consistent with in the marshy river as compared to July and October. Agricultural drainage nearly happened in August. Therefore, agricultural drainage has an influence on the concentrations and existing forms in river water-bodies. Some impacting factors of agricultural drainage on the biogeochemical process of iron in river water-bodies can be involved as follow: (1) Groundwater irrigation. In the Sanjiang Plain, groundwater irrigation is applied widely in the most of farms. The mixing between groundwater with lower concentration of iron and river water means perturbations to the system (such as variable inputs, dilution, and transformation of circumstance). (2) Fertilization. It is known that adding fertilizer in the cultivated land will indirectly make the concentrations of element of N and P being higher in the agricultural drainage waters, which may accelerate the growth of microbe. A mass of microbe are able to consume the organic matter in water and prevent the production of organic ligands from binding with iron. (3) The rainfall. August is the high flow period for river as it is the rainy season in the Sanjiang Plain. Because of high rainfall, the overall controlling factor is river flow, which may not only dilute the concentration of iron but also change the environmental condition in river waters. Iron may be more easily adsorbed to particles during the high flow periods, especially in the marshy river.

3.4 Competitive Complexation of Iron by Organic Ligands (Ferrozine)

The ferrozine (monosodium salt hydrate of 3-(2-pyri-dyl)-5,6-dipheny l-1,2,4-triazine-p, p'- disulfonic acid) reagent proposed by Stookey (1970) which reacts with divalent Fe to form a stable magenta complex species is used. Ferrozine reacts extremely rapidly with inorganic Fe(II) at pH 8.1 to form a purple colored complex with maximum absorbance at 562 nm in 2 min and continue to replace weak organic ligands from complexed iron in about 30 h (Ohji and Yoh, in prep). These results suggested that the slow increase in absorbance is explained by the slow displacement of Fe(II) from the organic ligands.

After 30h, the concentrations of both ferric and ferrous ion increase significantly (Fig.6). The results show that Ferrozine, as a kind of strong organic ligands, has ability to replace complexed iron from weak ligands. The result of iron concentration can represent free iron and complex iron at 3 min and 30h respectively and the concentrations of ferric and ferrous iron are about 2 and 6 times higher respectively at 30h than those of at 3 min. In other words, ferrous iron exists primarily as form of complex iron in river waters.

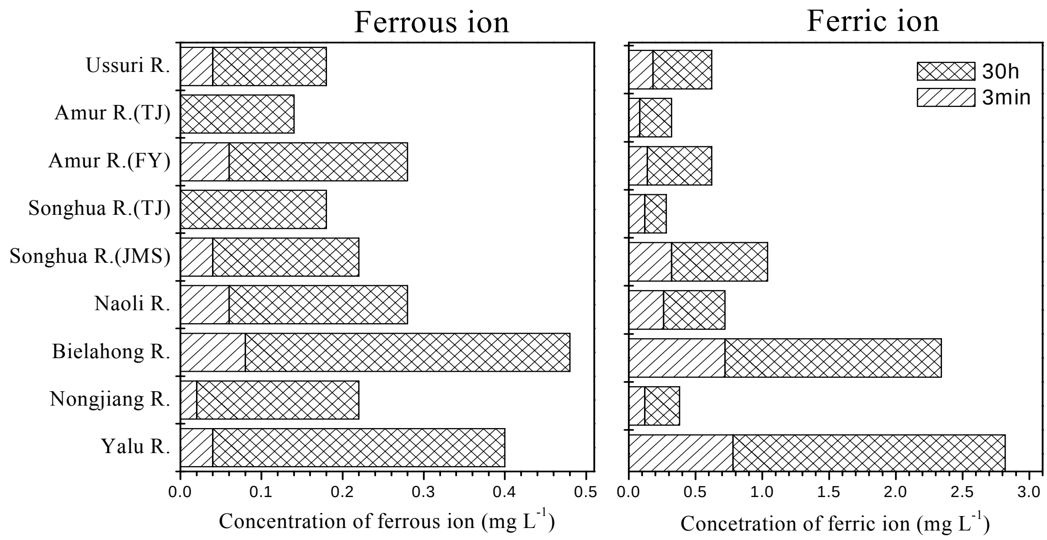

Fig.6 Changes in concentration of free iron with time after adding the FZ to water samples

3.5 Variation of Iron Concentration with the Sample Preservation Method

To check the effect of different method of water sample preservation on the concentration of iron, we introduce two kinds of sample bottle to preserve the water samples: plastic battle and ground-glass stoppered flask, which can represent opened system and closed system respectively. The water samples were collected from 15 sample stations including surface water and groundwater by two types of sample bottle. Fig.7 and Fig.8 show the free iron concentrations for samples using different method of sample preservation in river waters and groundwater. There are little difference between the two methods for free iron concentrations in river waters. However, the concentrations of ferrous ion preserved by plastic bottle are 30.2% lower compared to those of stoppered flask and the concentration of ferric ion preserved by plastic bottle are 54.8% higher in groundwater.

It is known that the circumstance of a groundwater is anaerobic and the redox balance of a groundwater is generally maintained by the relative rates of atmospheric O2. Therefore, the extraction of a groundwater may destroy the redox balance of iron, which may cause a conversion between ferrous ion and ferric ion. Indeed, both of the methods affect the result of concentration of iron, but the circumstance of closed system of stoppered flask may be more closed to the actual groundwater environment. So we collected groundwater samples in stoppered flask in 2007.

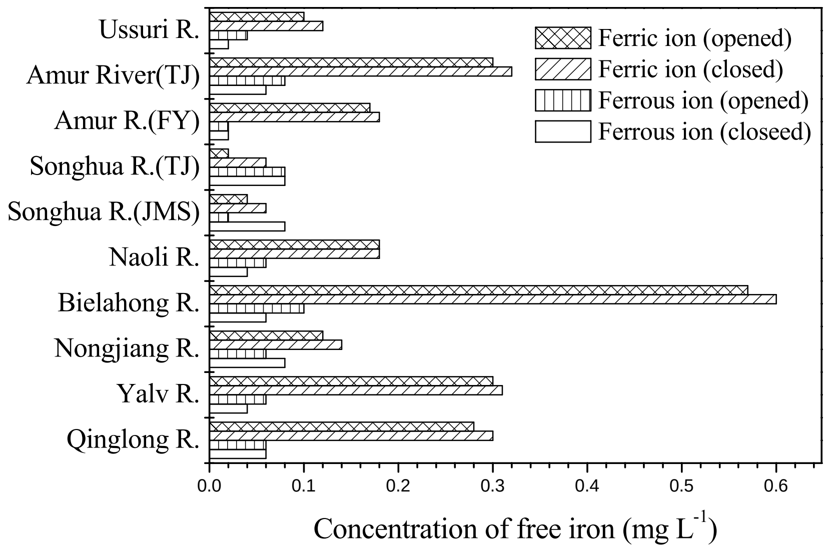

Fig.7 Comparison between different method of sample preservation about free iron concentration in river waters

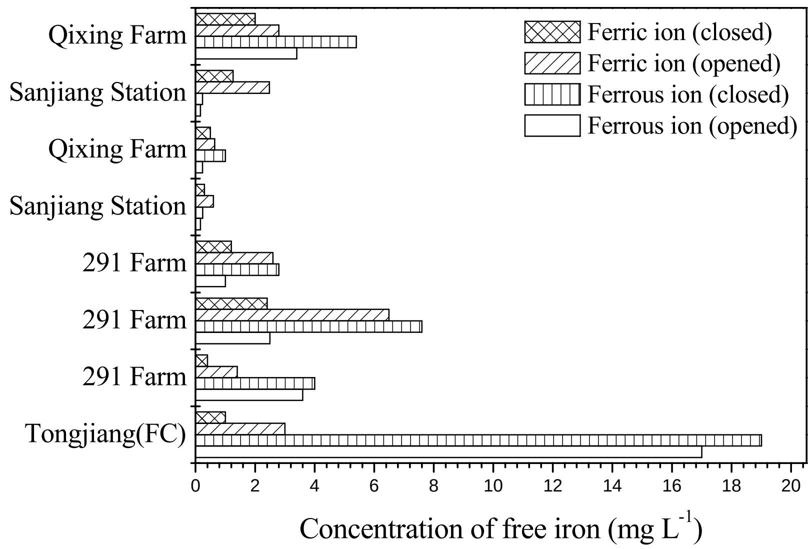

Fig.8 Comparison between different method of sample preservation about free iron concentration in groundwater

3.6 Runoff Outflux of Iron from River Waters in Sanjiang Plain

Sanjiang Plain is locates in temperate zone and has a character of continental monsoon climate. Annual rainfall is about 550-600 mm and there is a frozen periods during November and April. Therefore, the variation of runoff flow is great at the different seasons.

Exploitation of wetland destroys the surface plant and water circumstance, accelerates drought of the climate, and affects the rainfall and runoff in the Sanjiang Plain, which cause the variation output flux of iron in river waters. With the rapid expansion of agriculture, rainfall and runoff of marshy river had a decreasing tendency since the 1950's (Yan *et al*., 2004).

Liu *et al*. (2003) collected and calculated the hydrological data of different rivers including China and Russia in the region (Tab.4).

Table 4 Average annual runoff of different rivers

River	Drainage basin acreage/km^2	Hydrological Station	Catchment acreage/km^2	Average several years runoff/10^8 m^3
Amur R.	1843000	Khabarovsk	1630000	2664.8 [a]
Ussuri R.	187000	New Soviet	186000	411.6 [b]
Songhua R.	545639	Jiamusi	527795	688.4 [c]

[a] The value is calculated from 1896-1990
[b] The value is calculated from 1940-1990
[c] The value is calculated from 1940-1990

Based on the flow data above and mean concentrations of four forms iron, the annual output of iron transporting with runoff from different rivers in 2007 is estimated in Tab.5. Compared with the data of 2005 and 2006 (Fig.9), the output of iron in 2007 was significantly low due to decreased concentration of iron.

Table 5 Annual output of different forms iron in 2007

River	Concentration/ runoff flux	Fe^{2+}	Fe^{3+}	Complexed iron	Acid soluble particulate iron
Amur R.	Average concentration/mg L^{-1}	0.04	0.16	0.19	0.12
	Average runoff flux/ 10^8 kg yr^{-1}	0.10	0.43	0.50	0.31
Ussuri R.	Average concentration/mg L^{-1}	0.02	0.13	0.16	0.10
	Average runoff flux/ 10^8 kg yr^{-1}	0.01	0.05	0.06	0.04
Songhua R.	Average concentration/mg L^{-1}	0.05	0.15	0.16	0.09
	Average runoff flux/ 10^8 kg yr^{-1}	0.03	0.10	0.11	0.06
Total	Average concentration/mg L^{-1}	0.11	0.44	0.51	0.31
	Average runoff flux/ 10^8 kg yr^{-1}	0.14	0.58	0.67	0.41

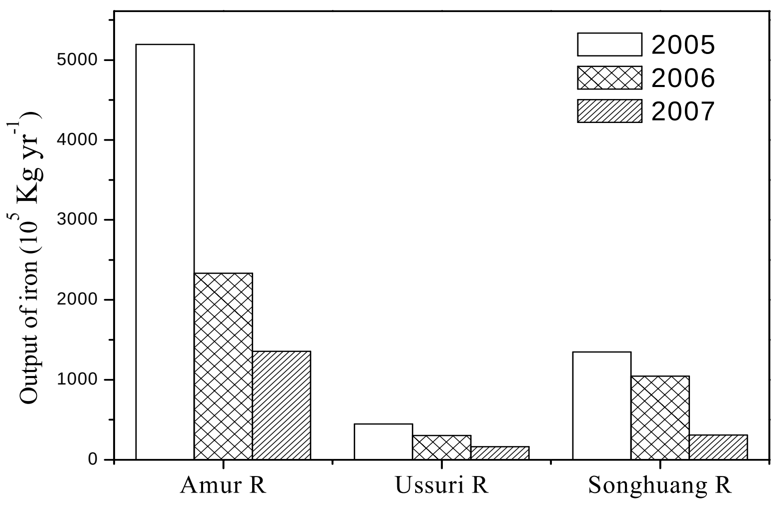

Fig.9 Different output of total iron in different time

CONCLUSION

The main results of this study can be summarize as follows: (1) In the study sites, the concentration of free iron exhibited a higher variation and the rapid expansion of agriculture reduced sharply the quantity of iron in river waters over past 50 years. This result led us to know that wetland is one of the major sources of iron. (2) Iron migrates mainly in ferric ion and complexed iron forms in river waters. There are significant differences in iron chemistry between high and low flow period due to internal process in river waters. (3) The concentrations of iron in marshy rivers are higher and more variable than those in the main rivers. Because marshy rivers are abundant in organic matters, an excess of ligands can be derived from marshy rivers. (4) Ferrozine is a high affinity and selectivity compounds, which can make equilibrium attain reasonably rapidly. Therefore, FZ reacts extremely rapidly with ferrous ion to form a purple colored complex in 2 min and continue to replace iron from other weak organic ligands in about 30 h. Through the experiment of competitive ligands, we found ferrous iron exists primarily as form of complex iron in river waters. (5) According to the data of average annual runoff from four rivers, the average runoff flux of four species can be calculated (see Tab.5).

LUCC has destroyed the wetland environment, changed the runoff outflux of iron to the ocean, and indirectly affect the ocean ecosystem. In addition, LUCC also changes iron forms in river water, which may affect the bioavailability and the fate of iron. Cultivation changes the aquatic condition (from anaerobic to aerobic environment), and influence indirectly the fate of iron.

PERSPECTIVE FOR FURTHER RESEARCH

Our field observation revealed that LUCC has destroyed the wetland environment, changed the runoff out-flux of iron to the ocean. In addition, LUCC also changes iron forms in river waters and groundwater, which may affect the bioavailability and the fate of iron. However, the biogeochemical process of iron in river waters and groundwater during the irrigation and discharge periods and composition of complex iron have not been known yet. Considering the bioavailability of complex iron which is primary forms in river waters, we should focus on the characteristic of organic matters binding with iron and understand the influence of the complex process on the bioavailability of iron. And also we should focus on what controls the soluble iron species in surface water and microcosmic factors in surface water environment with the development of LUCC. Some results may implicate LUCC is an important factor to variation of iron concentration. But how does it influence? Marshy wetland only functions as supply of iron? Maybe some problems must be considered further.

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