CONCENTRATION AND SPECIES OF DISSOLVED IRON IN WATERS IN SANJIANG PLAIN, CHINA

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ABSTRACT

Water samples were collected from May to October in 2005-2008 to investigate the concentrations and fractions of dissolved iron in rivers, wetland and agricultural drainage in Sanjiang Plain, where land-use has been changing greatly since last fifty years although was formerly the largest concentrative distribution area of freshwater marshes in China. cross-flow technique was used to separate iron species by size fraction. The aim of this study is to reveal the iron fraction and to evaluate the effect of land-use change on transport and output flux of dissolved iron. The results show that marsh and marshy rivers exhibited higher concentrations of dissolved iron than in Amur River, Songhua River and Ussuri River and are the primary sources of dissolved iron for the rivers. Low molecular weight (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. Ferrous iron accounted for 80.45% of dissolved iron in groundwater. The concentrations of high molecular weight and medium molecular weight iron (colloid iron) increased in paddy waters and ditch waters compared with in groundwater. Ferric and ferrous concentrations in Naoli River decreased between 1960's and 2008. Land-use change in Sanjiang Plain reduces the output of dissolved iron, especially LMW iron and resulted in a great reduction of output flux of dissolved iron to Amur River.

Key words: Fraction of dissolved iron; land use change; Sanjiang Plain; wetland; Amur River; Naoli River

1. INTRODUCTION

As an essential redox-active transition metal, iron can control the geochemical cycle of other trace elements. More importantly, it is a key nutrient in the ocean system that limits the primary productivity in many ocean areas and can also exacerbate problems caused by cyanobacterial blooms (Mills, et al., 2004; Morel and Price, 2003; Schulz et al., 2004). Previous studies have widely focused on the bioavailability of iron species in coastal water and seawater. The northern North Pacific is known as the ocean of high-nitrate and low-chlorophyll (HNLC) contents where dissolved macronutrients in the surface water cannot be fully utilized by phytoplankton because of the low availability of iron (Narita et al., 2004).

The neighboring Sea of Okhotsk is also characterized by sufficient nutrients supplied by winter convective mixing of surface and deep water. The Sea of Okhotsk is, however, not an HNLC region (Narita et al., 2004). This is probably because of sufficient dissolved iron that can be mainly transported from the Amur River. The Amur River brings a rich supply of dissolved iron into the Okhotsk Sea (Pan et al., 2007). As the Sanjiang Plain is widely underlain by freshwater marsh, and dissolved organic carbon in marshy waters can reach 27.07-44.59 mg/L, which can greatly improve the solubility of iron, the dissolved iron is mainly formed as a complex of iron and fulvic acids (Nagao et al., 2007). Therefore, the Sanjiang Plain may actually play a critical role in iron export. Wetland in Sanjiang Plain is located in a low-lying alluvial floodplain along the river, and this area experienced slow sedimentation, which lead to iron enrichment in groundwater and sediments. Moreover, complexation by natural organic matter (NOM) may either prevent or retard the precipitation of the oxyhydroxides. The formation process of dissolved iron and how it is transported to rivers are yet to be understood.

In fact, typical coastal waters receive large iron loads from river water, groundwater inputs and direct terrestrial runoff. In surface water, Fe (Ⅱ) species are rapidly oxidized with a half time of the order of several minutes (Millero et al., 1987; Rose and Waite, 2002) to either organically complexed Fe(Ⅲ) or to inorganic Fe(Ⅲ) species, which rapidly hydrolyze and subsequently precipitate as iron oxyhydroxides (Kuma et al., 1996; Liu and Millero, 2002). Consequently, insoluble ferric oxyhydroxide and organically complexed Fe(Ⅲ) are the dominant iron species in aquatic environments. Iron complexed by organic ligands may be assimilated by organisms via redox and ligand-exchange processes (Sunda, 2001; Rose et al., 2005).

With the rapid development of the drainage channel system and reclamation of marshes to upland and paddy land in the past 50 years there, the cultivated land area has increased to 5.24 Mha in 2000 from about 0.79 Mha in 1949. Accordingly, the wetland area has decreased to 0.84 Mha in 2000 from 5.35 Mha in 1949 (Liu, 2000; Li, 2002). Our previous studies showed that intensive cultivation in the plain changed the unique geological geomorphology, redox conditions, pH value, NOM contents and long waterlogged environment of wetland ecosystem (Pan et al., 2007, 2008), which caused the changes in iron chemical forms and concentration, finally reducing the iron output flux. On the other hand, groundwater irrigation brings vast iron supply to surface water. However, when groundwater is brought to surface land, the transformation of ferrous iron immediately occurs. Therefore, a much clearer understanding of various forms of iron present in the natural waters is needed to properly relate land-use change to the variability of iron. Therefore, the aim of this study is to reveal the chemical forms and migration process of dissolved iron in different waters in the Sanjiang Plain and to evaluate its output flux.

2. MATERIAL AND METHOD

Water samples were collected from river, wetland, well, paddy and canal from May to October in 2005~2008 (Fig. 1). Chemical speciation of iron was conducted using filtration and ultrafiltration methods. Dissolved iron species separated by cross-flow method and Whatman membrane(0.7μm) filtration were divided into three fractions: high-molecular-weight iron (HMW, 0.7~0.05 μm,), medium-molecular-weight iron (MMW, 0.05~0.01μm), and low-molecular-weight iron (LMW, <0.01 μm). Indication of the size distribution of iron species present was obtained by measuring the concentration in the 0.01, 0.05, and 0.7 μm filtrates. LMW iron fraction includes ion (Fe^{2+}) and complexed iron (organic iron). Ferrous iron was analyzed by Ferrozine Spectrophotometry *in-situ*.

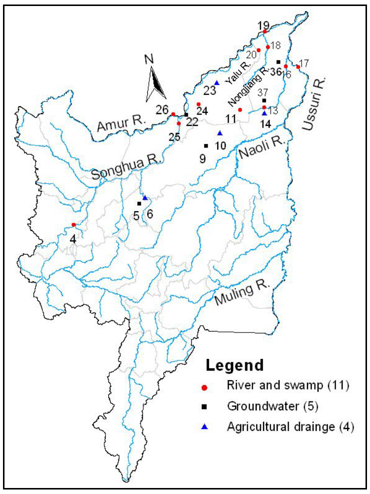

Fig.1 Location of samples in the Sanjiang Plain

The water samples were partially acidified to pH 2.0 and filtrated with Whatman membrane. The other samples were filtrated with Whatman GF/F glass fiber filters, acidified to pH 2.0 to reduce iron oxidation significantly, and then stored at 4°C prior to further treatment. The latter (pre-filtrate) subsequently flowed into the cross-flow filtration device with a membrane pack of nominal molecular weight cutoff of 50,000 Dalton. The retentate was analyzed immediately, and the filtrate or permeate flowed into 10,000 Dalton MWCO membrane. All filtrates were collected for measurement of total iron concentrations. The colloidal fraction is operationally defined here as a material that passes through 0.7 μm prefilter, while retentate is defined by a CFF membrane with a nominal molecular weight cutoff of 10,000 Dalton.

RPA-100 Fe analyzer was applied for the measurements of ferrous iron, AAS GBC 906 (Australia) for dissolved iron, Shimadzu TOC-VCPH Model Analyzer for DOC, and Horiba Water Cheker Model U-10 for water temperature and pH in-situ, respectively.

3. RESULT AND DISCUSSION

3.1 Temporal variation of dissolved iron concentration in different waters

3.1.1 River water

The concentrations of dissolved iron ranged between 0.050-1.010 $mg \cdot L^{-1}$ in Songhua River, 0.020-0.880 $mg \cdot L^{-1}$ in Amur River, 0.128-0.980 $mg \cdot L^{-1}$ in Ussuri River, and 0.430-4.874 $mg \cdot L^{-1}$ in marshy rivers (Naoli R., Bielahong R., Nongjiang R. and Yalv R.). The peak of dissolved iron concentrations mainly presented in the period between spring and flood season, namely May and June (Fig. 2), when is the irrigation period. The elevated concentration in rivers may attribute to the supply of iron from agricultural drainage, where the iron concentration reached 0.27~0.68 mg·L^{-1} during the irrigation period.

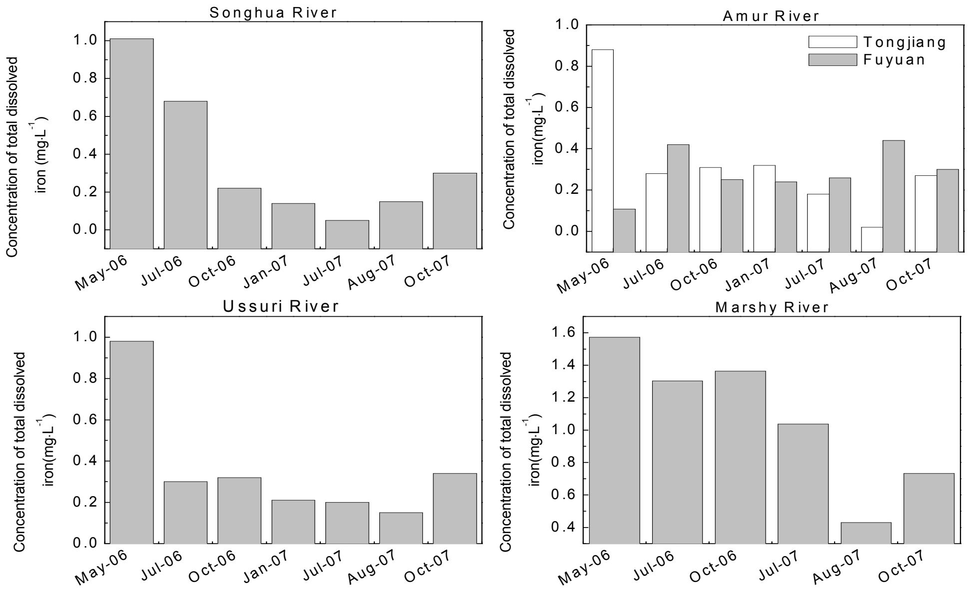

Fig.2 Seasonal variation of dissolved iron concentration in main rivers and marshy rivers in Sanjiang plain

The concentrations of dissolved iron between 2005 and 2008 were higher in marshy rivers than main rivers (Fig.3). The mean concentrations of dissolved iron in main rivers were 0.300 mg·L^{-1} (0.143-0.490 mg·L^{-1}) in Amur River, 0.422 mg·L^{-1} (0.160-0.830 mg·L^{-1}) in Songhua River, 0.373 mg·L^{-1} (0.128-0.647 mg·L^{-1}) in Ussuri River, respectively, while the mean concentrations were 1.401 mg·L^{-1} (0.733-2.965 mg·L^{-1}) in marshy rivers.

Dissolved iron concentration was higher in Songhua River than Amur River, but DOC concentration was consistently higher in Amur River than in Songhua River（Fig.4）. As DOC has the character with high affinity and selectivity for iron, this abnormity may attribute to the composition of DOC. Area and the proportion of wetland and forestland are higher in Amur River basin, while land use has intensively been changing from anthropogenic activity in Songhua River basin. Thus, the component of NOM may have been influenced. More organic matter should be supplied mainly by natural source from wetland and forestland in Amur River, and that the proportion of anthropogenic source should be upgraded in Songhua River. Guo and Ma (2005) found that the component of NOM in Songhua River followed the order fulvic acid（37%） > humic acid（27%） > hydrophilic fraction（18%）, and the soluble aliphatic hydrocarbons was the predominant fraction of DOM. Fulvic acid was observed higher in Amur River using fluorescent techniques（Nagao, et al., 2007）. Both dissolved iron and DOC concentrations in marshy rivers were higher. The DOC concentrations ranging from 7.710 to 13.054 mg·L^{-1} were generally 10.280 mg·L^{-1} in marshy rivers. The iron solubility may be greatly improved by forming the complexed iron due to much higher DOC concentration in marshy water.

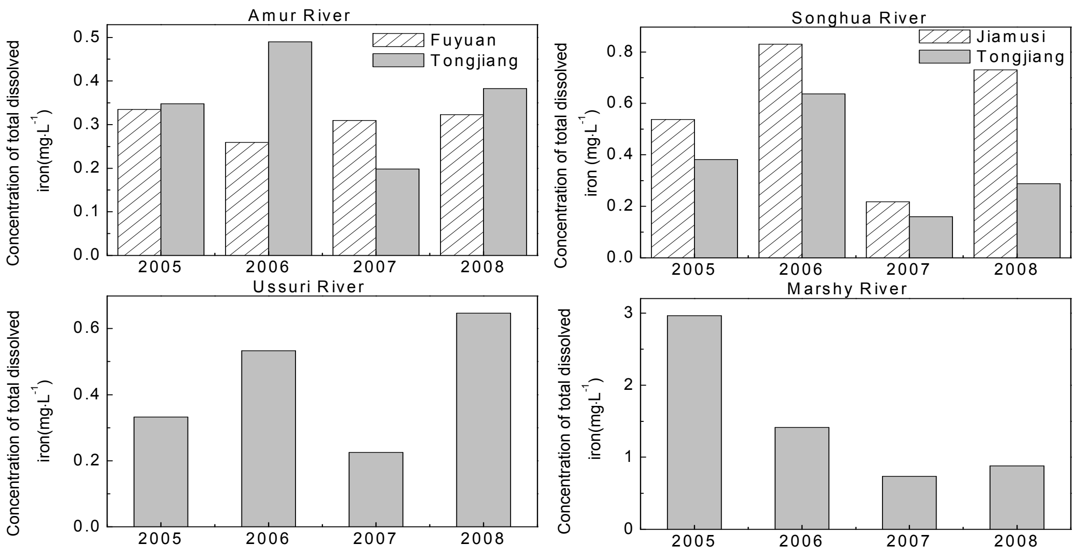

Fig.3 Year-to-year variation of averaged total dissolved iron concentration in river waters in Sanjiang Plain

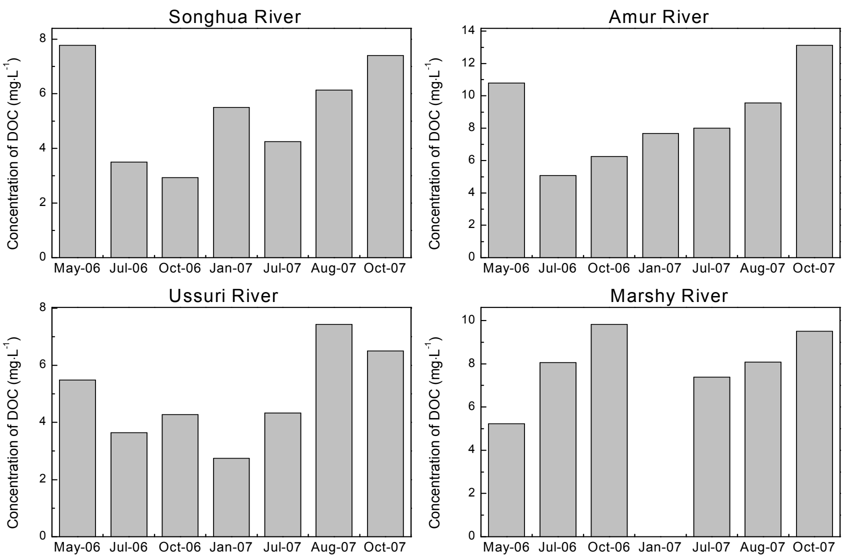

Fig.4 Seasonal variation of DOC in the river waters

3.1.2 Agricultural drainage waters

The Sanjiang Plain is crisscrossed by a network of agriculture ditches because of the water-logging prevention and irrigation for paddy field. Iron contents in agriculture drainage also visualized the variation with years and seasons (Fig.5). Dissolved iron concentration sporadically increased in May and Sep, which may result from drainage from agricultural activity, and overflow or lateral seepages during a storm. As the flows and concentrations of dissolved iron in both rain and seepage water were lower, their effects on concentrations of dissolved iron in ditch water may be finite.

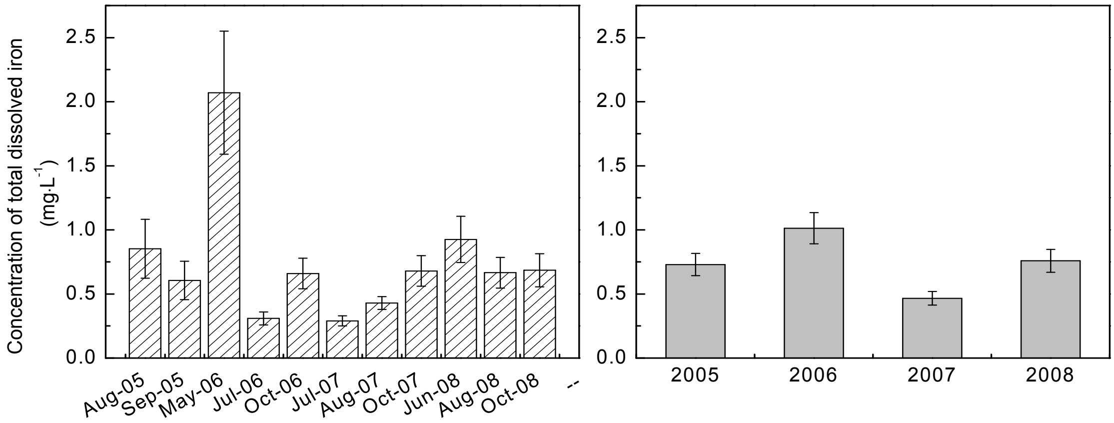

Fig.5 Variation of total dissolved iron concentration in agricultural distrainage (Qianfeng)

3.1.3 Groundwater

In Sanjiang Plain, irrigation water for rice growing mainly comes from groundwater. The groundwater was universally rich in dissolved iron, which can reach 21.3 $mg·L^{-1}$ in some areas. The concentrations were lower in Honghe Farm, reaching to 0.46±0.30 $mg·L^{-1}$, and higher in 291 Farm and Qixing Farm, reaching to 2.91±2.67-12.63±4.86 $mg·L^{-1}$, and the highest concentration was found in Fuchuan County located at the west of Tongjiang City (Fig.6). Dissolved Fe concentration in ground water at same site showed a considerable variation with seasons, being in the following order in some cases: flood season (July + August) > mean flow season (May + June+ September) > dry flow season (October-April) in level of $P<0.05$. This variation was apparently related with the ups and downs of groundwater level (Fig.7). The concentrations increased with the falling of groundwater level, and decreased with the rising of groundwater level within a year. The fluctuation of groundwater level was induced from lift irrigation. Mostly, lower groundwater level emerges during May and July due to intensive irrigation pumping.

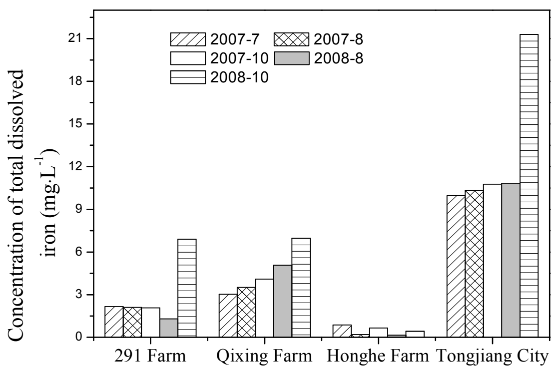

Fig.6 Total dissolved iron concentration in groundwater in different regions

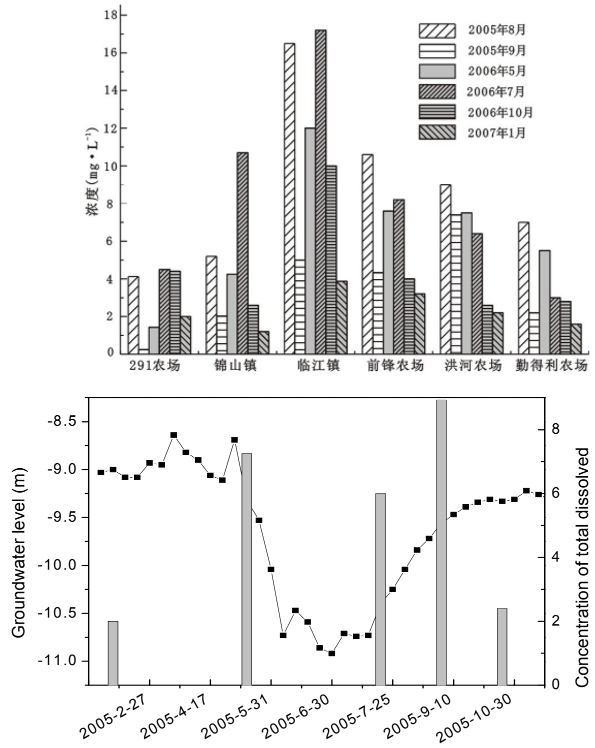

Fig.7 The relationship between dissolved iron concentration (bars) and groundwater level (line with dot) in Honghe Farm

3.1.4 Marshy water

Fig.8 presented the seasonal and annual variations of dissolved iron concentrations in surface water in the marsh located in the experimental field of Sanjiang Station. Water sample were collected from July to October between 2006-2007. The concentrations of dissolved iron range from 0.490 to 1.075 mg/L. The concentration was higher in July than in September and October. Marsh water has rich organic matter, DOC concentrations are generally 35.65 mg/L or more and have a little variation. Moreover, the pattern of water supply for marsh system is mainly rainfall-fed and snowmelt-fed. The dissolved iron concentration measured for a 17 mm rain event on July 31, 2007 in Sanjiang Experimental Station was quite low only at 0.107mg/L. Therefore, the season fluctuation of dissolved iron in marsh might partly be influenced by rainfall. The analytical results show the relative proportion of dissolved iron in marsh lowered after a storm event in the summer of 2007 (Fig.9).

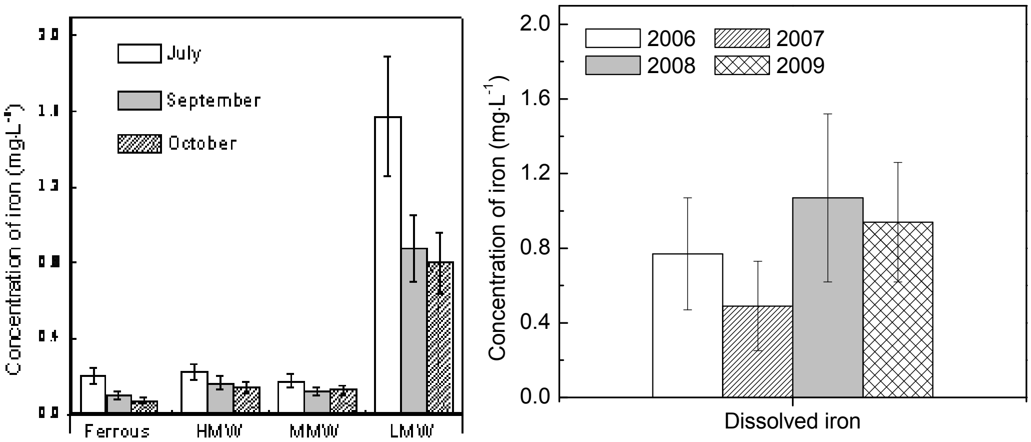

Fig. 8 Seasonal and annual variations of concentration of dissolved iron in marsh in Sanjiang Station

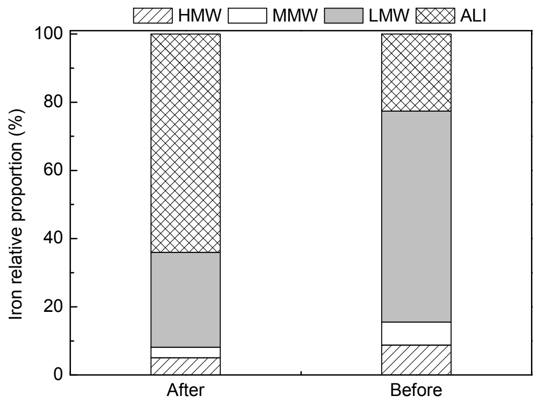

Fig.9 Relative proportion of dissolved iron in marsh water before and after a heavy rain event

3.2 Iron species

Low molecular weight iron (most of them are complex iron.) was the primary species of dissolved iron in all waters. Ferrous iron content were much higher in groundwater, and the acid-labile iron (ALI) concentrations were greatly higher in paddy and marsh than those in river waters (Fig.10).

The relative proportion of iron species in paddy water, groundwater and marshy water show that the highest complexed iron concentration was found in marshy water, and the lowest was observed in groundwater (Fig. 11,Tab.2), which indicated that complexed iron concentrations had obviously relationship with DOC concentrations. The DOC concentrations in marshy waters, paddy waters and groundwater were 35.65 $mg \cdot L^{-1}$, 7.37 $mg \cdot L^{-1}$, 4.30 $mg \cdot L^{-1}$. Ferrous iron is the main form of dissolved iron in the groundwater, which may attribute to the reductive conditions and less abundant organic matter in aquifer.

The marshy rivers have its source in the wetland or they flow through the wetland. However, when marshy waters flowed into marshy rivers, dissolved iron concentration decreased by 52%, the ferrous and complexed iron concentrations decreased by 75% and 57%, respectively. ALI concentration increased 46.7% and the colloid iron changed little (Tab.2). The difference between the marshy waters and marshy rivers in the water environment is obvious. pH (6.87), electric conductivity (0.129 $ms \cdot cm^{-1}$) and Eh is higher in marshy rivers than that in marshy waters. Therefore, the conversion of Fe^{2+} to Fe^{3+} and the selective flocculation would occur when marshy waters flowed into marshy rivers. Otherwise, DOC content may control the iron species and concentrations in marshy rivers and main rivers. DOC content in marshy rivers was 11.41 $mg \cdot L^{-1}$, which is higher than in the main rivers (8.64 $mg \cdot L^{-1}$). Furthermore, LMW iron concentration in marsh was 1.20 $mg \cdot L^{-1}$, which is higher than that in the main river (0.32 $mg \cdot L^{-1}$). Therefore, the marshy rivers become the main iron source for the Amur River.

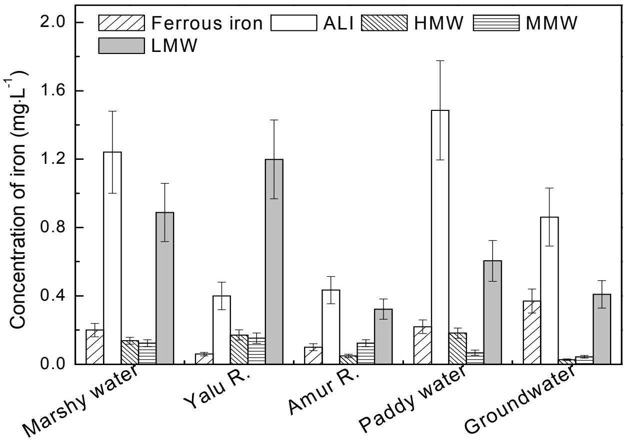

Fig. 10 Characteristics of iron species in different type waters in the Sanjiang Plain

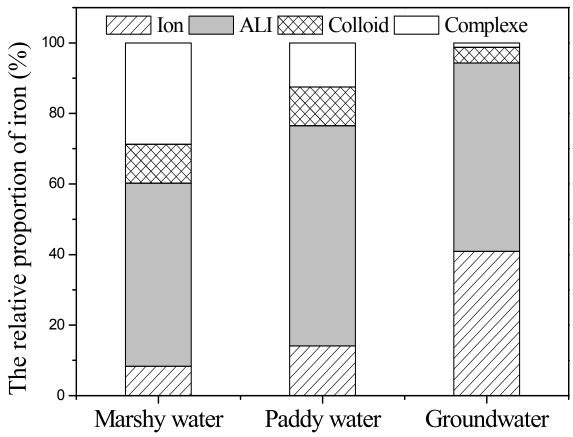

Fig.11 The relative proportion of iron specie in marshy water, paddy water and groundwater

Tab.2 The distribution of iron species in different water bodies（May, 2009） mg·L-1

Type	Total dissolved iron	Ferrous iron	Complexed iron	Colloid iron	Acid-labile iron	pH
Marshy waters	1.53±0.29	0.32±0.14	0.91±0.62	0.30±0.13	0.58±0.27	5.94±0.22
Marshy rivers	0.73±0.12	0.08±0.02	0.39±0.28	0.26±0.11	1.10±0.53	6.87±0.69
Paddy waters	1.94±0.37	0.15±0.05	1.57±1.07	0.22±0.09	4.52±2.24	7.08±0.32
Canal waters	0.96±0.17	0.18±0.07	0.54±0.38	0.24±0.10	0.76±0.36	7.12±0.43

3.3 The impact of land use change on dissolved iron concentration of Naoli River

The Naoli River is a typical marshy river in Sanjiang Plain. Land use has been enormously changing there due to the large scale of wetland reclamation in the last 50-year. The runoff reducing, temperature warming and groundwater table falling had been continually observed in the watershed (Yan, et al., 2004; Luan, et al., 2007). The contribution from human activities to runoff decrease in Naoli River accounted for71.19 % for the upstream, and 62.21 % for the middle-stream (Luan, et al., 2007). Therefore, dissolved iron concentration and transportation flux are influenced by anthropogenic activities. By contrasting our research data and sporadic historical data in 1960's and 1980's from hydrological department, we found that concentrations of ferrous and ferric iron decreased gradually between 1964-2008 (Fig.12). The sequel may attribute to the decrease in wetland area and falling of groundwater table. One the one hand, the conversion wetland to upland will lead rare runoff from upland as dry soil particles suck almost all precipitation. On the other hand, agricultural drainage from paddy field has been strictly controlled by agricultural management although there could be additional iron supply from the irrigation of ground water. Otherwise, precipitation and wetland water fleetly reinforce groundwater as a result of falling of groundwater table. Consequently, no more water (or runoff) and dissolved iron from wetland and farmland flows into rivers, which irresistibly induced the decline of dissolved iron export to Amur River. In conclusion, the land-use change is inferred to be the predominant factor leading to the great decreasing of dissolved iron in rivers.

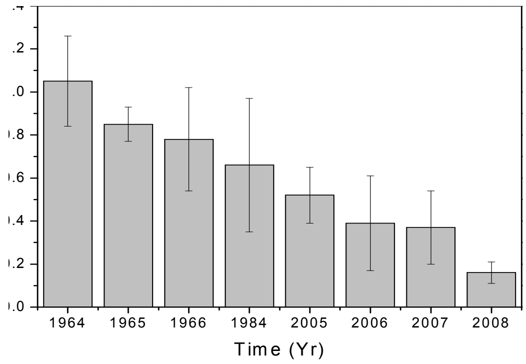

Fig.12 The variation of ferrous and ferric iron concentration in Naoli River

4. CONCLUSION

Marshy waters and marshy rivers exhibited higher concentrations of dissolved iron and are the primary sources of dissolved iron for the main rivers. The iron solubility is improved greatly by forming the complexed iron due to much higher DOC content in marshy water. The concentrations of dissolved iron in ground water was found to increase with the falling of groundwater level and decrease with the rising of groundwater level within a year. Low molecular weight iron, most of which are complex iron, was the primary species of dissolved iron in wetland and marshy streams, and 71% of LMW iron was in organic form in wetland. Ferrous iron content were much higher in groundwater. The concentration of ferrous and ferric iron decreased gradually between 1964-2008, possibly due to wetland reclamation of large scale. Thus, it is likely that land-use change in Sanjiang Plain reduces the output of dissolved iron, especially LMW iron and resulted in a great output flux reduction of dissolved iron to Amur River.

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