Distribution of dissolved iron in surface and groundwater in Sanjiang plain, Northeast China

Yan B. X., Zhang B., Pan Y. P., Wang D. X.

Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences

1. INTRODUCTION

LUCC is one of the important factors controlling the biogeochemical process of elements, especially in the Sanjiang Plain, which is located in the northeastern end of Heilongjiang province, Northeast China and is bordered by Russia in north and east sides. 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 5.24 Mha in 2000 from about 0.79 Mha in 1949. Accordingly, the wetland area was decreased to 0.84 Mha in 2000 from 5.35 Mha in 1949 (Liu, 2000; Li, 2000). Sanjiang Plain has become a representative region in China and East Asia to know the influence of LUCC on dynamics of transport mechanism and biogeochemical cycle of iron and other elements. Therefore, the purpose of this subject is to know the concentration and chemical forms of dissolved iron in surface water and groundwater, including rivers water, agricultural drainage and groundwater used to irrigation. Based on the four times field investigation and sampling analyses in the fiscal year of 2006, we put emphasis on the temporal, spatial and species distribution of iron in different water types, as well as the influence of human activities.

2. MATERIALS AND METHODS

2.1 Water Samping

Water samples were collected from rivers, agricultural drainages and wells in May 2006, July 2006, October 2006 and January 2007, respectively. The sampling schedules were depicted in table 1 and the sampling sites were showed in Fig1.

Table 1 Sampling information of 2006 in Sanjiang Plain

No	mm/dd/yy	Groundwater samples number	River watersamples number	Agricultural drainage samples wnumber	Total samples numbere
1	May 16-20,2006	8	14	6	28
2	July26-29,2006	6	10	6	22
3	Oct 8-11,2006	8	9	4	21
4	Jan 11-14,2007	7	8	0	15
Sub-total		29	41	16	86

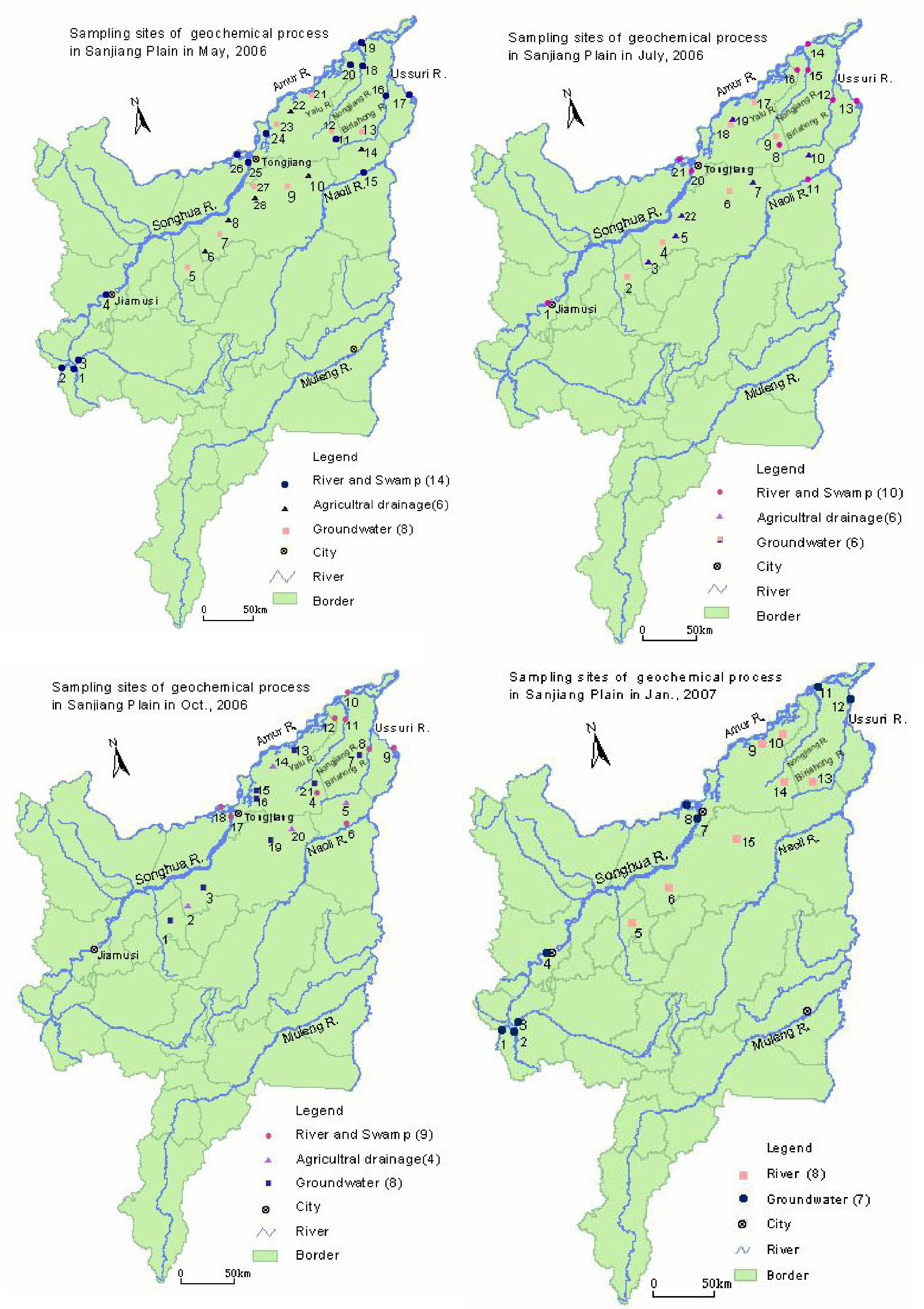

Fig 1 Sampling location in 2006 in Sanjiang Plain, Northeast

2.2 Pre-treatment and analyzing

After water sample collected, 1.00ml conc. HCl was added to the 100 ml bottles for the determination of acid soluble Fe, other samples were stored in a portable refrigerator (0-4℃) until further treatment(filtration and acidification) and determination of free Ferrous , ferric and the total dissolved ionic Fe, bicarbonate.) at the lodge that evening. Chemical analysis of the rest items were carried out at the laboratory of Northeast Institute of Geography and Agricultural Ecology, CAS (Table 3) within one week after the collecting. The measurement methods of all items are listed in Table 2.

Table 2 Measurement method and analyzer

items	method	analyzer	remark
NH_4^+,NO_3^-,NO_2^-,PO_4^{3-}	orimetry/colorimetry	SKALAR-SAN^{++} continuous flow analyser	In lab
K, Na, Ca, Mg, acid soluble Fe Total dissolved Fe and Mn	AAS	GBC 906 atom absorption spectrophotometer	In lab
SiO_2	colorimetry		In lab
DOC	TOC-Vchp	TOC analyzer	In lab
Fe^{2+} and Fe^{3+}	Ferrozine absorption spectrophotometer method	Fe^{2+} analyzer	Field*
HCO_3^-	titration		Field*
pH, EC, WT, SAL (Salinity), TURB(turbidity)	electrode method	HORIBA U-10	In situ

*measured within 12 hours

Ferrous iron was determined with classical Ferrozine spectrophotometric method (Stookey L. L.,1970). Only where there is a difference from this published report, will it be specified below. After reduced with Ascorbic acid, the water samples will be determined by the method mentioned above, and the readings are considered as the total dissolved ionic Fe including ferrous and ferric. The concentration of ferric will be calculated with subtraction method.

3. RESULTS AND DISSCUSSION

3.1 Spatial and seasonal variation of Fe in groundwater

Concentration of total dissolved Fe (TDFe) in groundwater samples ranged between 0.06 and 19.83 mg/l , which of most were above WHO recommendations criterion for drinking water. The mean was 5.38 mg/l, which is bigger than its background value 4.85 mg/l (Wang ,2004).

The shortage of rainfall usually occurred during the rice-growing season from May (seeding) to August. So, irrigation pumping groundwater is an important and extensive mean for rice growing in the region owing to rich groundwater resorce and shallow groundwater level. More iron will be input into paddy field with groundwater in the irrigation process due to higher concentration of TDFe in groundwater.

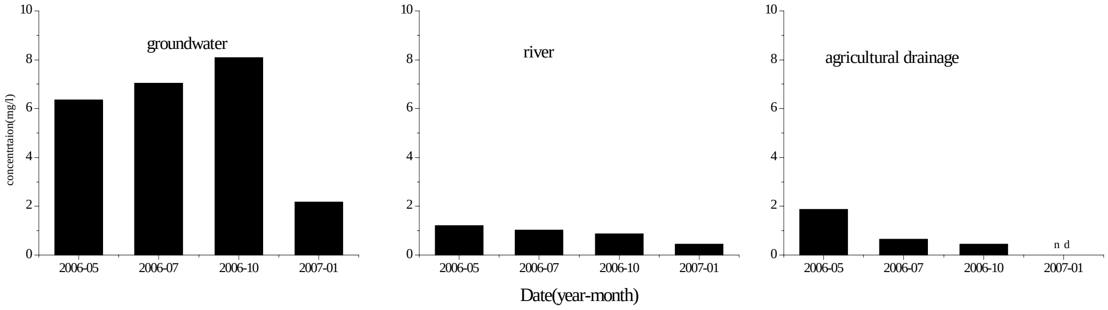

Fig. 2 Total dissolved Fe concentration in groundwater, river water and agricultural drainage

Figure 2 shows mean concentration of TDFe in grounwater in different seasons. It is clear that the concentration of TDFe is highest in fall (October) and lowest in winter (January), the concentrations in summer and spring are little less than, but very closed to than that in fall. The temporal distribution was opposite to the seasonal change of groundwater level in Sanjiang Plain (Fig.3). Form this interesting phenomenon, we concluded that concentration of TDFe increased with the falling down of groundwater level. The assumptive link will be approved in next year through further synchronous investigation, and it was helpful to assessment the TDFe output flux from the groundwater to the surface water.

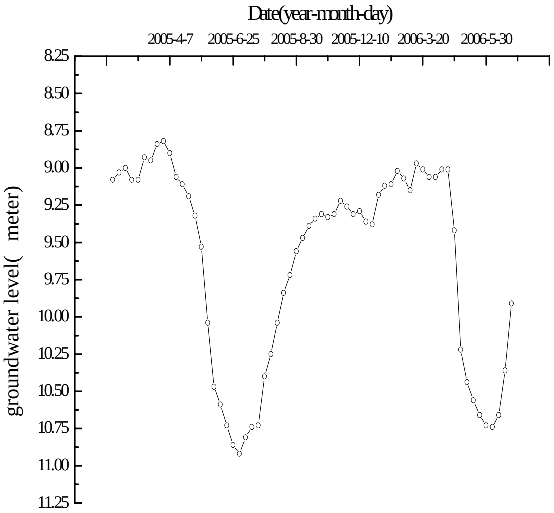

Fig.3 Temporal change of groundwater level in Sanjiang Experimental Station

It is interesting to note that the dissolved Fe concentration was higher at sites near the Songhua River(Jiamusi and Tongjiang) than Amur River. Although the reason for such difference among these sites is unknown, this phenomenon deserves attention in view of the spatial distribution of Fe.

The chemical form of Fe in the groundwater in May 2006 is showed in Figure 4. Organic Fe generally accounted for 30 % or less of dissolved Fe; i.e., free ferrous iron was the main fraction of dissolved Fe in most of the groundwater. In addition, particulate Fe accounted for only a small portion of dissolved Fe among all samples.

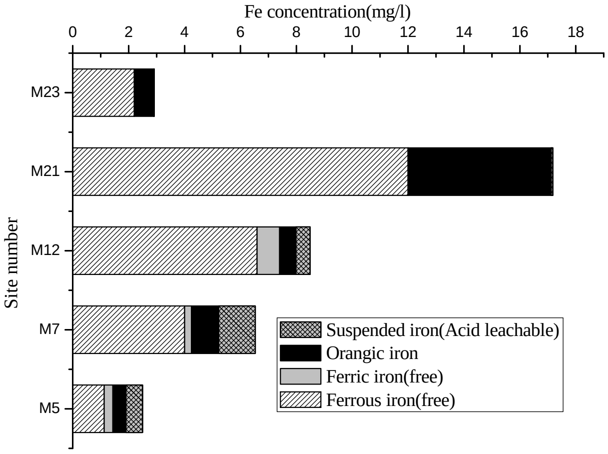

Fig.4 Concentrations of dissolved Fe, free ferrous Fe, and suspended Fe in groundwater (May., 2006). Organic Fe was estimated from the difference between dissolved Fe and free Fe (including ferrous and ferric Fe) Acid leachable Fe was the difference between ASFe and TDFe.

3.2 Spatial and seasonal variation of Fe in river water

TDFe concentrations in river water also showed a definite difference among the sites. Throughout the year of 2006, the TDFe concentration was somewhat lower in river water than that in agricultural drainage during periods of spring flood, whereas the opposite was observed during the rest of the year. However, the Fe concentration both in agricultural drainage and rivers showed a slowly decrease from spring to winter (Fig. 2). Among all the sites, the concentration of TDFe in river water was slight lower than that in groundwater.

Dissolved Fe concentrations in all samples of river water and swamp waters throughout six observations (August and September in 2005; May, July, October in 2006 and January in 2007) ranged between 0.08 and 10.40 mg/l (averaging 0.89mg/l) in the river water, having a large variation of two orders of magnitudes among the samples. The range was 0.21 to 2.16 mg/l in “forested” sites, while 0.19 to 10.40 mg/l in “swamp” sites. Thus, we found a clear tendency that the swamp area has higher dissolved Fe concentrations.

Figure 5 shows the mean concentrations of TDFe in different type river waters. It also showed a definite difference among the sites as described above; low level in rives derived from forest and high level in rivers derived from wetland.

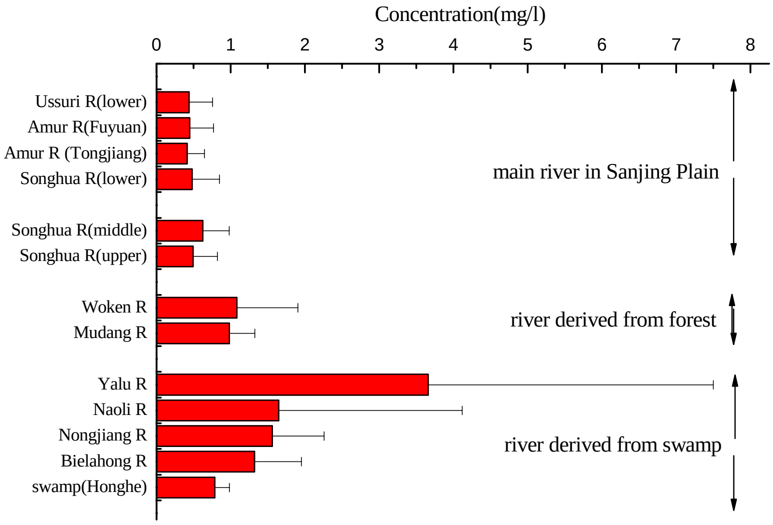

Fig.5 Concentration of TDFe in river waters(X ±SD)

Moreover, an interesting phenomenon was found that both of rivers from forest and wetland had higher TDFe concentration than the main rivers, i.e., Songhua River, Amur River and Ussuri River. It is confirmed from these results that the rivers in Sanjiang Plain act as the source of dissolved iron to Amur River. Furthermore, we observed that the concentration of TDFe in Usuuri River was similar to that in Amur River and the concentration in Songhua River was slight higher than that in Amur River (Fig. 5). This result indicates that the Songhua River export much Fe to Amur River based on its higher annual discharge (711.8 m^3/a) than Usuuri River(413.7 m^3/a).

The seasonal variation of dissolved Fe concentration among Amur River was compared in Figure 6. It is interesting to note that dissolved Fe concentration in river water had a common feature. The maximum concentration often occurred in May 2006. In addition, the concentrations of TDFe were nearly stable in other observations period except Songhua River. The result indicated that Songhua River exported high concentration TDFe to Amur River all the year, and Ussuri River exported high concentration TDFe to Amur River only in Spring flood period. Although the reason for such high concentration in Songhua River water is unclear, this phenomenon deserves attention in view of the transport flux of Fe.

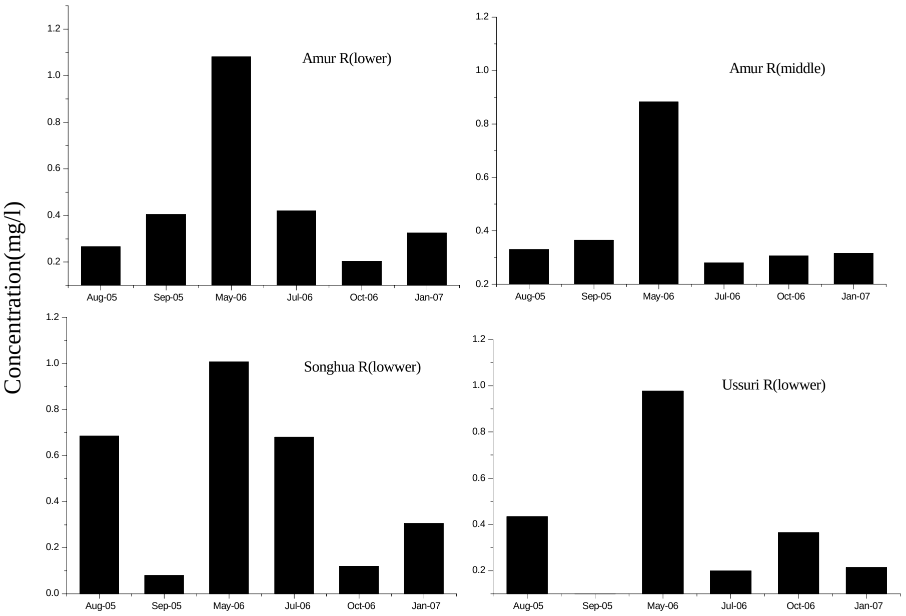

Fig.6 Temporal distribution of TDFe concentration of river

The chemical form of Fe in the river waters of different types in May 2006 is shown in Figure 7. Free Fe generally accounted for 30% of dissolved Fe except for a few samples; i.e., organic iron was the main fraction of dissolved Fe in most of the river water. Relative proportion of organic Fe showed no significant difference between the rivers from wetland and rivers from forest, whereas the absolute value of free ferric iron in the river from wetland was high than that from forest. Relative proportion of particulate Fe accounted for only a small portion of dissolved Fe within a few exceptional samples. It is interesting to note that the particulate Fe concentration in the middle Songhua River was higher than that in the lower where the dissolved Fe was similar, maybe indicating the precipitation of Fe to the sediment through the transport process. Fe distribution in the sediment and the exchange flux between river water and sediment can be an important issue for further research. In addition, it was observed that river water from swamp watersheds contained a significant amount of particulate Fe, such as Bielahong River and Yalu River. It is likely that dissolved Fe was translated into Fe hydroxides suspended in river water.

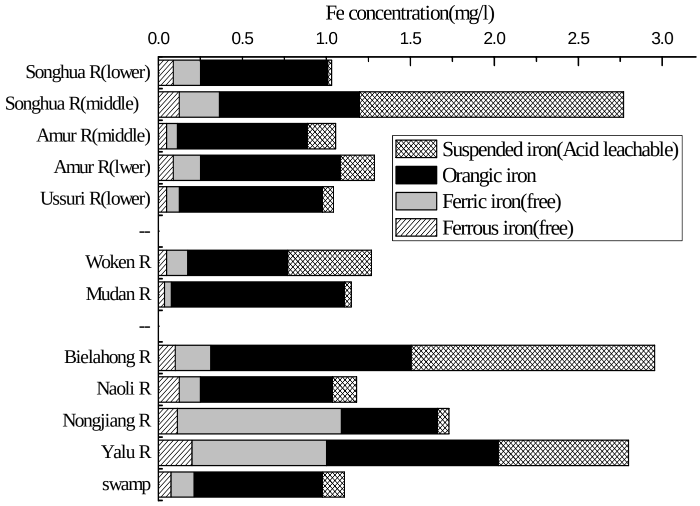

Fig.7 Concentrations of dissolved Fe, free ferrous Fe, and suspended Fe (May., 2006). Organic Fe was estimated from the difference between dissolved Fe and free Fe (including ferrous and ferric Fe). Acid leachable Fe was the difference between ASFe and TDFe.

All rivers exhibit high concentrations of dissolved organic carbon (DOC), ranging from 6.04 to 12.15 mg/l, averaging 8.05mg/l, which is typical for rivers draining boreal wetlands (Gordeev et al., 1996; Ingri et al., 2000; Millot et al., 2003). Although the DOC concentration was also higher in the rives than that in groundwater (Fig. 8), the relationship between DOC and TDFe in river was weak (Fig. 9), which is inconsistent with the result published by others (Yoh M.,2007).

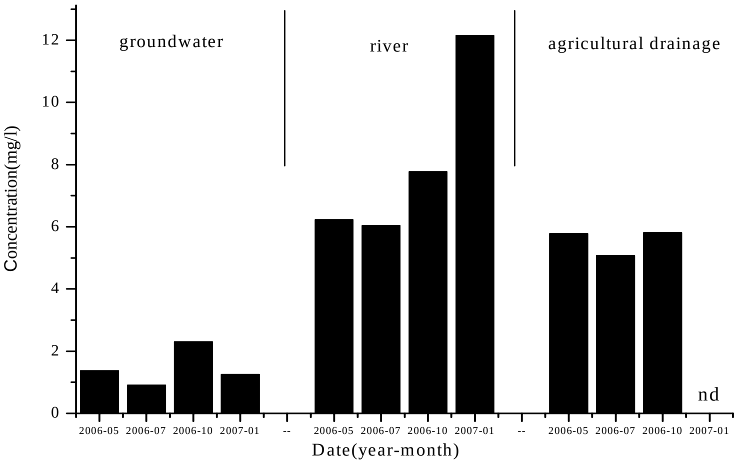

Fig.8 DOC concentration in groundwater, river and agricultural drainage

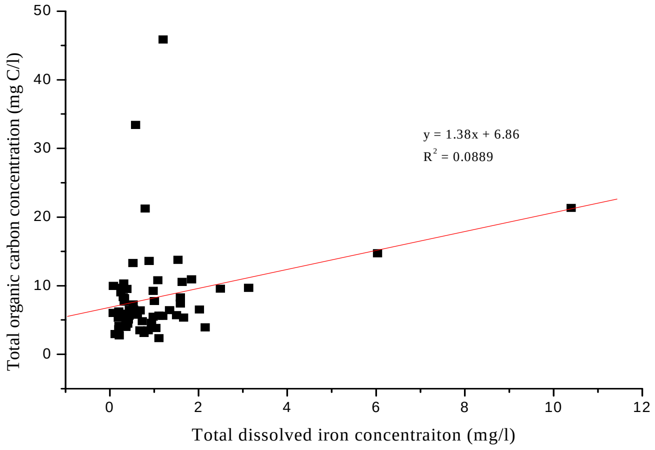

Fig.9 The relationship between DOC and dissolved Fe concentrations in river water

3.3 Spatial and seasonal variation of Fe in agricultural drainage water

The seasonal variation of mean dissolved Fe concentration among all agricultural drainage waters were compared in Figure 2. Throughout the year 2006, the Fe concentration in agricultural drainage showed a slowly decrease from spring to winter, which was similar with the change trend of river waters(Fig 2). Compared with the river water, TDFe concentration was somewhat higher in the agricultural drainage during periods of spring flood (i.e. in May, 2006), whereas the opposite was observed during the rest of the year. The max concentration appeared in May 2006. That maybe ascribe to the irrigation process in this season. During this intensive season of lift irrigation, higher TDFe concentration was input from the groundwater, then pumped into the paddy field and discharged to the agricultural drainage. But, this phenomenon was not obvious in other period.

Dissolved Fe concentrations in all samples of agricultural drainage waters throughout six observations (August and September in 2005; May, July and October in 2006; January in 2007) ranged between 0.09 and 8.29 mg/l. The average concentration is 1.46mg/l, which was slighter higher than that in river water (0.89mg/l). The result indicated that the agricultural drainages were important TDFe source of rivers owing to its higher mean TDFe concentration than that in rivers. But the link between flux and paddy field area where a certain agricultural drainage control is still unclear. Thus, a watershed covered by paddy field should be selected as a key and typical area in order to quantify the relationship between the discharge flux and agricultural region.

Figure 10 compares the seasonal variation of dissolved Fe concentration in 4 typical agricultural drainages. It is interesting to note that dissolved Fe concentration in these drainages had a common feature mentioned above. The concentration was nearly decreased from spring to fall except site 14 in October. The maximum concentration often occurred in Spring owing to the irrigation with groundwater. In addition, the drain activity before harvest of paddy filed had no strong influence on the drainage water owing to the lower TDFe concentration in October.

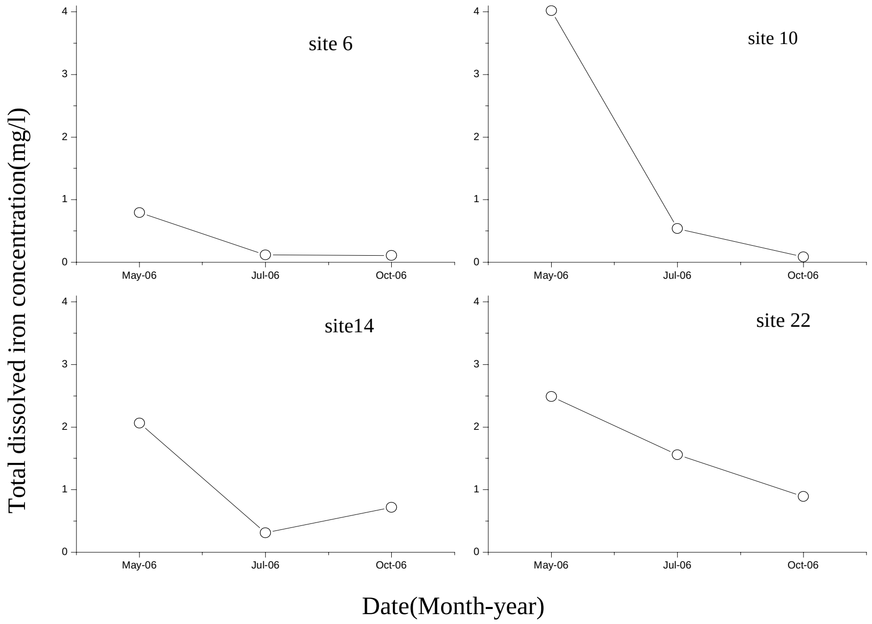

Fig.10 Temporal distribution of TDFe concentration of agricultural drainage waters(May., 2006)

The chemical form of Fe in the agricultural drainage waters in May 2006 is shown in Figure 11. Free Fe generally accounted for 20 % of dissolved Fe except for fewer samples; i.e., organic iron was the main fraction of dissolved Fe in most of the drainage waters. In addition, particulate Fe accounted for only a small portion of dissolved Fe with all samples.

Fe concentration in agricultural drainage water showed a better relationship against DOC concentration than river water (Fig. 12) .It suggests the presence organic-Fe complex with a certain composition such as humic substances in agricultural drainage.

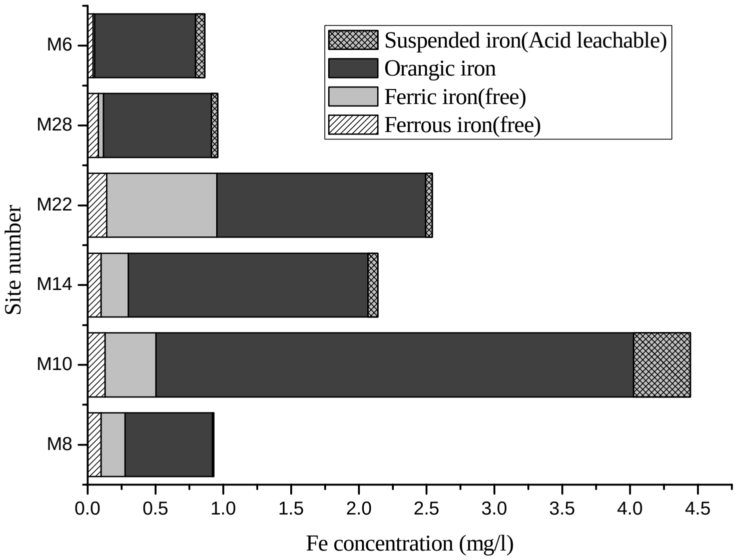

Fig.11 Concentrations of dissolved Fe, free ferrous Fe, and suspended Fe (May., 2006). Organic Fe was estimated from the difference between dissolved Fe and free Fe (including ferrous and ferric Fe) Acid leachable Fe was the difference between ASFe and TDFe.

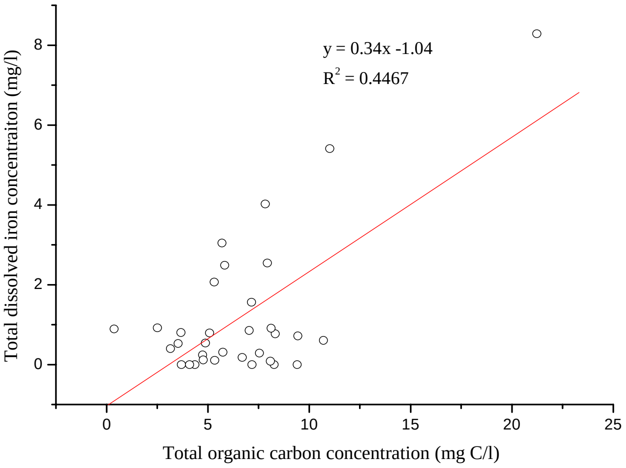

Fig.12 The relationship between DOC and dissolved Fe concentrations in river water

3.4 Distribution of free iron in Sanjiang Plain

The concentrations of ferrous and ferric ionic Fe were determined separately with raw water, and results were showed in Figure13.

All samples in different season exhibit high concentrations of dissolved ionic Fe including ferrous and ferric Fe, ranging from 3.81 to 11.23 mg/L, averaging 6.92 mg/l, which is much higher than surface water (river and agricultural drainage). Concentrations of dissolved ionic Fe in the river and agricultural drainage were 0.68 (ranging from 0.35 to 1.42 mg/l) and 0.95 mg/l(ranging from 0.27 to 2.21 mg/l), respectively (Fig.13).

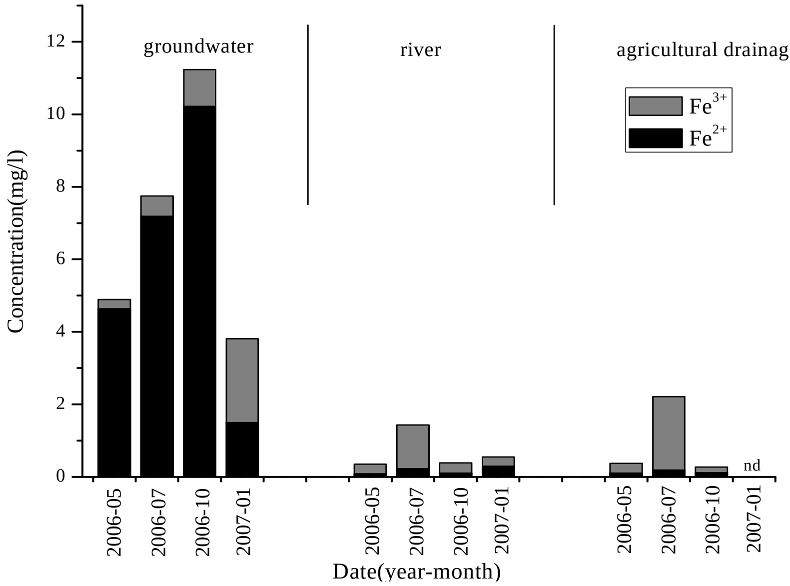

Fig.13 Total ionic Fe concentration and species distribution in well, river and agricultural drainage

During the periods of spring and summer flood (i.e. May and Jun., 2006), the concentration of dissolved ionic Fe was slight higher in the agricultural drainage than in river, whereas during the rest of the year the opposite was observed (Fig. 13). The temporal distribution of dissolved ionic Fe in groundwater was similar to the TDFe.

As for the species, groundwater was predominated by the ferrous ionic Fe whereas agricultural drainage and river by ferric ionic Fe through 2006(Fig. 13).

3.5 Flux change of free iron in Naoli River

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 14). On the other hand, the water discharge of Naoli River was also decreased with the wetland reclamation (Fig 15). As a whole, it can be concluded that the flux of free iron was decreased with the wetland reclamation. However, due to the lack of concentration of other fraction of iron, i.e., organic and acid leachable suspended iron, if the TDFe *(including ferrous and ferric iron)* flux in the river decreased with time is still a question to study in the future.

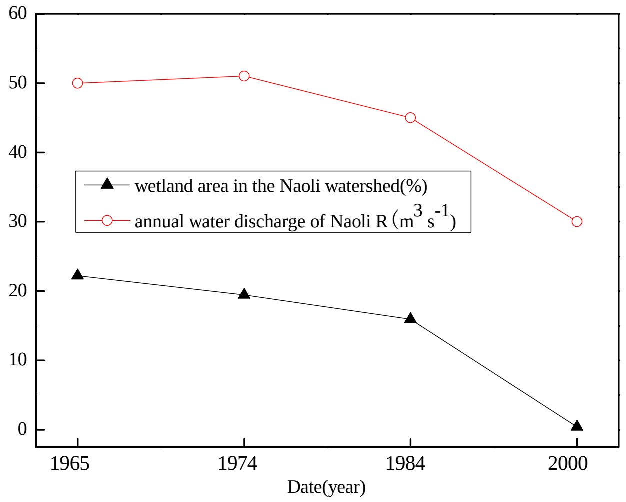

Fig 14 Changes of water discharge and wetland coverin Naoli River watershed (according to Liu, 2005)

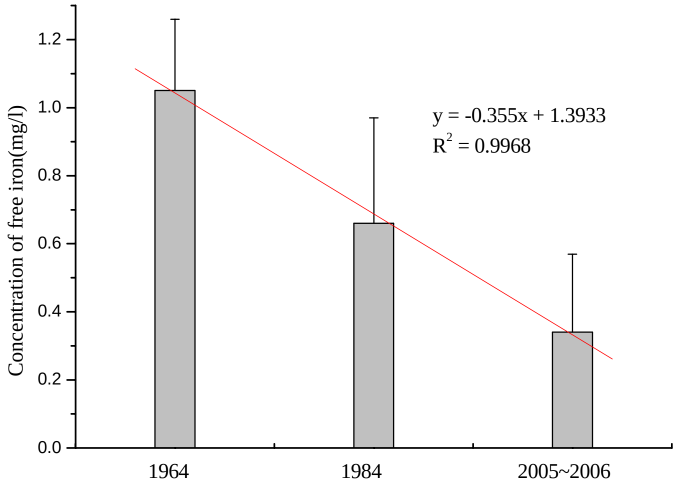

Fig 15 Flux change of free iron of Naoli River

4. PERSPECTIVE

Based on field observation, the temporal distribution of dissolved iron in groundwater, river water and agricultural drainage were analyzed. The difference between these types were also described in detail. However the reported results are based on the very limited observation temporally and spatially, indicating that more comprehensive and integrated observation would be needed. To quantify the transport flux of dissolved iron from the agricultural drainages to the rivers, then to the Amur River, a typical watershed will be selected to quantify the export flux from every land type including wetland, paddy field and upland to the river next year.

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