

Iron Forms in river water, agriculture drainage and ground water in Sanjiang Plain

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1. INTRODUCTION

Iron is an abundant and reactive element with a variety of geochemical and environmental roles. Iron can be found in dissolved or particulate phases in freshwater, sediment and suspended substance, and undergo significant interactions with natural organic matter (chiefly humic substances). Dissolved iron-organic complexes and iron oxide-humus colloids are important in the transportation and fate of the element in rivers and estuaries (Sholkovitz and Copland, 1981; Ross and Sherrell, 1999). According to Perdue et al. (1976) and Koenings (1976), soluble iron-humus complexes are significant components of surface freshwaters. The speciation of iron in natural water significantly affects water quality, bioavailability and biogeochemical behaviors. Therefore, physicochemical status of iron in aquatic ecosystem has been widely studied because of its importance in the prediction of transportation, bioavailability and the fate of iron.

Our research results from 2005 to 2007 in Sanjiang Plain showed that wetland, groundwater and agricultural drainage are the important sources of dissolved iron. In the Sino-Japan joint research on biogeochemical cycling of iron in Sanjiang Plain in 2008, the distribution of iron concentration has been investigated in different water bodies. Moreover, iron species as an important aspect was synchronously analyzed in marshy water, paddy water, marshy river, main rivers and agricultural drainage. According to the size fraction of iron species, Cross-Flow Filtration (CFF) technique was introduced to separate the chemical forms of iron in waters. The purpose is to recognize the mechanism of iron transportation in water system and the impact degree of land use change on iron species in different waters.

2. MATERIAL AND METHODS

2.1 Sample Collection and Analyses

Water samples in regional scale were collected from rivers, agricultural drainages and wells in June, August and October 2008, respectively. The sampling scheme is depicted in Table 1, and the sampling location is shown in Fig.1.

Moreover, a series of experiments of iron species separation in different waters were carried out in Sanjiang Ecological Experimental Station from June to October 2008.

Table 1 Sample numbers in 2008

Sampling order	mm/ dd / yy	Groundwater	River water	Agricultural drainage	Total samples number
1	June 6-7, 2008	1	2	2	5
2	August 4-8, 2008	5	11	4	20
3	October 9-14, 2008	6	11	3	20
Sub-total		12	24	9	45

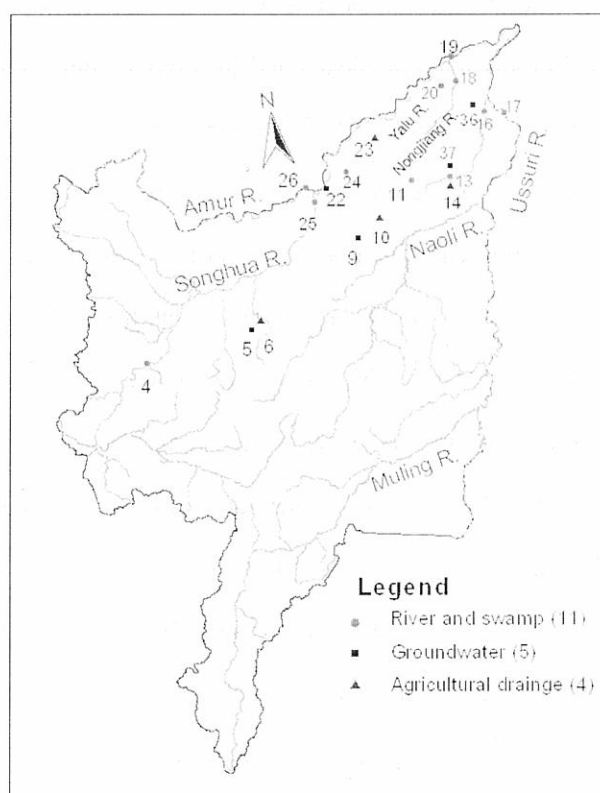


Fig.1 Sampling Locations in the Sanjiang Plain in 2008

2.2 Iron Species and Treatment

Stumm and Morgan (2000) had divided iron species into six parts, including ion, organic iron, inorganic iron, colloidal iron, surface bound, solid bulk phase, but it is too difficult to separate

each species completely under field condition due to its instability. Iron species determined in this study are defined in Table 2, and the treatment procedure is described in Fig. 2.

Table 2 Fractionation scheme of iron species in water

Particle size	>0.45 μ m	50KD~0.45 μ m	10~50KD	<10KD
Name of the fraction	Acid soluble particulate iron(ASPI)	High molecular weight iron(HMW)	Middle molecular weight iron(MMW)	Low molecular weight iron(LMW)
Phase	Particulate and Colloid	Colloid	Colloid	Complex and ionic iron

D (Dalton) is an unit of molecular weight, and 1 KD is close to the particle diameter in 1 nm.

Acid soluble particulate iron is equal to acid soluble iron minus total dissolved iron.

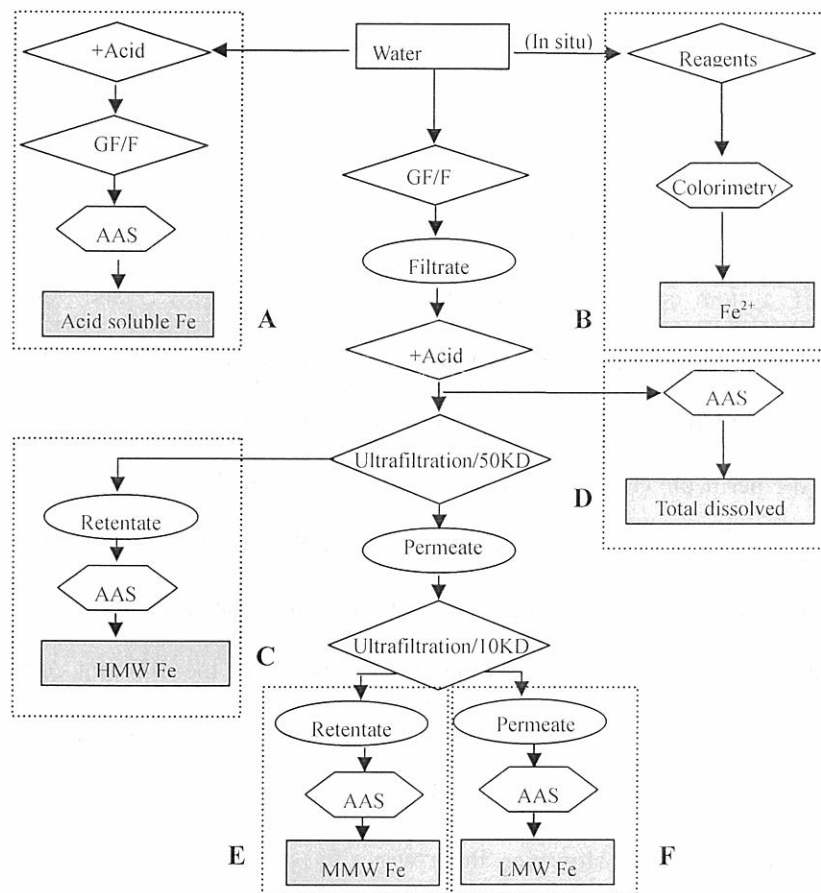


Fig.2. Flow diagram of water samples treatment. Total dissolved Fe includes ion and complexed iron. A-D=acid soluble particulate iron (ASPI); Fe^{2+} was determined with ferrozine spectrophotometric method (Stookey L. L., 1970); Retentate means the water including big-size element that could not pass through the membrane stay in the retention reservoir.

2.3 Cross-Flow Filtration (CFF)

Ultrafiltration technique is used to collect and enrich the suspended colloids in water sample for

analysis. The particles intercepted by ultrafilter membrane are concentrated in the retention reservoir, while the material smaller than ultrafilter cutoff will pass through to permeate (Fig.3). As the fractionation progress, the sample in the retention reservoir becomes more concentrated.

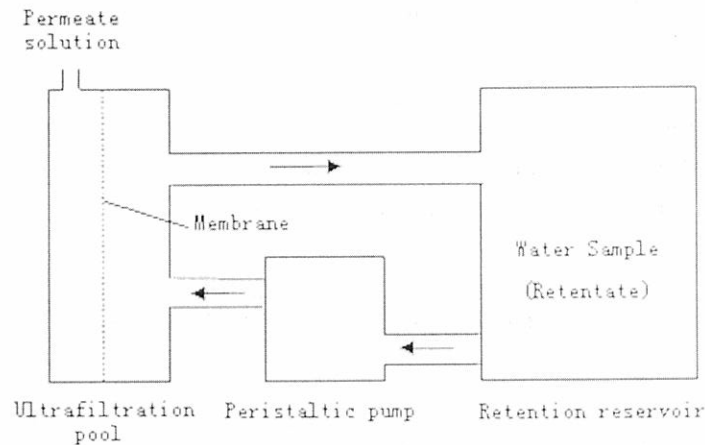


Fig. 3 Sketch of CFF system working

The CFF system consists of a 1L retention reservoir, a 10 KD and 50KD ultrafiltration membrane (PES, 200 cm² surface area) with a cassette holder (VIVA) and peristaltic pump (Masterflex[®] L/S[®]) which ensures the tangential circulation of water in the membrane at about 10 mL/min for the permeate (Fig.3). Prior to the sample fractionation, the system is cleaned orderly with 0.1M hydrochloric acid, deionized water, 0.1M sodium hydroxide and deionized water. The first 100mL is processed and discarded to prevent the sample contamination during filtration.

Presented in Fig. 4 are the membrane characteristics for the different concentration factor represented by retentate, permeate and loss percentages. The mass balance was quite good at low concentration factor (loss terms -1.2%~5%) indicating neither significant contamination nor losses of iron from the membrane. However, there was a 9%~15% loss of iron at high concentration factor during the fractionation which is attributed to sorption to the membrane. We have noted previously that losses of high molecular weight substances onto the CFF membranes may occur preferentially at higher CFF concentration factors (Dai *et al.*, 1998).

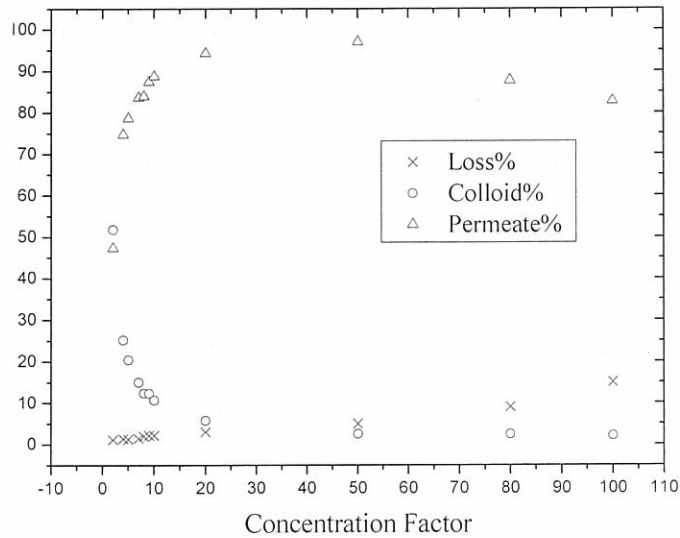


Fig. 4 Calibration of ultrafiltration performance

3. RESULTS AND DISCUSSION

3.1 Iron Species in River Waters

3.1.1 Concentration of Dissolved Iron and Acid Soluble Particulate Iron in River Waters

The data showed that the concentration of acid soluble particulate iron (ASPI) was higher and total dissolved iron was lower in August, 2008 in river waters (Fig.5). The marshy rivers (Yalu R., Nongjiang R., Bielahong R. and Qinglong R.) had high concentration both for ASPI and total dissolved iron comparing with other rivers, and the average concentrations of total dissolved iron

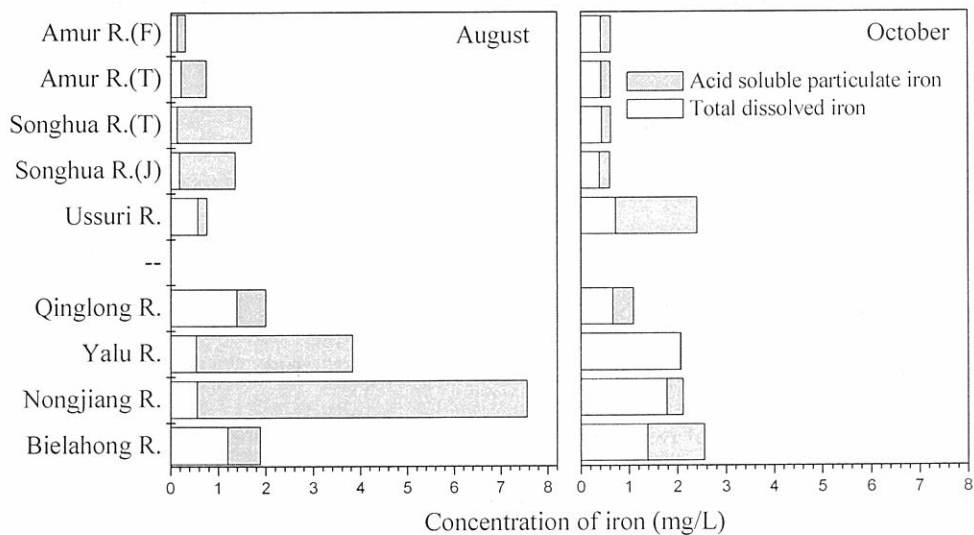


Fig.5 Concentration of iron in river waters in August and October,2008 (Songhua R.(J):sampling at Jiamusi city; Songhua R.(T):sampling at Tongjiang city; Amur R.(T):sampling at Tongjiang city; Amur R.(F):sampling at Fuyuan county)

and ASPI in river waters were 0.920, 2.897 mg/L in August and 1.471, 0.487 mg/L in October, respectively. In main rivers (Amur R., Songhua R. and Ussuri R.), the concentrations of ASPI and total dissolved iron were 0.253, 0.720 mg/L in August and 0.474, 0.500 mg/L in October 2008.

The result in 2007 also showed the same variation trend: the concentration of ASPI was greatly high during flood period (July and August), which result from the flow change. The river flow is high in summer, the rainy season in the Sanjiang Plain. High river flow may not only dilute the concentration of iron, but also change the physical and chemical conditions of river waters. During rainy season, the intensive precipitation-runoff process enhances the Eh value in river, which would promote the conversion of Fe^{2+} to Fe^{3+} . However, Fe^{3+} could form iron hydroxide and be bound by particles in water, which result in the increase of ASPI concentration with increasing of content of suspended substance during flood season. Some Fe^{3+} possibly transform into complex iron or colloidal iron at the same time. High flow also leads to turbidity for river waters, accelerates the release of sediment under river bottom, increases the quantity of suspended substance, and finally these processes result in the higher concentration of ASPI in river waters during high flow period. The concentration of ASPI in river waters was approximately three times higher than that of total dissolved iron in August 2008, but only half of total dissolved iron in October 2008. In other words, the concentration of total dissolved iron in river waters would decrease during flood period, and increase during normal river flow period. In Sanjiang Plain, the mean concentration of total dissolved iron for all rivers were 0.549 and 0.917 mg/L in August and October, 2008, respectively.

3.1.2 Iron Species in River Waters

CFF technique was introduced to separate iron species in river waters in the research of 2008 financial year. Taking Amur R. and Yalu R. as examples, Amur R. represents the main river, and Yalu R. is a typical marshy river in Sanjiang Plain. The results of the distribution and fractionation of iron in marshy rivers and main rivers are shown in Fig.6. ASPI and LMW iron (<10KD) are predominant species in both of two types of water. The concentration of LMW iron is much higher in Yalu R. than that in Amur R. LMW, MMW, and HMW iron account for 78.7%, 10.0% and 11.3% of total dissolved iron in Yalu R., and 84.9%, 13.0%, 2.2% of total dissolved iron in Amur R., respectively.

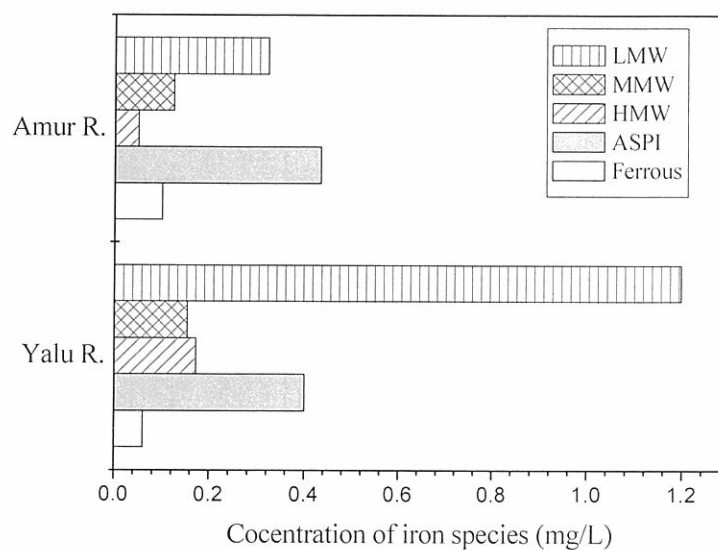


Fig.6 Iron distribution in River waters

The difference of DOC concentration between Amur R. and Yalu R. led to this result. As expected, marshy river has high DOC concentrations (11.41 mg/L), which is coherent with the obviously brown color of the water. Therefore, DOC is the key to determine the concentration of low molecular weight iron in Sanjiang Plain. Moreover, DOC plays an important role not only in formation of complex iron, but also redox condition and adsorptive capacity of organic matters in rivers. Also, low concentration of Fe^{2+} and appreciably high concentrations of HMW and MMW are found in marshy river.

3.2 Concentration and Species of Iron in Agricultural System

3.2.1 The Concentrations of Total Dissolved Iron and ASPI in Agricultural Drainage

Bielahong Agricultural Drainage is one of the biggest drainage channels in Sanjiang Plain, which flows into Ussuri R. finally. The mean concentrations of total dissolved iron and acid soluble particulate iron were 0.633, 0.486, 0.633 mg/L and 1.482, 0.645, 1.611 mg/L in the drainage in June, August and October 2008, respectively (Fig.7). The concentrations of both total dissolved iron and acid soluble particulate iron were appreciably high in June and October. The result is different from that in river water where the concentrations of total dissolved iron increased and ASPI decreased in October. This may be attributable to the local farming practices, because the standing water in paddy field would be discharged partly or entirely in late of May and early of September every year in order to meet the need for seedling growth or rice ripeness in the plain. Therefore, iron will be expelled from paddy field, and flow into trenches. But then, the

concentration appeared in river would be later due to hysteresis.

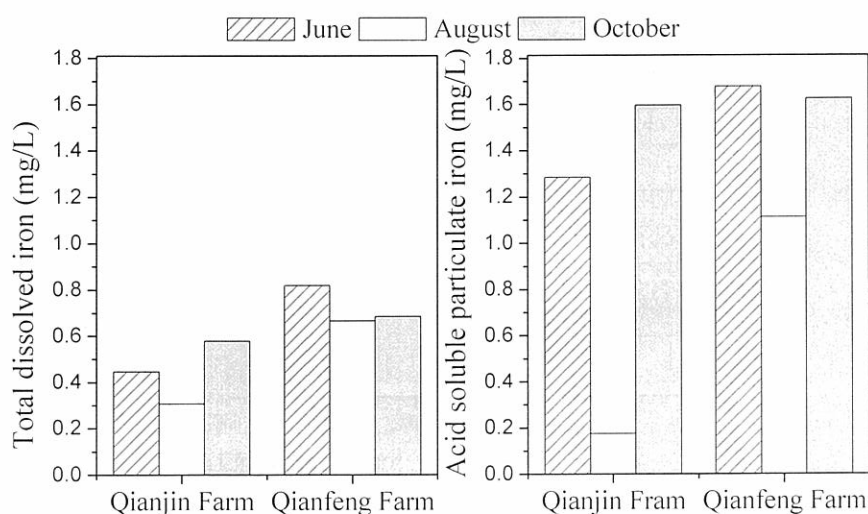


Fig.7 The concentration of iron in agricultural drainage in June, August, October, 2008

At other period, the paddy water flowed infrequently into channel, except on the occasion of heavy rain in rainy season. That suggests that irrigation water from paddy field will flow into trenches mainly as form of soil solution in most growing season. Therefore, iron supply of paddy field may restrict the iron concentration in drainage channels due to slow and long transportation of irrigation water in soil solution. So, the high concentration of iron may not be found in the flood period. The same result was also found in 2007.

In the process of drainage water flowing into Bielahong Agricultural Drainage, drainage water, pollutants and elements including iron would stay and move through countless small trenches. A series of physical (coagulation, sedimentation and absorption) and chemical (oxidation, complexation, etc.) processes would take place. From the result in 2008, whether total dissolved iron or acid soluble particulate iron, their concentrations were higher in lower drainage (0.759, 2.200 mg/L for total dissolved iron and ASPI in Qianfeng Farm) than in upper drainage (0.529, 1.460 mg/L in Qianjin Farm), which proved that the afflux of small irrigation channel into agricultural drainage play an importance role in the source of iron.

3.2.2 Iron Species in Paddy Water and Groundwater

The irrigation pattern of pumping groundwater for paddy is widely adopted in Sanjiang Plain. This suggests that the iron, especially Fe^{2+} , would be brought from underground into surface soil. So, the paddy water should keep more iron. The result showed that the concentrations of most iron

species except ferrous iron were higher in paddy water than those in groundwater, and ASPI and LMW were the predominant species both in groundwater and paddy water (Fig.8).

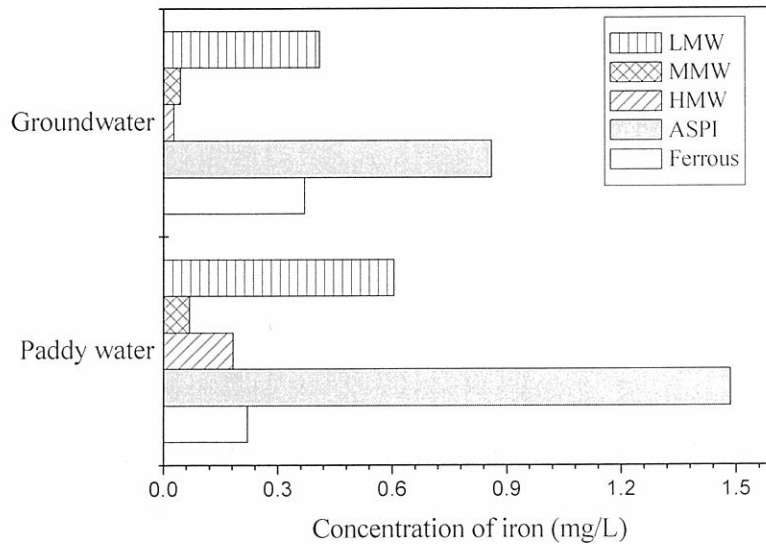


Fig.8 The concentration of iron in paddy water and groundwater

When groundwater is pumped to surface land, the transformation of ferrous would immediately occur. Therefore, the concentration of ferrous iron in paddy water is lower than in groundwater. Moreover, the paddy water has more particulate due to cultivation disturbance, ASPI concentration in paddy water also is higher than in groundwater. From another point of view, the concentration of DOC was 9.87 and 4.17 mg/L in paddy water and groundwater respectively, which also influence on the concentrations of LMW, MMW and HMW in water.

3.3 Iron Species in Marshy Water

The concentrations of Ferrous, LMW, MMW and HMW iron decreased gradually and acid soluble particulate iron increased from July to October in marshy water. This did not accord with the result in river water where the concentration of total dissolved iron is high in October. The previous studies carried out in wetland system showed that there was a positive correlation between dissolved iron concentration and the land surface's temperature. The litter decomposition, which had an ability of adsorption or release iron, possibly was another one of important role in determining the concentration of dissolved iron in marshy water. Zheng, *et al.* (2005) proved that the function of absorption is bigger than that of release for *Carex lasiocarpa* system (a kind of meadow). Dissolved iron would continually be absorbed by wetland plants or be fixed by wetland soil.

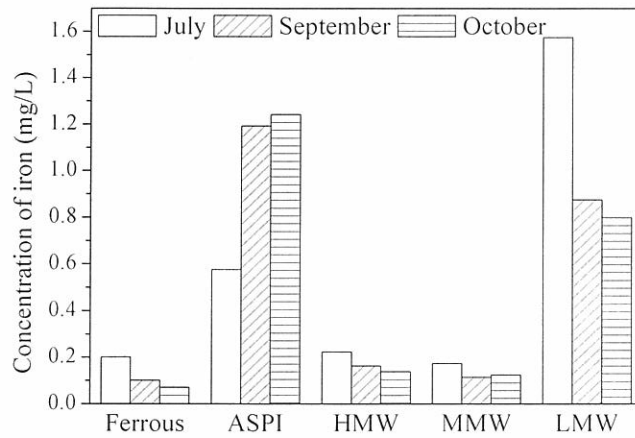


Fig.9 The concentration of iron species at different time in marshy water

3.4 The Estimate of Iron Outflux from Rivers in Sanjiang Plain

Based on the data of average annual runoff of main rives (Liu, 2003) and iron concentrations in the plain in 2008, the annual iron output flux is estimated in Table 4.

Table 4 Annual output of iron speciation in 2008

River	Concentration/ runoff flux	Total dissolved iron
Amur R. (Fuyuan)	Average concentration/mg L ⁻¹	0.30
	Average runoff flux/ 10 ⁸ kg yr ⁻¹	0.80
Ussuri R.	Average concentration/mg L ⁻¹	0.65
	Average runoff flux/ 10 ⁸ kg yr ⁻¹	0.27
Songhua R. (Jiamusi)	Average concentration/mg L ⁻¹	0.29
	Average runoff flux/ 10 ⁸ kg yr ⁻¹	0.20
Total	Average runoff flux/ 10 ⁸ kg yr ⁻¹	1.27

Contrast with the fluxes of last fewer year, the iron output flux in 2008 was appreciably high in Ussuri River and Songhua Rives (Fig.10). The annual precipitation was not comparatively high in 2008, but the work of silt dredging was put in practice in Bielahong agricultural drainage last summer. Resuspending of sediment would lead high iron concentration in Ussuri River, especially acid soluble particulate iron.

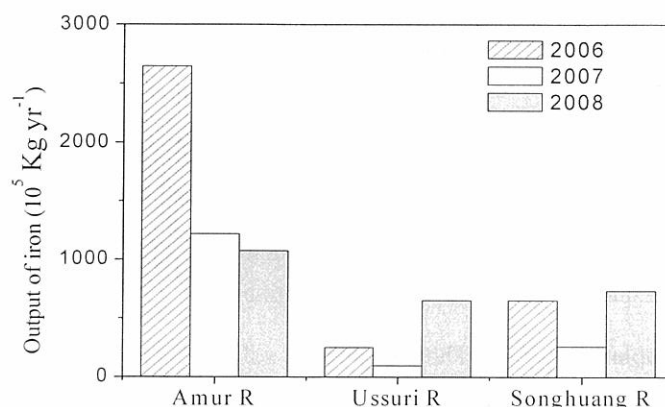


Fig. 10 Output of iron in main rivers in 2006, 2007 and 2008

4. CONCLUSION

From above results, some conclusions could be generalized:

(1) The concentration of total dissolved iron was comparatively low and acid soluble particulate iron was high in raining flood period;

(2) Agricultural drainage (stem channel and small ditch) partially provide iron to river in a certain extent, but the hysteresis of supplying from paddy field water would possibly occur in agricultural ditch;

(3) The low molecular weight (LMW) and acid particulate iron (ASPI) is predominant species in water bodies in Sanjiang Plain and high DOC concentration would lead to high LMW and ASPI concentration;

(4) Water temperature and litter decomposition in wetland possibly influence iron speciation;

(5) In Sanjiang Plain, the raining flood which happens in July and August every year brings great changes (pH, Eh) in aquatic system influencing the fate of iron. Moreover, lift irrigation and agricultural drainage not only influence iron speciation in agricultural system but also the transport of iron from paddy to channels and rivers.

ACKNOWLEDGEMENTS

The authors thank Dr. Hui-cong Cao, Dr. Shu-yuan Liu, Dr. Yu-hong Yang, Mr. Li-lu Zhu and Ms Ying-ying Xu for their invaluable help in the field sampling.

REFERENCES

Dai M. H., Buessler K. O., Ripple P., *et al.* 1998. An evaluation of two cross-flow ultrafiltration membranes to isolate marine organic colloids. *Marine Chemistry*, 62:117-136.

Liu H. Y., Li Z. F. 2003. 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)

Werner Stumm & James J. Morgan. 1996. *Aquatic Chemistry* (3rd ed.) .New York: John Wiley & Sons, Inc. 257-258.

Zheng Y. Q., Liu J. S., Wang J.D. 2000. Variations of chemical elements of *Carex lasiocarpa* litter in Sanjiang Plain. *Grassland of China*, (3):12-16. (in Chinese)

Sholkovitz E. R. & Copland D. 1981. The coagulation, solubility, and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Journal of the Geochemical Society and the Meteoritical Society*, 45:181-189.

Ross J. M. & Sherrell R. M. 1999. The role of colloids in trace metal transport and adsorption behavior in New Jersey Pinelands streams. *Limnology & Oceanography*, 44:1019-1034.

Perdue E. M., Beck K. C. and Reuter J. H. 1976. Organic complexes of iron and aluminium in natural waters. *Nature*, 260: 418-420.

Koenings J. P. 1976. In situ experiments on the dissolved and colloidal state of iron in an acid bog lake. *Limnology & Oceanography*, 21: 674-683.