



Temporal variability of iron concentrations and fractions in wetland waters in Sanjiang Plain, Northeast China

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Abstract

Chemical forms, reactivities and transformation of iron fractions in marshy waters were investigated with cross-flow filtration technique to study the iron environmental behavior. Iron fractions were divided into four parts: acid-labile iron (pre-acidification of unfiltered marshy water samples, $> 0.7 \mu\text{m}$), high-molecular-weight iron ($0.7\text{--}0.05 \mu\text{m}$), medium-molecular-weight iron ($0.05\text{--}0.01 \mu\text{m}$), and low-molecular-weight iron ($< 0.01 \mu\text{m}$). The cross-flow filtration suggested that iron primarily exist in both the $> 0.7 \mu\text{m}$ and $< 0.01 \mu\text{m}$ size fractions in marshy waters. Rainfall is the key for rain-fed wetland to determine fate of iron by changing the aquatic biochemical conditions. By monitoring the variation of iron concentrations and fractions over three years, it was found that dissolved iron and acid-labile iron concentrations exhibit a large variation extent under different annual rainfalls from 2006 to 2008. The seasonal variation for iron species proved that the surface temperature could control some conversion reactions of iron in marshy waters. Low-molecular-weight iron would convert to acid-labile iron gradually with temperature decreasing. The photochemical reactions of iron fractions, especially low-molecular-weight iron had occurred under solar irradiation. The relative proportion of low-molecular-weight in total dissolved iron ranging from 28.3% to 43.2% were found during the day time, which proved that the observed decreasing concentration of acid lability iron was caused by its degradation to low molecular weight iron.

Key words: iron species; cross-flow filtration; wetland waters; photochemical behavior

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Introduction

Iron is a key nutrient in aquatic system that limit primary productivity in many ocean areas and can also exacerbate problem cyanobacterial bloom (Mills et al., 2004; Morel and Price, 2003; Schulz et al., 2004). Iron oxyhydroxides and complexes typically exhibit large surface areas per unit mass and, as a result, control the behavior of other elements which readily partition to their surface. Many studies have revealed that dissolved iron-organic complexes and iron oxide-humic colloids were important in transport of other elements in rivers and estuaries (Sholkovitz and Copland, 1981; Ross and Sherrell, 1999), while how iron fractions and biochemical process controlled by climate, DOM variation and intensity of solar irradiation in wetland waters are still unknown.

According to Perdue et al. (1976) and Koenings (1976), soluble iron-humic complexes are primary components of freshwaters. Most ($> 99\%$) of the dissolved ferric iron is present as organic iron complexes in marine surface waters (Powell and Donat, 2001; Rue and Bruland, 1995, 1997; Vandenberg, 1995) and probably also in rivers and lakes. In

surface waters, inorganic Fe(III) are formed through light-induced redox cycling of iron (Powell and Wilson-Finelli, 2003). Biogeochemical and physiochemical reactions of iron are complicated in the system of surface water and soil, including co-precipitation and adsorption, oxidation and reduction, complexation and photochemical process which are still not fully understood. Therefore, besides pH-dependent precipitation, two important reactions are complexation of iron by dissolved organic compounds, including humic substances, siderophores and other organic acids, and sorption of humic substances by iron oxides through surface complexation reactions (Evanko and Dzombak, 1998). In addition, dissolved organic material (DOM) and iron reactions also control energy transfer through photochemical or microbial pathways (McKnight et al., 2001).

The surface waters in wetland are highly colored, organic rich natural waters, which may improve solubility of iron and cause significant changes in the flux of dissolved iron. The interaction between organic matters and iron is a complicated process. Humic substances participate in redox, complexation and adsorption reactions with Fe(III) (Szilágyi, 1971; Lovley et al., 1996, 1998; Scott et al.,

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1998). However, the swamp system from Sanjiang Plain area is believed to play a crucial role in species control and export of iron (Pan et al., 2007). Clearly, a full understanding of iron chemistry in marshy waters needs to take into account the diversified reactions and fractions of iron and also competitive reactions of iron and other metals with humic matter.

In this study, the evaluation of the potential for environmental factors to control the variation of iron concentration were conducted at year-span, month-span, day-span in wetland, DOM-rich waters. The results associated with existing information would illustrate some biochemical behaviors of iron in natural waters, and conversion characters of iron fractions.

1 Material and methods

1.1 Study area

Sanjiang Plain (43°49′–48°27′N, 129°11′–135°05′E) is the largest concentrative distribution area for freshwater marshes in China, and is a low-lying alluvial floodplain of about 66,600 km². Currently, the total area of wetlands in Sanjiang Plain is 11,000 km² (nearly twice the size of the Everglades), making it the most notable wetland in China. The floodplain ecosystem consists of a mosaic of sedge (*Carex* spp.) and reed (*Phragmites communis*) marshes, wet grass meadows (*Peyuxia angustifolia*), oxbow lakes, riverine Salix scrub, and wooded hummocks of birch (*Betula*) and poplar (*Populus*). Its main soil types are albic soil, meadow soil and marsh soil, and its natural vegetations are mainly of marsh vegetation, with woodland meadow scattered on relatively high altitudes. The mean annual precipitation is around 600 mm and the mean annual temperature is 1.91°C. Water and soil in marshes are completely frozen from late October to the following April and begin to melt in late April.

1.2 Iron fractions and treatments

Stumm and Morgan (2000) divided iron fractions into six parts, including ion, organic iron, inorganic iron, colloidal iron, surface bound, and solid bulk phase. But it is difficult to separate each fractions completely under field condition due to its instability. Iron fractions determined in this study with cross-flow filtration (CFF) method are divided into four parts: acid-labile iron, high-molecular-weight iron, medium-molecular-weight iron, and low-molecular-weight iron. The details of iron species are described in Table 1.

Water samples were collected in *Carex* swamp from 2006 to 2008 to monitor the variation of iron concentrations and other elements. For the removal of suspended solid, the marshy water samples were vacuum-filtered with 0.7 μm membrane filters (Whatman) and then stored in acid washed polyethylene containers. The long term water quality for wetland waters system is presented in Table 2.

Fe²⁺ was analyzed with Ferrozine colorimetric method *in situ*; total dissolved iron and acid lability iron were analyzed with atomic absorption spectrophotometer (AAS).

Table 1 Fractionation scheme of iron species in water

Size (μm)	Fraction	Phase
> 0.7	Acid-labile iron ^b	Particulate and colloid
0.7–0.05 ^a	High-molecular-weight iron	Colloid
0.05–0.01	Medium-molecular-weight iron	Colloid
< 0.01 ^a	Low-molecular-weight iron	Complex ^c Ionic iron ^d

^a molecular weight cutoff of membrane are 10 and 50 kDa, respectively. 1 kDa ≈ 0.001 μm; ^b acid-labile iron represents pre-acidification of unfiltered samples; ^c complexed iron represents ferric iron binding with organic and inorganic matters and hydrolysis products of ferric iron; ^d ionic iron mainly represents ferrous iron.

To separate iron species based on their size, 0.01 μm (10000 MWCO PES), 0.05 μm (50000 MWCO PES), and 0.7 μm (Whatman GF/F, Whatman International Ltd., England) filters were used. Water samples were partially acidified to pH 2 and filtrated with Whatman membrane, the other samples were filtrated with Whatman GF/F glass fiber filters, acidified to pH 2 to significantly reduce iron oxidation, and then stored at 4°C prior to further treatment. The latter (pre-filtrate) subsequently flowed into cross-flow filtration device with a membrane pack of nominal molecular weight cutoff of 50 kDa. The retentate was analyzed immediately, and the filtrate or permeate flowed into 10 kDa MWCO membrane. All filtrates were collected for measurement of total iron concentrations. The colloidal fraction is operationally defined as being material that passes through 0.7 μm prefilter and retentate by a CFF membrane with a nominal molecular weight cutoff of 10 kDa.

1.3 Apparatus

All sample bottles were immersed in a diluted HCl (0.5 mol/L) solution more than 24 hr and rinsed with deionized water over 5 times. All dilutions and sample preparations were made using deionized water produced by ion-exchange system (Shanghai Gaoying Water Purification Ltd., China). Fe²⁺ measurements were performed with RPA-100Fe analyzer (Jiangsu Jianghuan Analytical Instrument Ltd., China). AAS GBC 906 (Australia) was applied for the determination of total dissolved iron and acid-labile iron. The filter was washed with 0.5 mol/L HCl and 1 L deionized water. The ultrafiltration membrane was cleaned with 0.1 mol/L NaOH, 0.1 mol/L HCl and deionized water prior to use.

1.4 Reagents

An acetic sodium solution (0.2 mol/L) was prepared by dissolving 8.2 g acetic sodium in 500 mL deionized water. Acetic acid (0.2 mol/L) was obtained by dissolving 16 mL of 38% acetic acid in 500 mL deionized water. Acetic buffer (pH 4.6) was prepared by mixing the corresponding amounts of acetic acid (0.2 mol/L) and acetic sodium solution (0.2 mol/L). The colorimetric reagent of Fe²⁺ was prepared by dissolving 0.125 g ferrozine in 500 mL acetic buffer.

1.5 Cross-flow filtration (CFF)

Ultrafiltration is used to collect and enrich the suspended

Table 2 Sampling time and physicochemical properties of marshy waters

Sampling date (yyyy/mm)	Water temperature (°C)	EC (mS/cm)	DOC (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	N (mg/L)	P (mg/L)
2006/05	8.0	0.04	34.23	2.47	2.44	3.53	1.11	43.92	5.33	nd
2006/07	20.0	0.05	31.22	2.14	1.05	6.05	2.09	51.24	9.31	nd
2006/10	9.8	0.06	33.41	6.00	4.41	3.42	1.55	266.45	7.59	nd
2007/07	22.4	0.07	44.59	1.57	2.49	11.27	7.79	38.13	14.58	0.07
2007/08	22.8	0.05	34.30	1.14	4.04	4.67	7.79	51.85	23.69	0.01
2007/10	2.97	0.04	27.07	10.18	1.91	4.74	5.08	231.80	7.75	nd
2008/06	12.1	0.04	39.52	2.22	2.54	5.45	1.32	44.39	7.54	nd
2008/08	21.7	0.04	33.55	1.21	2.49	4.73	7.83	49.41	7.83	nd
2008/10	6.5	0.08	36.29	4.77	10.67	3.41	7.04	39.65	23.62	0.04

Sampling site is located at Sanjiang National Research Station of Wetlands Ecosystem. N: inorganic nitrogen (NH₄⁺+NO₃⁻+NO₂⁻); P: inorganic phosphorus (PO₄³⁻); water temperature and EC were measured *in situ* by a Horiba Water Checker Model U-10 (Japan). Concentration of DOC was measured with a Shimadzu TOC-VCPH Model Analyzer (Japan). Major cations (Na, K, Ca and Mg) were measured by an atomic absorption GBC Avanta spectrometer. HCO₃⁻ was measured *in situ* by the method of titration. nd means not detected.

colloids in the retentate solution for analysis. The larger moleculars captured by ultrafilter membrane are concentrated in the retention reservoir, while the material smaller than ultrafilter cutoff passed through to permeate. As the fractionation progress, the sample in retentate reservoir becomes more concentrated. The concentration factor (cf) is described by Eq. (1):

$$cf = \frac{V_P + V_R}{V_R} \quad (1)$$

where, V_P and V_R are permeate and retentate volume, respectively.

The abundance of a chemical element in the colloidal fraction is calculated as Eq. (2):

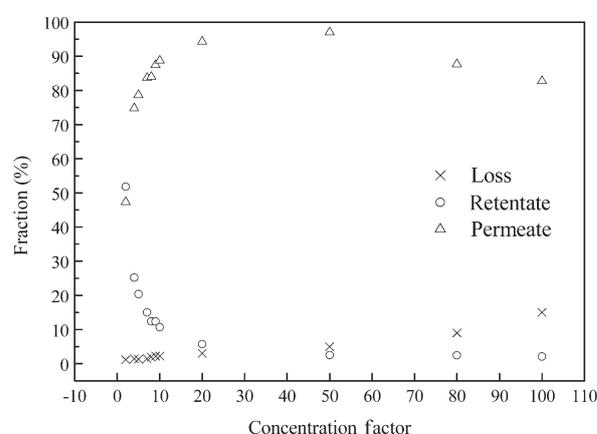
$$C_{Me-coll} = \frac{C_{Me-ret}}{cf} \quad (2)$$

Equation (2) is valid at any point during the fractionation and also on the integrated fractions at the end of a fractionation. The mass balance is evaluated by comparing the sum of the colloidal component and permeate component with total filter passing component:

$$\text{Mass loss} = \frac{C_{Me-tot < 0.45 \mu m} - (C_{Me-coll} + C_{Me-perm})}{C_{Me-tot < 0.45 \mu m}} \times 100\% \quad (3)$$

The CFF system consists of a 1-L reservoir, a 10 and 50 kDa ultrafiltration membrane (PES, 200 cm² surface area) with a cassette holder (VIVA) and peristaltic pump (Masterflex[®] L/S[®]) which ensures the tangential circulation of the fluid in the membrane at about 10 mL/min for the permeate. Prior to the sample fractionation the system was cleaned in order with 0.1 mol/L HCl, deionized water, 0.1 mol/L NaOH and deionized water. The first 100 mL was processed and discarded to prevent the sample contamination during filtration.

The three crucial issues related to CFF's applicability are system blanks, mass balance and cf issues. Blank tests represent an essential check of the performance of ultrafiltration system. A low procedure blank suggests the absence of the contamination. A high procedure blank may suggest material gain or contamination from other

**Fig. 1** Calibration of ultrafiltration performance.

components during the processing. Therefore, a high blank means that the system is not clean enough, and constitutes a potential contamination source for the natural sample. Retentate blank refers to deionized water being concentrated by a factor of 20 with CFF. After careful cleaning, the blank were no significant with respect to Fe in water samples. Both of the permeate blank and retentate blank of iron is < 0.001 mg/L.

Figure 1 shows the membrane characteristics for the different concentration factors 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 loss of iron to or from the membrane. However, there was a 9%–15% loss of iron at high concentration factor during the fractionation which was attributed to the sorption to the membrane. We have noted previously that the loss of high molecular weight substances onto the CFF membranes may occur preferentially at high CFF concentration factors (Dai et al., 1998).

2 Results

2.1 Annual variation for total dissolved iron and acid lability iron

Figure 2 presents the annual variation of iron concentrations in wetland waters in Sanjiang Plain. For the monthly

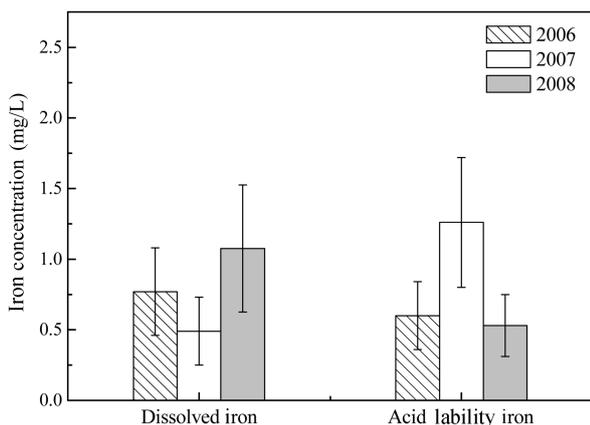


Fig. 2 Iron concentration in wetland waters in 2006, 2007, and 2008.

studies conducted during the different rainfall conditions after snowmelt in May, June, August, September and October, the range of total dissolved iron concentrations were from 0.490 to 1.075 mg/L, more than 2-fold range. The range of ALI (acid lability iron) concentrations were from 0.490 to 1.260 mg/L. The large extent of this range in total dissolved iron and ALI concentrations provided support for some control on iron concentration by biogeochemical process associated with DOM, precipitation and microbial oxidation.

2.2 Seasonal variation for iron fractions

Based on size fraction by ultrafiltration coupled with chemical and spectroscopic analyses, the seasonal variation for iron species is shown in Fig. 3. The variation of iron concentrations in different months was obvious. The concentrations of ferrous iron, LMW, MMW and HMW iron decreased gradually from July to October in the marshy waters. The marshy waters exhibited a high concentration of ALI in October (1.241 mg/L). Nevertheless, the concentrations of LMW and ferrous iron decreased to 0.798 and 0.070 mg/L, respectively in October.

The factor which could have limited steady state iron concentration could have been microbial metabolism of

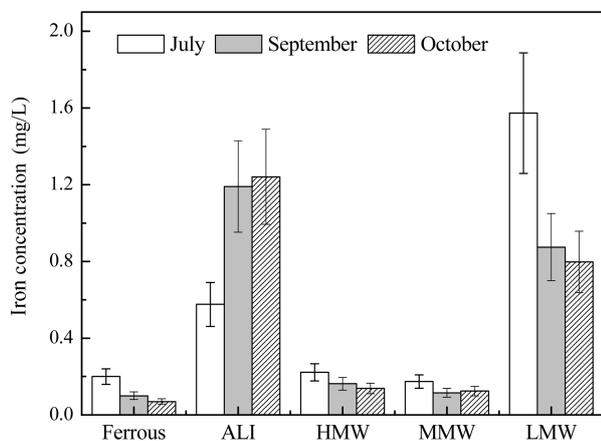


Fig. 3 Concentration of iron species in different seasons in marshy waters. July: flood season; September: normal river flow period; October: dry season.

DOM associated with oxidation and complexation of iron. In such organic-rich environment, LMW iron and ALI were the predominant fractions. LMW iron collected in marshy waters consists of both iron ion (Fe^{2+}) and complexed iron (organic Fe). Early study (Macrellis et al., 2001) had shown that relatively simple, low-molecular-weight DOM which often accompanied with specific functional group could easily chelate with ferric iron. In addition, ALI in the marshy waters consists in Fe oxides and Fe-organic particle. Therefore, both of LMW and ALI iron acting as the most trace carrier in freshwaters have related with DOM derived from litter decomposition during waterlogged conditions.

2.3 Diurnal variation for iron fractions

Figure 4 shows that the variation trend of pH value occurred in marshy waters during different intensity of solar irradiation conditions. The pH value decreased gradually from 03:30 to 12:30 and increased appreciably at 15:30. This phenomenon proved that there were some biochemical reactions happening in marshy waters during the process of sun irradiation, which lead to a variation of pH value. Iron, as a redox sensitive element, participates in some major water environmental reactions and acts as an intermediate species in the sunlit surface water, regarding both iron bioavailability and roles of ferrous iron as reducing agent.

Figure 5 presents the temporal variation of iron proportion in marshy waters. The percentage of ALI decreased continuously with the increase of the light intensity during the morning and decreased to the lowest level at 15:30 in marshy waters. At the same time, an apparent increase in the percentage of dissolved iron, especially LMW iron, was observed after 12:30. The results from Fig. 4 suggested that a fraction of particulate iron (or colloidal iron) was transformed into dissolved iron during the irradiation period. The particulate iron was degraded into LMW iron preferentially. The interplay of precipitation/dissolution, photochemical, and microbial reactions can be readily observed in the diurnal variation of iron.

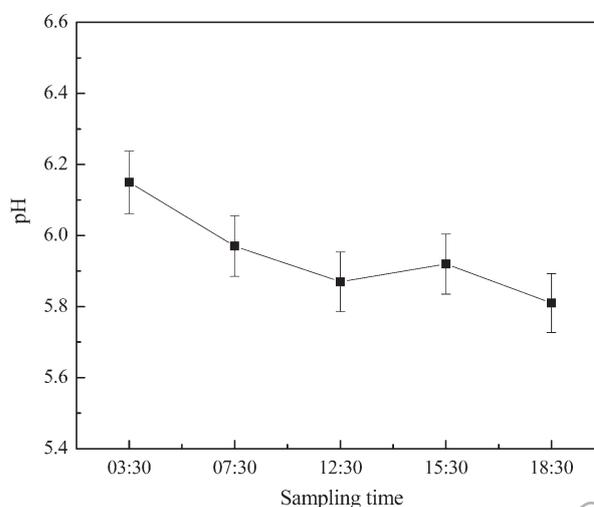


Fig. 4 Diurnal variation of pH value in marshy waters on July 27, 2008.

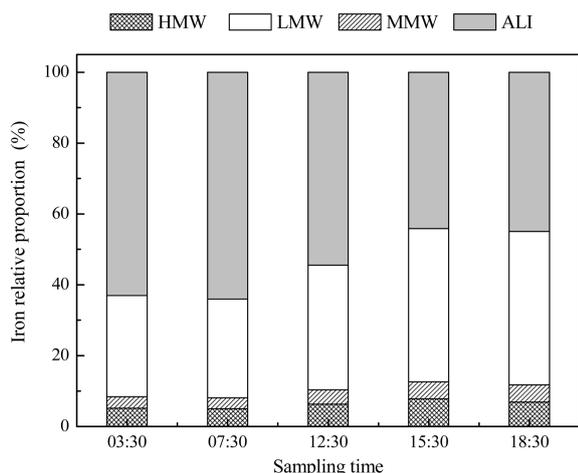


Fig. 5 Diurnal variation of iron relative proportion in marshy waters on July 27, 2008.

3 Discussion

The DOC concentrations which are strongly controlled by surface litter decomposition are generally 30 mg/L or more in wetland waters system (Table 2). However, annual variations in DOC chemistry and concentrations were not great and would not contribute much to variation in iron concentrations. It is more difficult to evaluate the factors controlling the rate at which microbial populations oxidize ferrous ion.

With the result of large variation of iron concentrations, it is informative to examine the precipitation data. In Sanjiang Plain, the pattern of water supply for wetland system is rainfall-fed and snowmelt-fed. Rainfall was highest from June to August through year, which contributed soil saturation at this time. Rainwater acts as an important iron source for wetland and could strongly influence the fate of iron by controlling the pH, Eh and turbidity in wetland surface waters. The concentrations of HMW, MMW, LMW and ALI iron were 0.005, 0.010, 0.092, 0.215 mg/L in rainwater, respectively. From the free iron (Fe^{2+} and Fe^{3+}) measurement for rainwater, we found the concentration of free iron was approximately zero, which indicated that LMW iron occurred almost exclusively as complexed iron. The annual rainfall in 2006, 2007, and 2008 was 538.2, 571.2 and 414.0 mm, respectively, which caused iron concentrations fluctuation. The total dissolved iron concentrations were lower during the great rainfall conditions in 2007 than that in other two years, reflecting a greater dilution of iron released from marshy waters during the heavy rain period. Nevertheless, ALI concentrations were higher during the great rainfall conditions compared with total dissolved iron, which would be related to the turbidity arising from the precipitation in marshy waters.

High rainfall may not only dilute the concentration of iron, but also change the chemistry of marshy waters. During rainy season, the intensive precipitation process enhances the Eh value, which would promote the oxidation of Fe^{2+} to Fe^{3+} . Subsequently, Fe^{3+} could form iron hydroxide or be bound by particles surface in water, which may result in an increase of ALI concentration with

the increase of suspended substance content during flood season.

The seasonal influence on iron concentrations and fractions can be particularly important in a cold climate, as near or below freezing temperatures and plant dormancy may affect important process. It is generally known that microbial activity is linked to temperature, with bacterial growth and metabolic rates strongly reduced with decreasing temperature (Atlas and Bartha, 1998). In Sanjiang Plain, seasonal variation of temperature was obvious, which resulted in a remarkable temperature variation of surface water (Fig. 6). Thus iron concentrations in wetland waters were constantly changing in respond to temperature, in a way which reflects both the seasonal climate pattern and the shorter-term vagaries of weather. Oxidation/reduction activities would be inhibited and rates of microbial decomposition of organic iron (absorbed at surface DOM or chelated with DOM) would be slow at low temperature in wetland waters, which would prevent dissolved iron conversion and release from particle. The decrease of the temperature would cause the increase of Eh and pH value promoting the precipitation of iron in waters.

Moreover, water temperature as a basic quality could strongly influence adsorption-desorption balance of dissolved iron. It is well known that adsorption is an endothermic process in comparison with an exothermic process of desorption. Comparatively high temperature could promote physical desorption from solid phase (suspended substance and sediment). But with decreasing temperature, influence of adsorption function is greater, which suggests that dissolved iron would transfer to solid phase. Besides, the transport of plant oxygen by convective flow, which is assumed to be the most efficient mechanism, decreases greatly at low temperature (Armstrong and Armstrong, 1991). For this reason, the chemical reactions of iron in wetland waters would be comparatively poor. Therefore, the positive correlation between dissolved iron concentration and surface water temperature is likely to exist.

Plant uptake was well documented (Kadlec and Knight, 1996). Litter decomposition, which had an ability of assimilating or release iron, possibly was also a important

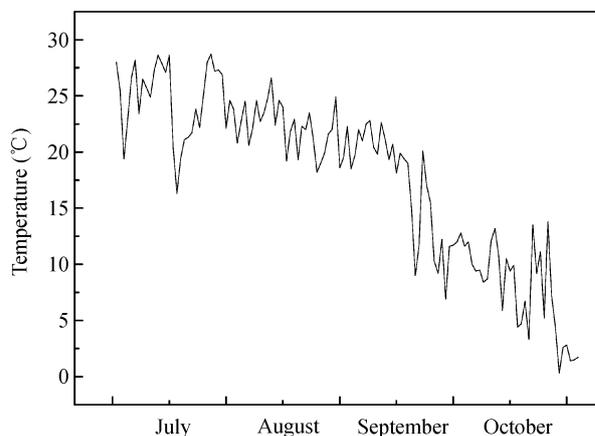


Fig. 6 Surface temperatures from July to October in Sanjiang Plain.

role in determining the concentration of dissolved iron in marshy waters. Zheng et al. (2000) proved that the effect of assimilating was bigger than that of release for *Carex lasiocarpa* system (dominant plant in meadow). Dissolved iron would continually be assimilated by wetland plants, transport to root of plants, and subsequently be fixed by wetland soil.

Complicated biochemical processes, involving oxidation/reduction, adsorption/desorption, precipitation/dissolution, photochemical processes, may occur in marshy waters. In the OM-enriched waters, complexed iron, colloidal iron and particulate iron are composed of organic matters. OM-iron complexes and iron oxide are stable phases existing in the water environment, whereas, some iron compounds adsorbed by colloid and particulate are unstable, which can be degraded into small or dissolved matters under the solar irradiation. The behavior of photolysis of iron complexes have been reported (Barbeau et al., 2001, 2002, 2003; Faust and Zepp, 1993; Gao and Zepp, 1998; Kuma et al., 1992; Voelker et al., 1997). The adsorbed iron compounds desorbed from colloid and particulate may be bound immediately by organic matters forming stable compounds. During the process of interaction of iron and organic matter, iron replace H^+ from organic matter, which leads to a decrease of pH value.

In addition to photolysis of iron complexes, another important reaction is the redox of iron with DOM. Increasing of light intensity during the morning causes increasing rates of photoreduction of dissolved Fe(III) and colloidal Fe oxides as well as concomitant increases in Fe(II) concentration (McKnight et al., 1988, Kimball et al., 1992). Similarly, photolysis of DOM is a daytime source of both superoxide and H_2O_2 . Superoxide can reduce Fe(III), whereas H_2O_2 can oxidize Fe(II) through the Fenton reaction. Therefore, different compositions of DOM caused contrary various trends in different marshy waters.

4 Conclusions

The separation of iron species by size fraction with CFF technique was used to characterize the fate of iron in wetland waters system. This study assessed the concentration and fractions for iron in wetland water during different time span to demonstrate the biochemical process of iron and the effect of environmental factor on iron fractions.

Based on the analysis of wetland waters in Sanjiang Plain, the results show that the organic compounds with an extremely high affinity and selectivity for ferric ion maintain more than 90% in low molecular weight organically complexed dissolved form. DOM affect iron species in the photochemical process to a great extent. A fraction of DOM, including the particulate, colloidal and complexed forms, can be photochemically degraded under solar irradiation. With the decomposability of OM-Fe colloid and Fe-oxides during daytime, the concentration of dissolved iron would increase, especially LMW iron. In addition, annual rainfall can influence annual concentration of iron in wetland waters. Large annual rainfall

can dilute the concentration of dissolved iron and improve the turbidity of waters, which can lead to an increase in concentration of ALI. Otherwise, rain primarily provides ALI and LMW iron for surface water in a certain extent, but not significantly.

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