ORGANIC MATTER AND IRON GEOCHEMICAL MIGRATION IN AMUR RIVER WATERS

LEVSHINA SVETLANA I.
Institute of Water and Ecology Problems FEB RAS, Khabarovsk, Russia

1. INTRODUCTION

Iron (Fe) is one of most common elements on the Earth [4], and Priamurye landscapes, especially their humus masses are not an exception [5, 10]. Due to its big Clarke number Fe is a permanent component of natural waters, and its concentrations fluctuate in a wide range from micrograms to several milligrams per 1 litre [2, 6]. Iron is an important nutrient for higher plants, algae and many other hydrobionts representatives. Fe deficit limits phytoplankton growth in marine waters. Its migration in drainage systems and water objects significantly affects migration of P, Mn and other elements (due to their adsorption by ferrum oxides). Increased Fe concentrations in water deteriorate its quality (smell, high colority).

Not only total content of iron in water objects, but also its water forms (suspended, colloid, dissolved and bottom sediment retained) determine Fe biochemical behavior and its effect on water ecosystems. The Fe dissolved form bound with dissolved organic matter (DOM) is most important and accessible for biota. Assessment of Fe concentrations and its forms in the Amur and its tributaries, as well as Fe discharge into the Amur liman seems quite essential to study biogeochemical processes in water ecosystems.

Although lots of data on Fe concentrations in Priamurye surface waters are available [3, 5, 10, 13 etc.], they are very contradictory. Moreover no attempts have been taken yet to study Fe bound with organic matter (OM) in Priamurye surface waters and especially Fe bound with humus acids (HFA), i.e., humic and fulvic acids.

The goal of the present research is to assess the content and distribution dynamics Fe bound with organic matter in Priamurye surface waters and with humus acids in particular.

2. RESEARCH OBJECTS AND METHORDS

The research was implemented in the Amur and Ussuri Rivers and the Amur liman in 2007–2008 under the Program of the Far Eastern Branch of the Russian Academy of Sciences entitled "Complex expedition research of the Amur Basin natural environment (2004-2008)".

Water was sampled from the surface (0.5 m) and near-bottom (0.5 m from the bottom) water layers at several hydrological measuring stations: the Amur River upper the Songhua juncture (Amurzet village); the Amur River lower the Songhua juncture (Nizhneleninskoe village); the lower Amur reaches (Nizhnyaya Gavan village); the Ussuri mouth; the Amur liman and in the area of river and sea water mixing.

Different water treatment and analytical methods were applied, including methods of membrane filtration, ion-exchange chromatography and inductively coupled plasma spectrophotometry with the Elan DRC II PerkinElmer (USA). For dissolved Fe analysis water samples were filtered (under vacuum) with 0.45 μm pore nuclear filters. Some samples were filtered with 0.2 μm pore filters. GF/F Whatman filters were used to filter samples for carbon form analysis. In summer water samples were filtered on expedition vessel board immediately after sampling and stored at 2–5^{o}C temperature for 2-4 days or freezed and carried to the laboratory for further analyses. To extract the forms of Fe bound with humus acids the method of concentration on DEAE-cellulose [8, 12] was use, followed by ICP-MS to estimate Fe. Dissolved organic carbon (DOC) in water samples was analyzed with standard methods of natural water chemical analyses [1, 3]. Humus acids (HFA) were estimated with the DEAE-method [8, 12]. Water pH and salinity were estimated with standard methods with portable devices.

3. RESULTS AND DISCUSSIONS

Research results showed that Fe distribution in the Amur at its different passages significantly vary both along and across the river and depends on water quality in the Amur tributaries (Table 1). The table makes clear that dissolved iron concentrations in the Amur River are within the range 0.2-05 mg·L^{-1}. Dissolved matter discharge prevails over suspended matter discharge in the Zeya and Bureya, the left Amur tributaries. Suspended matter concentrations in these rivers are not high (~10 mg·L^{-1}). Minimal concentrations (0.5 mg C·L^{-1}) of suspended organic matter are also registered in Bureya water. However Bureya and Zeya waters contain high concentrations of DOM and humus acids (50%-75% of DOC) in particular [9]. The rest part of DOC is made of products of organisms' functioning (polysaccharides, polypeptides, fatty and amino acids, etc.) or substances of anthropogenic origin with similar chemical properties.

The smallest pH values are specific to Amur left-bank water (Amurzet Station), where high concentrations of Fe bound with humus acids were also registered (up to 60% as average).

Several authors [4, 7] indicated that most amounts of dispersed elements, including iron, in river water, are bound with suspended matter, i.e. migrate in the composition of suspended matter, but not in the solution. High concentrations of Fe dissolved forms, found at the Amur left bank (Amurzet Station) are not typical for river waters. In general, in most rivers Fe is transported in its suspended form [7]. Fe is transported in its dissolved form only in rivers, which basins are composed of a poorly broken relief, or with increased annual temperature, or with low water turbidity.

Table 1. Distribution of dissolved organic carbon, humus acids, dissolved Fe, Fe bound with humus acids and pH of river water in Priamurye in 2007-2008 (numerator – concentration range; denominator – mean value, number of samples (n) equals 6).

Sampling date	*pH*	DOC	HFA	Fe		
		mg·L^{-1}		dissolved	bound with HFA	
				mcg·L^{-1}	mcg·L^{-1}	% of dissolved Fe
Amur River, Amurzet Station						
20.08.07	6.70–7.03 / 6.92	10.5–11.1 / 10.9	4.45–4.87 / 4.70	191–220 / 204	82.5–190 / 135	43.4–86.4 / 65.3
27.02.08	6.65–6.70 / 6.68	8.5–9.9 / 9.2	4.42–4.87 / 4.69	100–345 / 212	72.8–170 / 125	50.0–72.8 / 63.6
Amur River, Nizhneleninskoe Station						
21.08.07	6.70–7.63 / 7.13	10.1–12.1 / 11.3	2.18–4.80 / 3.20	228–460 / 305	< 0.001–152	< 0.001–66.6
29.02.08	6.61–6.89 / 6.77	8.1–9.4 / 8.5	1.53–4.51 / 2.60	54.4 –224 / 126	< 0.001–0.162 / 0.105	< 0.001–72.0 / 55.3
Ussuri River						
24.08.07	6.97–7.25 / 7.15	3.7–4.8 / 4.2	2.21–2.28 / 2.24	128–151 / 141	41.3–44.0 / 42.3	27.3–31.2 / 28.4
03.03.08	7.02–7.05 / 7.03	4.0–5.7 / 4.7	1.65–2.05 / 1.80	64.7–85.3 / 74.8	21.6–24.2 / 22.9	28.2–32.8 / 30.5
Amur River, Nizhnyaya Gavan Station						
20.09.07	7.25–7.29 / 7.26	7.2–8.1 / 7.5	3.15–3.42 / 3.24	250–362 / 297	100–152 / 130	40.0–43.8 / 42.8

One of the reasons of high Fe mobility in Priamurye region is abundance of ancient parent iron-ore deposits and mountain rocks (basalts, andasite-basalts and andesites) rich in ferriferous minerals [11]. In greater or lesser quantities and this or that form iron is constantly present in accumulative deposits in river valleys and soil cover of mountains in the Amur basin. Grains of Fe-bearing minerals (epidote, hornblende, hypersthene, etc.) prevail in alluvium of the upper and middle part of the Amur basin. In the lower part of the basin within the Maly Khingan, Bureinsky Mountain ranges and further east iron is present in dark concretions and ferriferous-manganese films, covering sand particles and pebbles in some swamped river areas [13].

Dissolved iron concentrations significantly varied across the Amur lower the Songhua juncture (Nizhneleninskoe Station). Fe bound with humus acids was found in trace quantities or no observed at all at the right river bank. Much higher pH values are typical to right-bank waters compared to Amur waters at its left bank. After water samples were filtered through 0.2 µm filters, no Fe dissolved forms were found in water samples from the right (Chinese) Amur bank and most samples from the Amur middle. Also no Fe bound with humus acids was found. In Ussuri water average dissolved Fe concentrations were about 85 mcg/l, i.e. much lower than in Amur water. The portion of Fe bound with humus acids was about 30% of dissolved Fe. Down the Amur at Nizhnyaya Gavan Station dissolved Fe concentrations were

300 mcg/l at average and the portion of Fe bound with humus acids was 43%.

Fe bound with humus acids was about 30% of dissolved Fe. When Amur water is discharged into the Amur water, water is not just diluted at different stages of fresh and marine water mixing, but also dissolved matter conversion into suspended matter and other processes take place (adsorption-desorption interactions, flocculation, biogeochemical transformations). Even at low salinity (over 1‰) in changing redox conditions organic matter, discharged from the Amur into the liman, undergoes transformations. Most intensive reduction of iron (by an order and more) occurs at salinity 3–10‰ probably due to rapid decomposition of iron-organic complexes. Iron may sediment in the form of ferric hydroxide.

4. CONCLUSIONS

Amur waters contain dissolved iron in significant concentrations, which vary both along and across the river. The iron fraction bound with humus acids also presents a diverse picture. Its maximal concentrations (over 80%) were registered in Amur left-bank water upper the Songhua juncture. Lower the Songhua juncture at the right Amur bank and in the river middle humus acid concentrations were found minimal and Fe lignites were found absent.

Most Fe, which migrates bound with DOM and with humus acids in particular, remains in the Amur liman due to a sharp alteration of redox conditions and does not actually get into the coastal seas.

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