The influence of seasonal changes on the formation of colloids and thin films of iron(III) hydroxide in Ob floodplain lakes

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Abstract: The research was conducted in the middle Ob floodplain. Several parameters (dissolved CO$_2$, pH, conductivity, temperature, humin substances, Fe) were measured in six floodplain lakes in summer and autumn periods 2018. Temperature, conductivity and dissolved CO$_2$ demonstrated the significant difference between these two samples.

1. Introduction

Floodplain is a territory, which is covered by water during the spring flood [1]. Suspended matter, dissolved chemical elements and gases move around the flood zone. The river spreads wide during the spring flood and provides the water exchange with the lakes. So the floodplain lakes influence huge territories [1].

Dissolved gases are very important in the floodplain water objects. Without oxygen (O$_2$) and carbon dioxide (CO$_2$) the life is impossible [2, 3]. pH shows the changes in alkalinity of water environment. The organic composition of natural waters is formed by substances entering water bodies as a result of natural biological processes and the interactions of these substances with surface slope and industrial effluents. Iron (Fe) plays an important role in geochemical processes, such as adsorption, desorption, and redox reactions in soils, sediments, and water. Biological activity of iron impacts the phytoplankton development and microbial population in the water body [4-7]. The natural aquatic environment is a complex system consisting of a dissolved and colloidal fraction, solid particles. Natural aqueous nanocolloids are usually defined as natural nanoparticles with a size from 1 nm to 1 μm [8, 9]. Natural colloidal materials play a decisive role as a mediator in biogeochemical processes, such as cycling of C, N and P, aggregation and sedimentation, as well as the fate of pollutants, as these colloids have a large surface area, high concentration and dense surface binding sites, contributing to strong interactions [10-12]. In addition to colloids formed in water layers when deep or soil waters are mixed, a significant part of the iron can pass into thin films on the surface of temporary puddles and small streams.

The aim of the work is to study the influence of seasonal factors on the deposition of dissolved organic carbon (DOC) with colloidal and thin-film iron(III) hydroxide in the floodplain of the Ob River and the synthesis of thin films.

2. Materials and methods
2.1. Study site
The researches were conducted in the Ob’s floodplain. The river Ob is 3650 km long and goes through Siberia from south (Altai mountains) to the north (the Gulf of Ob). Ob’s floodplain is tens km wide and is the second floodplain in the world. Ob is the long river and in dependence on geomorphological, hydrological and climatic conditions can be divided into three parts: the lower Ob (from Altai mountains to Tom mouths), the middle Ob (from Tom mouth to Irtysch mouth), and the upper Ob (from Irtysch mouth to Gulf of Ob) [13, 14]. Our researches were conducted in the floodplain lakes in the middle course of Ob, Tomsk region, the station Kaibassovo; N57.246142°, E84.181919° (Figure 1). This part of Ob is ice-covered six months per year; the average thickness of ice before the ice-breaking in April is about 90 cm [15].

2.2. Data sampling and analysis
We measured and sampled six floodplain lakes in the summer and autumn 2018. We measured dissolved CO₂ in water using a data-logger with an underwater sensor (GM70 Hand-Held Carbon Dioxide Meter, Vaisala®). We put the logger in water at the depth 15 cm and waited for the reach of the curve’s saturation on the indicator before noticing the measured value. Conductivity, pH, and temperature were measured by WTW Multi 3320 with data-loggers: pH-Electrode Sen Tix® 41 and WTW Tetra Con 325. The loggers were put in the water, and then we fixed the value.

The water samples were filtered in pre-washed 30-ml polypropylene Nalgene® flacons by Minisart single-use filter units (0.45 μm pore size, Sartorius, acetate cellulose filter). We analysed filtered water samples with a spectrometer in a 1-cm quartz cuvette (Eppendorf BioSpectrometer®).

To determine the concentration of organic acids, total content of iron and iron(III) used atomic absorption spectrometer 3300 manufactured by Perkin-Elmer. To obtain the coloured complexes by the spectrophotometric determination of the total content of iron and iron(III) we used sulfosalicylic acid (chemically pure), ammonia solution (chemically pure) and ammonium chloride (chemically pure). After the color emergence we measured the optical density of the solutions. The intensity of the color depends on the iron content and follows the Bouguer-Lambert-Beer law, if iron content in the analyzed water is up to 2 mg/ml. The measurements were carried out at a wavelength of 425 nm. Cuvettes have a working layer thickness of 2-5 cm. The calibration curve was constructed using iron ammonium alum with different concentrations at the same wavelength. According to the calibration graph, the iron content in the source water was calculated. To determine the content of organic acids measurements were carried out at a wavelength of 440 nm. To construct the calibration graph we used standardized samples of organic acids provided by the Siberian Research Institute of Agriculture and Peat.

IR spectra of dried solutions were analyzed on Agilent Cary 630 FTIR IR spectrometer in the frequency range of 400…4000 cm⁻¹.
Obtained data were analyzed using the software Statistica 6.0 and Excel 2010. The non-parametric Mann-Whitney U test was performed; a significant difference was set at $P < 0.05$.

For experimental (laboratory) modeling of the formation of colloids and thin films upon mixing of deep reduced waters and surface waters rich in dissolved organic carbon based on in situ measurements were selected iron, silicon, and humic organic compounds.

As raw components were taken FeSO$_4$·7H$_2$O (Russia) with a concentration of 2.5 mg/ml, dissolved organic matter isolated from peat bogs in the Tomsk Region, provided by the Siberian Research Institute of Agriculture and Peat (Tomsk) with a concentration in the range from 0.02 to 4.0 mg/ml, Na$_2$SiO$_3$·9H$_2$O (Russia) with a concentration in the range from 5 to 20 mg/ml.

For the synthesis of model solutions, combinations of components were selected: iron compounds and dissolved organic substances (sample 1), iron compounds and silicon compounds (sample 2), iron compounds, dissolved organic substances and silicon compounds (sample 3).

The stability of the synthesized solutions was evaluated by changing the optical density of the solution, changing the concentration of colloidal iron in the solution and particle size.

For a system of combining iron, dissolved organic substances and silicon compounds (sample 3), the coating thickness was determined using the method of ellipsometry on a laser ellipsometer SE400advanced.

3. Results and discussion

Lake water contains different dissolved elements and gases. The carbon dioxide is the product of the organisms’ life activity. Iron (Fe) is one of the most abundant metals in freshwater. The chemical form of Fe (its chemical speciation) has a great influence on the mobility and availability of the element itself, as well as other nutrients and potentially toxic trace elements. Dissolved iron may have ionic form (the form of complex compounds with mineral and organic substances). In summer and autumn baseflow periods, the lake feeding is mostly groundwater, so the values of iron concentration remain almost unchanged (figure 2a, b). However, for the lake 4, the summer and autumn values of iron differ 1.5 times. The change in iron concentration in the Ob River for the summer and autumn period remains constant at 0.7 mg/ml.

The values of CO$_2$ in two seasons differ 6.7 times. Dissolved CO$_2$ is stable in different floodplain lakes during the summer and during the autumn (figure 3a). Figure 3b shows that for all the studied floodplain lakes, the pH in the autumn period is in the range of 7.34–8.08, and in the summer it is slightly lower, but within the slightly alkaline region from 7 to 7.4. As is known [9], in an alkaline and slightly alkaline medium in water there is a large amount of iron(III) bound in complexes with humic
acids. The concentration of organic acids in the summer-autumn period remains practically unchanged and ranges from 0.1 to 0.2 mg/ml.

**Table 1.** Biogeochemical parameters and their significance by P<0.05.

| Parameter                  | Mean ± st.dev. Summer | Mean ± st.dev. Autumn | Criteria U | Significance level p |
|----------------------------|-----------------------|-----------------------|------------|----------------------|
| Temperature t, C           | 23.51 ± 1.14          | 3.62 ± 0.48           | 0          | 0.002700             |
| pH                         | 7.27 ± 0.11           | 7.78 ± 0.24           | 2          | 0.006494             |
| Conductivity               | 145.18 ± 40.38        | 173.83 ± 67.78        | 13         | 0.667806             |
| Dissolved CO₂, ppm         | 6258.33 ± 2688.33     | 1498.57 ± 365         | 0          | 0.002700             |
| Humin substances, mg/l     | 0.018 ± 0.003         | 0.015 ± 0.005         | 12         | 0.150786             |
| Fe(III), mg/l              | 1.17 ± 0.49           | 1.165 ± 0.38          | 18         | 0.773885             |
| Fe total, mg/l             | 1.31 ± 0.51           | 1.295 ± 0.4           | 16         | 1                    |

Table 1 shows that only temperature, pH and dissolved CO₂ showed the significant difference. The significant difference of temperature values in different seasons are natural because of climate peculiarities of Siberia region.

Our previous research [4, 16] demonstrated the negative correlation between dissolved oxygen and carbon dioxide in floodplain water. So we can suppose that dissolved oxygen significantly differs at different seasons. At summer the living activity is more intensive and the living organisms produce great quantities of CO₂. At autumn the flora and fauna start to die off and get to hibernation, but the photosynthetic rate is still high.

The forms of iron and their content in water are greatly influenced by pH, the concentration of organic acids (humic acids), dissolved oxygen and carbon dioxide, microorganisms that oxidize and reduce iron. In oxygen-rich water, breaking of the bonds of iron with organic matter is accompanied by the formation of Fe(III). In the absence of big amounts of organic matter, Fe(II) is rapidly oxidized with dissolved oxygen to Fe(III), and can precipitate as iron(III) hydroxides. The pH for the Fe(OH)₃•nH₂O deposition should be in the range 2.5-4.5, which is much lower than pH observed in the floodplain lakes. The probability of precipitation of iron hydroxides is low. Figure 3b shows that
for all the floodplain lakes the pH in the autumn period is in the range of 7.34-8.08, and in the summer period it is slightly lower (from 7 to 7.4), but still within the weakly alkaline range. It is well known [1, 4, 9] that in the alkaline and weakly alkaline ranges in water there is a large amount of iron(III) bound in complexes with humic acids. On the other hand, the migration of iron in surface waters largely depends on the activity of microorganisms. Biological transformation of iron is carried out with the participation of groups of iron-reducing and oxidizing microorganisms, and the rate of biogenic processes of iron oxidation is many times higher than chemical oxidation. It has been proven [10-12], Fe is characterized by the highest affinity of all metals for complex formation with organic matter. Our research demonstrated that the concentration of organic acids in the summer-autumn period does not change. Thus, the concentration of humic acids, pH, CO₂ are the determining factors of the water geochemistry of iron. 

The work carried out experimental (laboratory) modeling of the formation of colloids and thin films upon mixing of deep water and surface water rich in dissolved organic carbon. The resulting colloidal solutions are resistant to the sedimentation process for 30 days. The formation of colloidal iron compounds in the presence of silicon compounds occurs in the entire studied range of silicon concentrations. At low concentrations of silicon ions, partial coagulation of iron compounds occurs, as evidenced by an increase in particle size. At low concentrations of silicon ions of 5.0 and 10.0 mg/ml, the average particle size of the dispersed phase is 180 nm. With an increase in the concentration of silicon ions to 20.0 mg/l, the particle size decreases to 70 nm. In the solution (composition 3), the concentration of dissolved organic matter is 4 mg/ml, the concentration of iron ions is 2.5 mg/ml. For the formation of a stable colloidal system, a concentration of silicon ion of 10 mg/ml is sufficient. In addition to colloids formed in the water column, a substantial part of the iron can pass into thin films on the surface. Therefore, thin films on a silicon substrate (model surface) were obtained from model solutions. To establish the uniformity of the formation of the film coating, the surface of the film was evaluated using a scanning electron microscope. Figure 4 shows a micrograph of the film surface, which is uniform over the entire surface.

![Figure 4. Film surface micrograph](image)

For composition 3, the coating thickness was determined using the ellipsometry method. At a silicon concentration of 5 mg/ml, the film thickness is 78 nm, an increase in the content of silicon ions in the system to 20 mg/ml increases the coating thickness to 160 nm.

4. Conclusion

The main feature of floodplain lakes in Western Siberia in the summer and autumn is the presence of iron compounds and dissolved organic acids, which concentration in the study period did not change.

The determining factors of the water dynamics of iron are the concentration of humic acids, pH, CO₂. In summer, living activity is more intense, living organisms produce large amounts of CO₂, so the concentration is high. In autumn, the flora and fauna begin to die off and go into hibernation, but the photosynthetic speed is still high. Thus, regardless of the concentration of DOC, colloidal solutions are formed that are resistant to the settling process. For the formation of a stable colloidal system, a concentration of silicon ions of 10 mg/ml is sufficient. It was found that film formations are formed on
the surface of natural waters, which have a thickness of up to 160 nm depending on the concentration of silicon ions in the system.

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