

Features of water chemical composition of oligotrophic and eutrophic bogs in the South of the Tomsk region

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Abstract. On the basis of the actual material the analysis of chemical composition of bog waters in the territory of the South of the Tomsk region is carried out. The data on average concentration of macro and trace components, organic matter, pH of bog waters are obtained. Significant distinctions in a chemical composition of surface water for different types of bogs are revealed. The composition and macrostructure of humic acids by the example of eutrophic bogs is studied.

1. Introduction

Western Siberia represents one of the largest accumulative low plains on Earth, which considerable part is boggy. Currently, wetlands range from 37 to 50% [1], and process of peat formation progresses. In regions with humid climate the content of dissolved organic matter in bog waters exceeds several times the content of ash elements [2]. Such waters are organogenic [3] and of keen interest for scientists of the world that defines the relevance of study in bog systems of the territory, including detection of the main features of chemical composition of bog waters, and study in organic matter structure.

The aim of this work is to study bog water for determination of the quantitative contents of macro- and trace components and characteristics of the elemental composition of organic matter.

2. Objects and methods

Field works were performed in the territory of right-bank part of the valley of the lower reach of the Tom River in 20–25 km from its confluence with the Ob River within the second upland fringe. The climate of the area is sharply continental, the average annual air temperature makes -0.6 °C. The amount of precipitation is of 400-600 mm/year. The evaporation capacity makes 450-470 mm/year. Precipitation evaporates incompletely because of the low humidity deficit, low air temperatures and the properties of bog soil and peat to detain moisture. The actual evaporation makes about 350 mm/year, keeping excess moistening of the area [4]. In the upper part of the section Neogene-Quaternary, Paleogene and Upper Cretaceous aquifers developed. The composition of water up to the depth of 500 m is HCO_3 Ca and becomes Na deeper [5]. The landscape is presented by generally ridge pattern.

Investigations included sampling of bog water, the subsequent determination of their chemical and organic composition, and statistical analysis of the received materials. Parameters of the rapidly



changing components were measured in situ: temperature, conductivity, ORP (oxidation-reduction potential), pH – by means of the WATER TEST Hanna instruments; NO_2^- , NO_3^- , NH_4^+ , HCO_3^- , SO_4^{2-} , Ca, Mg, Fe – by photometric and colorimetric methods. The water analysis was carried out in the Accredited Problem research laboratory of hydrogeochemistry of the scientific and educational center "Voda" of Tomsk Polytechnic University.

Elemental analysis of the humic and fulvic acids was performed in the Baikal Nature Management Institute of the Siberian Branch of the Russian Academy of Sciences according to [6, 7] by automatic elemental analyzer «CHN-1106» of Carlo Erba firm, the oxygen content was calculated by the difference. The functional groups were approved by the A.F. Dragunova and T.A. Kukharensko methods.

3. Results and discussion

3.1. Bog water chemistry

The results of the summarized data on chemical composition of bog waters are presented in Table 1. Investigation of the chemical composition of oligotrophic bog water shows that it is mostly acid, slightly acid and neutral (pH varies from 3.1 to 7.2, averaging 4.4); as for the value of TDS, it is ultra-fresh (average value makes 18 mg/L). According to ion composition, the water of oligotrophic bogs is hydrocarbonate calcium-magnesium, sulfate calcium-magnesium, and calcium-sodium.

The water of eutrophic bogs considerably differs under the terms of inflow and chemical composition. Eutrophic peat underlies on the unconsolidated sediments and receives its primary recharge from surface and underground water [8]. In terms of pH, natural waters of these bogs are characterized as slightly acid, more rarely acid and neutral (pH varies from 4.0 to 7.6, on average 5.5); as for the value of TDS, it is ultra-fresh (on average 38 mg/L). According to ion composition, the water of eutrophic bogs is hydrocarbonate calcium-magnesium, sulfate calcium-magnesium being not typical.

There are close synergies between the values of pH of bogs water and its chemistry, especially the concentration of HCO_3^- . In acid water of oligotrophic bogs this ion often is not found at all, and the carbon is contained therein as dissolved dioxide and organic compounds [9]. The latter is formed in the maximum concentration in water of oligotrophic bogs, reducing the pH to 3.1, and considerably exceeding the total content of the dissolved salts. The general content of organic substances in eutrophic bog water in terms of C_{org} makes from 7 to 110 mg/L that is much lower than their content in waters of oligotrophic peat sediments, where C_{org} varies from 20 to 190 mg/L. As compared to eutrophic bogs the average concentrations of organic substances in oligotrophic bogs water are almost twice as higher. Among organic compounds, humic and the fulvic acids sharply dominate which are formed at decomposition of biological material and make the most share of gross organic substance [10, 11]. The average value of fulvic acids content in water of oligotrophic sites is much higher than in eutrophic ones, and can reach 160 mg/L, accounting for 85% of the total organic content in the water. The concentrations of humic acids are lower, 13 on average in the eutrophic bogs water, up to 25 mg/L in the oligotrophic ones.

The high content of organic substances in the studied bodies contributes to concentration of ammonium ions significantly. The average concentration of NH_4^+ in oligotrophic bog water is 4.1 mg/L, in the eutrophic one - 2.3 mg/L, which exceeds twice the Clarke value [2].

Among trace components, in bog water heavy metals prevail. The maximum content of Zn, Pb, Cu, Mn and Al can testify the possibility of their forming complex compounds with organic substances which are found in large amount in the studied water. Among the metals, the content of Fe is the highest; concentration in 3-9 mg/L prevails. Especially, they are abnormal in water of eutrophic bogs, where they can reach 46 mg/L. This is due to the large amount of organic matter in the water, since iron acts as the main element in the competition forming organometallic complexes that promotes its retention and accumulation in water [12].

Table 1. Average, minimum, and maximum concentrations of the dissolved substances and value of physical and chemical parameters of bog water.

| Parameter | Unit | Oligotrophic bogs | | | Eutrophic bogs | | |
|-------------------------------|---------------------|-------------------|------|-------|----------------|------|-------|
| | | Average | Min. | Max. | Average | Min. | Max. |
| Conductivity | uS/cm | 55.9 | 16.0 | 408.0 | 63.7 | 25.0 | 382.0 |
| pH | | 4.4 | 3.1 | 7.2 | 5.5 | 4.0 | 7.6 |
| CO ₂ | mg/L | 72.1 | 2.6 | 141.0 | 57.2 | 3.5 | 154.0 |
| HCO ₃ ⁻ | | 5.0 | N/D | 159.0 | 17.9 | 2.6 | 238.0 |
| SO ₄ ²⁻ | | 4.3 | N/D | 11.3 | 2.5 | 1.5 | 16.5 |
| Cl ⁻ | | 2.0 | 0.4 | 5.8 | 3.4 | 0.8 | 20.6 |
| Ca ²⁺ | | 4.3 | 0.5 | 13.8 | 6.4 | 1.6 | 46.0 |
| Mg ²⁺ | | 0.9 | 0.2 | 8.4 | 3.0 | 0.5 | 8.5 |
| Na ⁺ | | 1.4 | 0.2 | 11.5 | 2.5 | 0.3 | 8.5 |
| K ⁺ | | 0.9 | 0.2 | 4.0 | 2.1 | 0.1 | 5.2 |
| TDS | | 17.8 | 3.4 | 214.0 | 37.6 | 5.5 | 414.0 |
| O ₂ | | 2.6 | 0.6 | 8.4 | 3.8 | 0.5 | 7.7 |
| C _{org} | | 79.6 | 19.9 | 185.6 | 46.9 | 7.5 | 108.0 |
| Fulvic acids | | 69.9 | 15.3 | 158.6 | 38.7 | 3.0 | 96.0 |
| Humic acids | | 24.2 | 1.1 | 61.5 | 13.2 | 0.3 | 46.1 |
| NH ₄ ⁺ | | 4.1 | 0.2 | 87.0 | 2.3 | 0.4 | 10.5 |
| NO ₂ ⁻ | | 0.03 | 0.01 | 0.28 | 0.02 | 0.01 | 0.73 |
| NO ₃ ⁻ | | 0.8 | 0.05 | 2.7 | 1.2 | 0.5 | 4.3 |
| PO ₄ ³⁻ | | 0.2 | 0.01 | 58.8 | 0.9 | 0.1 | 3.4 |
| Fe _{gen} | | 2.8 | 0.4 | 18.3 | 9.3 | 0.4 | 46.2 |
| Mn | | 0.03 | 0.01 | 0.7 | 0.2 | 0.01 | 5.9 |
| Si | | 4.2 | 0.3 | 11.6 | 5.0 | 0.9 | 10.2 |
| F | | 0.1 | 0.02 | 0.3 | 0.1 | 0.1 | 0.2 |
| Al | | 0.2 | 0.04 | 1.2 | 0.5 | 0.3 | 0.8 |
| Total petroleum hydrocarbons | | 2.9 | 0.10 | 16.10 | 0.05 | 0.01 | 0.40 |
| Permanganate value | mgO ₂ /L | 99.5 | 14.0 | 176.8 | 43.1 | 3.6 | 264.0 |
| Zn | | 49.5 | 8.0 | 250.0 | 24.4 | 0.03 | 267.0 |
| Cd | | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.7 |
| Pb | | 1.8 | 0.2 | 265.0 | 2.1 | 0.6 | 19.0 |
| Cu | µg /L | 2.5 | 0.7 | 25.0 | 3.6 | 0.6 | 706.0 |
| As | | 1.8 | 0.3 | 5.0 | 5.7 | 5.0 | 54.0 |
| Li | | 7.1 | 1.0 | 30.0 | 2.7 | 0.01 | 46.0 |
| Sr | | 6.4 | 3.0 | 124.0 | 1.3 | 1.0 | 18.6 |
| Number of samples | | 38 | | | 32 | | |

3.2. Elemental composition of humic substances

To understand the mechanisms of natural organometallic complexes formation and assess the chemical properties of humic substances, first of all, it is necessary to analyze their elemental composition. In this regard three tests of water samples of eutrophic bog are analyzed.

The results of the humic substances composition are presented in Tables 2 and 3. The elemental composition of HA and FA (Table 2) corresponds to the average content of the humic acids elements released from natural waters [7, 13-15]. The amount of carbon in the HA and FA varies between 42.52 - 49.54 %. The hydrogen content of humic acids ranges from 3.82 to 4.13 %, the minimum value is characteristic for FA₁, maximum - for HA₂. The ratio of H:C reaches its highest value in the samples of HA₁ and FA₃, decreasing to 1.01 (HA₂ and FA₁). The observed fluctuation of the H:C ratio results mainly from different proportions of carbon in the aromatic lattice and carbon in the peripheral aliphatic chains.

Table 2. Elemental composition of humic and fulvic acids of bog water

| | Weight percentage | | | | Atomic percentage | | | | Atomic ratio | | |
|-----------------------|-------------------|------|------|-------|-------------------|-------|------|-------|--------------|------|-------|
| | C | H | N | O | C | H | N | O | H:C | O:C | C:N |
| HA₁ | 45.31 | 4.07 | 2.06 | 48.46 | 34.33 | 36.77 | 1.37 | 27.59 | 1.12 | 0.80 | 25.06 |
| FA₁ | 42.52 | 3.61 | 1.72 | 52.15 | 33.78 | 33.97 | 1.15 | 31.11 | 1.01 | 0.92 | 29.37 |
| HA₂ | 49.54 | 4.13 | 2.18 | 41.82 | 44.15 | 37.02 | 1.43 | 25.10 | 1.01 | 0.68 | 25.89 |
| FA₂ | 44.74 | 3.82 | 2.11 | 49.33 | 34.73 | 35.11 | 1.40 | 28.76 | 1.02 | 0.83 | 24.81 |
| HA₃ | 48.32 | 4.19 | 2.21 | 45.28 | 36.02 | 37.19 | 1.42 | 25.38 | 1.03 | 0.70 | 25.37 |
| FA₃ | 43.21 | 4.11 | 1.93 | 50.75 | 32.79 | 36.99 | 1.27 | 28.96 | 1.13 | 0.88 | 25.82 |

The aromatic part of molecules (the degree of benzenoids) is more expressed in HA₂ than in HA₁. The degree of benzenoids of FA in all samples (except sample 1) is lower than that of HA.

The relations of O:C, which are caused by the content of oxygen in the carboxylic, alcoholic, phenolic and methoxy groups, reach the maximum values in FA₁, decreasing among FA₃ – FA₂ – HA₁ – HA₃ – HA₂. The amount of oxygen in humic substances is inversely proportional to the amount of carbon. C:N ratios for humic acids change in a narrow range (25.06-25.89), for fulvic acids – over a wider range (25.82-29.37).

Table 3. Characteristics of humic and fulvic acids of bog waters

| | Oxidation level | Functional groups, mmol/g of specimen | | | Benzenoids |
|-----------------------|-----------------|---------------------------------------|----------|-------------------|------------|
| | | Sum of functional groups | Carboxyl | Phenolic hydroxyl | |
| HA₁ | 0.53 | 10.6 | 6.8 | 3.8 | 0.24 |
| FA₁ | 0.35 | 10.2 | 6.7 | 3.5 | 0.29 |
| HA₂ | 0.38 | 11.2 | 6.3 | 4.9 | 0.42 |
| FA₂ | 0.69 | 11.3 | 7.5 | 3.8 | 0.38 |
| HA₃ | 0.64 | 11.4 | 6.5 | 4.9 | 0.39 |
| FA₃ | 0.64 | 11.6 | 7.2 | 4.4 | 0.22 |

4. Summary and Conclusions

Thus, bog water of the studied area is ultra-fresh, with extremely high content of dissolved organic compounds, P, Fe, NH₄ and some trace components (Zn, Pb, Cu, Mn, Al). The tendency of increasing in concentration from the oligotrophic bogs to the eutrophic is typical almost for all elements of macrostructure; the inverse pattern identified for organic substances is presented mostly by fulvic and

humic acids. In the composition of humic acids there are about 45 % carbon, 45 to 52 % oxygen, 4 % hydrogen and up to 2 % – nitrogen.

Acknowledgments

The reported study was funded by RFBR, according to the research project No. 16-35-60084 and by the State Assignment “Nauka” № 5.1931.2014/K.

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