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## Spatial-Temporal Regularities in Changing Chemical Composition of Bog Waters in Taiga Zone of Western Siberia

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### Abstract

The generalization of data on bog water chemistry has been performed in taiga zone of Western Siberia within 1998–2011. It is shown that the decrease in dissolved salt concentrations over the territories included in the row «eutrophic swamp – mesotrophic swamp – oligotrophic bog» is observed in the course of deterioration of water-mineral supply for bog plants, in the cross-section of peat formation – from inert layer to the upper part of active layer. It is stated that during a year there are maximums in trace element contents, biogenic matter, organic acids in spring and most of principle ions – in summer.

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### 1. Introduction

The West-Siberian Plain is characterized by high quantity of mires reaching 60–80 % in some sites, besides, nowadays, firstly, further boggiess of the territory is observed, particularly in the subzones of South and Middle Taiga, where a number of authors have noted the average rate in vertical growth of peat formation of 0.39–0.80 mm/year size at maximums up to 2.62 mm/year, but the rate of mire square increase – nearly 100 km<sup>2</sup>/year<sup>1-3,10</sup>. Secondly, river basin boggiess is accompanied by deterioration of surface and underground water quality due to the intake of bog water into rivers, lakes, and underground aquifers. It contains a great amount of organic and organic-mineral compounds formed in the process of peat formation and transformation.

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One can assume that in different parts of the region, in different dryness years and in different hydrological phase bog impact on hydrochemical catchments' conditions is various, which is necessary to take into account in solving scientific and applied problems, for example, at long-term planning of water use and protection, evaluation of impact on the environment. Hence, there appears the necessity for study of spatial-temporary changes in bog water composition in taiga zone of Western Siberia. At present thanks to investigations by <sup>5, 10-14</sup> and other researchers, a great amount of data has been accumulated, but there is a need in their generalization and analysis that defines the objective of the given work.

## 2. Material and Methods

The initial data were obtained by the authors together with S. L. Shvartsev, V. A. Bazanov and others in the process of scientific investigations, engineering surveys, state water monitoring in the territory of Tomsk and Tyumen Oblasts performed in 1998–2012 in Tomsk Polytechnic University (TPU), Joint Stock Company "Tomskgeomonitoring", "INGEOTECH" Ltd., and partly published in the articles<sup>1,2,8,10-13</sup>. Some materials including the results of many years' study in changes of chemical composition of the Vasyugan bog water are published for the first time. The research was included: 1) bog water sample selection and conservation for further determination of their chemical composition in stationary certified laboratories of Tomsk Polytechnic University and Joint Stock Company «Tomskgeomonitoring», organic trace compounds – in Oil Chemistry Institute of Russian Science Academy (Siberian Branch), defining the concentrations of quick changing components in field condition; 2) generalization and statistical analysis of materials from TPU, Tomsk State University (TSU), JSC «Tomskgeomonitoring», «INGEOTECH» Ltd. and a number of other institutions and authors.

The object of investigation is more than thirty bogs (mostly out of the zone of intensive anthropogenic impact) basically located on the territory of Tomsk Oblast, partly – in Khanty-Mansiysk Autonomous District and Novosibirsk Oblast (Fig. 1) including the eastern sites of one of the greatest bogs in the world – Vasyugan. In one of the transition valley bogs in Tomsk suburbs the study in bog water chemical composition changes was additionally performed in the cross-section of peat formation using downhole equipment and core sampler designed by A. V. Shmakov and permitting for water sampling from the given depth without mixing water of different aquifers<sup>6</sup>. Bog water sampling (excluding particular case of studying vertical changes) was mostly made from active layer of peat formation. Under active layer, in accordance with<sup>15</sup>, the layer of active bog water exchange is meant, which is a transition from peat profile to vegetation cover.

When determining hydrochemical and geochemical indexes in the certified laboratories of TPU and "Tomskgeomonitoring" the following methods were used: pH, F<sup>-</sup> – potentiometric; SO<sub>4</sub><sup>2-</sup>, – turbidimetric; Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, dichromate oxidizability (DO), permanganate oxidizability (PO), humic acids (HA), fulvic acids (FA), CO<sub>2</sub> – titrimetric; nitrogen compounds, phosphates, Si, Fe – photometric; substances identified as «petrochemicals», phenols, Al – fluorometric; Na<sup>+</sup>, K<sup>+</sup> – flame-emissionic spectrometry; Zn, Pb, Cu, Cd, Mn, Li – atomic absorption, stripping-voltammetric; suspended matter – gravimetric. More research details are presented in the articles<sup>8, 10-13</sup>. The data analysis involved exclusion of indistinctive (extremely high) values, evaluation of average values, errors in their determination and average quadratic deviations, different sample inspection for homogeneity using the Fisher, Student, and Wilcoxon tests according to Land Hydrology<sup>14</sup> as well as comparison of hydrochemical, geobotanical and water management data. In cases when matter concentrations were lower than detection level, the values equal to the half of detection level were used in calculation of statistic characteristics according to Land Hydrology<sup>14</sup> and A.A. Golovin et al<sup>15</sup>. In studying spatial changes the classification of bog ecosystems adopted on Roshydromet and bog zoning of western part of Tomsk Oblast developed by V. A. Bazanov with coauthors<sup>1,2</sup> were applied.



Fig. 1. Location of the research area

### 3. Result and Discussion

Conventionally, differentiation of bog water chemical composition is carried out in terms of bog type which, in its turn, distinguished by the conditions of water-mineral nutrition (eutrophic, mesotrophic and oligotrophic). For instance, similar generalizations for Western Siberia were presented in research<sup>5, 6, 7, 8, 10, 11, 12, 13</sup> on the basis of which one can state that bog water of the area in its natural state is referred to as weak acid (oligotrophic and mesotrophic, less frequently eutrophic) or neutral (eutrophic), fresh with low and average TDS (to 200 and 200–500 mg/dm<sup>3</sup>, respectively; Table 1). Water mineralization of oligotrophic and mesotrophic bogs is usually noticeably lower than that of eutrophic. In this case in the cation composition of oligotrophic bog water the part of Na<sup>+</sup> and Mg<sup>2+</sup> ions grows significantly, but in anion one – the part of Cl<sup>-</sup> ions increases, in some cases – SO<sub>4</sub><sup>2-</sup>. Content of organic matter in bog water amounts about 25–50 mgC/dm<sup>3</sup>. Its significant portion includes fulvic acids, which concentrations are on the average equal to 76.4 mg/dm<sup>3</sup> in water of oligotrophic bogs, but in eutrophic ones – 44.4 mg/dm<sup>3</sup>. Besides, our own and other authors' research generalization<sup>10</sup> has shown that in bog water of the region different groups of organic compounds are also present: carboxylic acid, phenols, aromatic and paraffinic hydrocarbons, organic phosphates, phthalates and other compounds. Particularly, the sum hydrocarbon concentrations in waters of oligo- and mesotrophic eastern sites of the Vasyugan Bog (sub-zone of South Taiga with extensive mire formation with average depth of peat profile 4–8 m) amounts from 4 to 66 mkg/dm<sup>3</sup>, but in downstream of the Tom River (the boundary between south taiga and forest-steppe with intensive but unstable mire formation in multi-year cross-section) – from 231 mkg/dm<sup>3</sup> in oligotrophic bog to 2657 mkg/dm<sup>3</sup> in eutrophic one. Such a considerable range is explained by the corresponding changes in bog water levels (0.3–1.5 m in catchment of the Tom River and 0.2–0.7 m in the Vasyugan Bog) and, hence, more profound transformation of organic matter and intake of these transformation products in water in the transition zone of peat formation. In this case it should be noted that in the zone of permanent eutrophication natural bog processes provide rather a high level of hydrocarbon content exceeding noticeably the accepted in the Russian Federation standards that is attested by the research data on bog water over 100 km and more distance from the sources of anthropogenic impact.

Table 1. Average-annual chemical composition of surface waters in non-contaminated undrained bogs during 1998–2009 [14], mg/dm<sup>3</sup>

Indicator	Eutrophic swamps		Mesotrophic swamps		Oligotrophic bogs		Water courses of eutrophic swamps	
	A	N	A	N	A	N	A	N
pH	6.59	44	5.17	9	4.41	28	5.55	4
TDS	256.3	45	58.2	9	30.9	28	153.5	4
Si	2.04	5	2.02	6	0.6	7	5.32	2
Fe <sub>total</sub>	1.315	44	1.691	9	0.144	28	3.465	2
NO <sub>3</sub> <sup>-</sup>	8.034	6	1.05	6	3.136	8	4.149	4
NO <sub>2</sub> <sup>-</sup>	0.064	6	0.052	6	0.053	8	0.070	4
NH <sub>4</sub> <sup>+</sup>	1.106	44	2.392	9	3.318	28	1.131	4
PO <sub>4</sub> <sup>3-</sup>	0.47	6	0.40	6	0.26	7	0.273	4
DO	134.9	3	123.7	4	93.1	4	161.55	4
Zn	0.0105	44	0.0082	9	0.0060	28	0.0130	4
Cu	0.0015	44	0.0032	9	0.0010	28	0.0030	4

Note: A – arithmetic mean; N – the number of samples; TDS – the sum of dissolved principle ions; DO – dichromate oxidizability

More detailed consideration of hydrochemical data in combination with cluster analysis has allowed for distinguishing not only the bog types mentioned above (oligo-, meso- and eutrophic) but also internal bog ecosystems defined in terms of inner-bog landscapes and phytocenosis in macrocomponent composition of bog waters of peat formation active horizon (Fig. 2). For example, minimal differences were stated between the sum of principle ions in bog waters of sphagnum biogeocenosis, ridge-hollow, ridge-hollow-lake and ridge-lake complexes with predominance of linear inner-bog water reservoirs. Oligotrophic bogs with sphagnum-shrub biogeocenosis and, to less extend, waters of hollow-ridge, hollow-ridge-lake and ridge-lake with inner-bog water reservoirs of non-linear form are similar to them. The group of mesotrophic swamps and oligotrophic bogs with pine-sphagnum biogeocenosis is isolated from other oligotrophic bogs and occupies a transition place between them and eutrophic swamps<sup>2</sup>. In this case the common feature of oligotrophic bogs is a decrease in the sum of dissolved salts in bog waters while increasing in the  $q_z$  characterizing the bog water exchange intensity (Table 2). For eutrophic swamps the opposite trend is stated that is, presumably, conditioned by the following features of composition water formation in bogs of different types and at different distance from the bog boundary.

At the boundary of bog and forest ecosystems the intensive surface water saturation with various inorganic and organic matters takes place. It is explained by, firstly, contact of acid bog waters with mineral ground and subsequent formation of water-dissolved and colloidal complexes. Secondly, at the edge of bogs significant quantity of water accumulates and forms the directed flows with which the formed compounds are carried away. Thirdly, at movement of water flows there is erosion of soil and formation of suspended and bed-load currents accompanied by increase in square of water contact and rock particles, sorption of some dissolved and colloidal matter on the surface of the latter etc. Therefore, increase in intensity of water exchange at the bog boundary (usually eutrophic and mesotrophic) results generally in growth of sum of dissolved salts in bog waters at flow increase. Within the boundary of extensive oligotrophic bogs characterized mostly by atmospheric water-mineral nutrition the flow growth is primarily associated with intensity of matter washout (as compared to its intake) and, consequently, decreases in TDS value. In this case it should be noted that for oligotrophic bogs with ridge-pool, ridge-pool-lake and ridge-lake complexes predominated the form of inner-bog water bodies can be used as an important indicator of water exchange intensity. Large number of lakes with linear form testifies the presence of increased water flow and less quantity of dissolved salts in bog waters. The lakes with non-linear (round) form are, on the contrary, characteristic of slow bog water exchange with environment and, hence, greater interaction time of water with mineral and organic-mineral compounds and higher content of dissolved salts in bog waters (Table 2).



Fig. 2. Dendrogram of Euclidian distances between average sum values of principle ions in water of different bog group ( $D$ ,  $\text{mg}^2/\text{dm}^6$ ); Note: bogs with prevalence of microlandscape: 1 – ridge-pool, hollow-ridge-lake and ridge-lake complexes (HRLC) with linear form of inner-bog reservoirs; 2 – sphagnum mires; 3 – sphagnum-shrub; 4 – HRLC with non-linear forms of inner-bog reservoirs; 5 – pine-sphagnum; 6 – woody-moss-grass mesotrophic; 7 – woody-moss-grass eutrophic; 8 – moss-grass eutrophic

Table 2. Average values of flowage and indicators of bog water chemical composition of Taiga zone (Western Siberia) with predominance of definite inner-bog ecosystems<sup>2</sup>

Indicator	Bog type							
	oligotrophic				mesotrophic		eutrophic	
	Predominated inner-bog ecosystem (Fig. 2)							
	1	2	3	4	5	6	7	8
$q_z$ , l/(s·km)	2.24	1.75	1.71	0.69	0.98	1.35	7.00	1.68
pH	4.6	4.1	5.5	4.3	4.6	5.0	4.6	6.6
TDS, mg/dm <sup>3</sup>	44.7	33.8	47.8	54.6	123.9	86.4	189.7	307.0
$N$	8	5	7	5	23	5	5	32

Note:  $q_z$  – average multi-year flowage value;  $q_z = K_f J \cdot (Z_0 - Z)$ , where  $K_f$  – average coefficient of filtration in filtering layer ( $Z_0 - Z$ ) at bog water level  $Z_0$ ;  $Z_0$  – thickness of active layer;  $J$  – bog surface slope; there presented the results of TPU, data generalization, JSC «Tomskegemonitoring», «INGEOTECH» Ltd, Siberian Institute of Peat, TSU within 1967–2004.

Hence, the basic regularities in changing chemical composition of bog waters (in active layer of peat profile) in the area of the region involved are: 1) decrease in the sum of dissolved salts in the “eutrophic swamp – mesotrophic swamp – oligotrophic bog” row; 2) increase in content of principle ions at the boundary of bog and forest ecosystems and their decrease as they move away from the bog boundary and deterioration in conditions of bog, underground and river water interaction; 3) the highest content of dissolved salts in valley eutrophic bogs and at the boundary of forest-steppe and southern taiga (in the Shegarka River basin, in the lower course of the Tom, Chulyum Rivers and in water catchments of their tributaries); 4) the least content of dissolved salts in waters of oligotrophic watershed bogs in the basins of small and medium rivers in the subzone of middle taiga (the Vasyugan and Tym Rivers, their tributaries). In the vertical cross-section the changes in chemical composition of bog waters are also connected with the intensity of water exchange – the minimal contents of dissolved salts are dated in generally to the top part of a peat profile – to its active layer. However, this dependence is not simple which is connected with the

character of bog water level fluctuations, which, in its turn, is determined by the present bog conditions, general wet conditions (in taiga zone of Western Siberia in the long-term average annual cross-section the wetness is basically excessive, in the sub-zone of southern taiga - normal) and drainage rate (being hampered over the whole considered site, but in combination with other factors, for example, erosion processes, can increase or decrease bogging). The layout of bog water levels and their amplitude of change define the layout of boundary of oxygen supply and change in filtration properties, in other words, the boundary of biogeochemical barriers location is the main factors of increase in element concentrations in the layers of peat formation.

The analysis of temporary changes in water chemical composition of watershed oligotrophic site of the Vasyugan bog enables for conclusion on absence of profound increase in water mineralization of oligotrophic site waters in winter, typical, for example, for regional river waters, that is conditioned by minimal impact of underground supply. Nevertheless, definite seasonal changes are noticed. In particular, they are observed at some increase in nitrogen and iron compound concentrations in summer-autumn period in comparison with spring (Table 3). In the first case (for nitrogen compounds) it is explained by gradual intensity in mineralization of organic matter at the end of summer, in the second one (for iron) – definite dilution of bog waters with snow in spring and more intensive formation in summer-autumn (in comparison with spring) complexes with fulvic acid. Thermodynamic calculations have shown that bog waters are not saturated in natural condition during the whole observation period with respect to all studied carbonate minerals, primary and secondary aluminosilicates. At the same time, bog waters are close to equilibrium with respect to slightly soluble compounds of calcium and magnesium with humic acids in spring and insignificantly oversaturated in summer-autumn<sup>12</sup>.

Table 3. Intraseasonal changes in chemical composition of bog water (active layer) in taiga zone of Western Siberia outside the anthropogenically contaminated area, mg/dm<sup>3</sup>

Indicator	oligotrophic		Bog type mesotrophic		eutrophic	
	IV-VI	VII-XI	IV-VI	VII-XI	IV-VI	VII-XI
TDS	64.0	51.3	126.6	88.0	321.4	198.8
NO <sub>2</sub> <sup>-</sup>	0.015	0.003	0.015	0.002	0.014	0.002
NO <sub>3</sub> <sup>-</sup>	0.600	0.115	0.032	0.138	0.263	0.064
NH <sub>4</sub> <sup>+</sup>	0.970	1.246	0.526	1.600	0.712	1.950
Fe <sup>total</sup>	0.883	1.325	1.383	6.990	1.953	10.723
DO	174.84	390.11	135.88	651.90	75.00	276.99

Similar results were obtained in studying temporal changes in chemical composition of mesotrophic valley bog waters within Tomsk city<sup>16</sup>. Among other things, maximal concentrations of most substances are observed either in spring (Na<sup>+</sup>, K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Si, permanganate oxidability, dichromate oxidability, HA, FA, Zn, Cd, Pb, Cu) or in summer (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, TDS). The fact is explained by, on the one hand, intake of a number of substances with snow melting and surface runoff from dry lands (including those from solution of dust particles by acid melt and bog waters), but, on the other hand, – intensification of biological processes in summer under the most optimal development conditions of macro- and microflora. It is just in summer period that there is increase in active aquifer bog water saturation with oxygen, growth in organic matter transformation intensity and shift in carbon balance towards increase in hydrocarbonate-ion concentration, and, consequently, growth in the sum of dissolved salts.

#### 4. Conclusion

Changes in bog water composition of the area is characterized by decrease in dissolved salt content in «eutrophic swamp – mesotrophic swamp – oligotrophic bog» row in the process of deterioration in water-mineral nutrition of bog vegetation, in the cross-section of peat deposit – minimal values of mineralization in the upper part of active layer, which is characterized by maximum values of flow and filtration coefficient. During a hydrological year maximums in trace element, biogenic substances and organic acid content are observed in these waters in spring due to the intake of definite substances in the bog with surface runoff from neighboring dry lands, with precipitations, at

solution of solid impurities in snow melt. Maximum of principle ions content (with exception of  $\text{Na}^+$  and  $\text{K}^+$ ) is observed in summer at intensification of biogeochemical processes. Similar spatial-temporary changes in chemical composition of bog waters are conditioned, first of all, by the processes of bog-formation and organic matter transformations, which, in their turn, connected with natural (excessive wetness, relatively low thermal supply and weak site drainage contributing to peat formation).

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