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# *STATISTICAL ESTIMATION OF IMPACT OF MAJOR NATURAL AND ANTHROPOGENIC FACTORS ON THE CHANGE IN THE CHEMICAL COMPOSLTLON OF SMALL LAKE WATERS IN WEST SIBERI[A](#page-0-0) \**

*SUMMARY. Thefactor, discriminant, andcorrelation analyses ofthe chemical composition of130 natural watersamples takenfrom the small lakes in West Siberia are carried out. Over 50 indicators describinggeneral and microelement composition ofthe waters are usedforthe analyses. Based on the results of the factor analysis, the main factors and processes are identified according to their impact on the chemical composition ofwaters: I) geographical zoning, 2) regionalfeatures (marine influence, humification, salinity), and 3) localfactors, both natural (bogginess, eutrophication) and anthropogenic (man-induced acidification). According to the results ofthe discriminant analysis, it is concludedthat thewater composition in the tundra and taiga zonesslightly varies, and a sharp variety in the water composition of theforest-steppe lakes is registered. The correlations between macro- and microcomponent contents ofnatural waters are determined.*

*KEYWORDS. Formation ofthe chemical composition ofwaters, microelement composition ofwaters, statistical methods.*

**Introduction.** The methods of statistical analysis are widely used in various fields of science. In geochemistry, the application of mathematical methods is rather specific. The actual material is generally presented by a set of numerical parameters that quantify the occurrence and distribution of chemical elements in the modem structure of geological objects (water bodies, rocks, the Earth's crust, the Earth as a whole) [1], [2]. To solve a wide range of tasks, mathematical and statistical methods summarizing and interpreting the data arrays are required. In particular, this problem arises while analyzing the chemical composition of natural waters.

The purpose of this paper was to study the impact of basic natural and anthropogenic factors on the formation of the chemical composition of small lakes in West Siberia

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and to determine correlations in the contents ofmacro- andmicroelements by statistical methods.

**The data and methods ofthe research.** The research was based on the summary ofthe data concerning the chemical composition of 130 small lakes in the territory ofWest Siberia from the tundra zones (Gydan and Yamal peninsulae) to the steppe zone in the south of the Tyumen Region, obtained in 2011 by the consistent methodological scheme [3]. The research included lakes not subject to any direct sources of pollution, with water surface area no more than 20 km<sup>2</sup>. The water samples were taken from the lake surface or from the overflow stream in the period from August (the tundra and forest-tundra lakes) till the late October (southern zones) using helicopter and air routes.

The chemical analysis of the samples was carried out in stationary conditions according to the standard methods. In the water samples, the following parameters were determined:

• pH, electrical conductivity ( $\chi$ ), and basic mineralization ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>,K<sup>+</sup>, Na<sup>+</sup>), alkalinity (Alk),  $SO<sub>4</sub><sup>2</sup>$ , Cl<sup>-</sup>);

• color index (Col), total organic carbon (TOC),  $NO_3$ ;  $NH<sub>4</sub><sup>+</sup>$ , total nitrogen (TNb),  $PO<sub>4</sub><sup>3</sup>$ , total phosphorus (TP), Si;

• contents of microelements (Sr, Al, Fe, Mn, Cr, Cu, Ni, Zn, Cd, etc.)

The above-listed parameters were determined as follows:

- pH: by the potentiometric method, with a glass electrode;
- electrical conductivity at 20<sup>o</sup>: by the conductometric method;

— color index: by the spectrophotometric method by the chromiumcobalt color scale at the wavelength of 380 nm;

concentrations of microelements ( $> 60$  elements): by the emission method of inductively coupled plasma by the *Element* (UK) mass spectrometer in Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science.

#### **The factor, discriminant, and correlation analyses ofthe data**

The factor, discriminant, and correlation analyses of the data were carried out using the *Statistics 6* and *SPSS17+* (standard software packages). To analyze the chemical composition, 137 samples of natural water were taken from the lakes of West Siberia, excluding zonal distribution. The data on the macro- and microelements (more than 50 indicators) and some general indicators of the chemical composition (pH, color, total organic carbon (TOC), alkalinity) were included into the processing. Aside from the chemical composition of the samples, the climatic (precipitation, evaporation, humidity  $(C_{\text{hum}})$ , the sum of active temperatures) and geographical data (forest coverage coefficient  $(C_f)$ , bogginess  $(C_{bog})$  and lake coverage  $(C_i)$  coefficients were used in the factor analysis. The elements with the concentration lower than the analytical detection limit (Ga, Hg, Sc, Ge, In, Pt, Ru, Pd, Те, Rh, Os, Ir) were not included into the analysis. After carrying out the correlation analysis on the whole data array for the lanthanides group (La, Ce, Nd, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb,

Tm, Th), the high correlation (0.94 - 1.0) between them was determined. The final table presents the data for two typical representatives (Ce and Yb).

## **The results of the factor, discriminant, and correlation analyses**

The composition of soils and soil-forming minerals in the water-producing area considerably affects the chemical composition of water in small lakes. The bedrock leaching is the main source of the elements input into the water bodies. Aside from the influence ofthe sources ofthe input and the zonal conditions of forming the water chemical composition, the microelement composition of the lake waters is subject to the transformation connected with the development of both natural (organic acidifying of waters) and anthropogenic processes such as eutrophication and man-induced acidification [4]. To estimate various factors in the formation of the water chemical composition, the factor analysis was carried out using the principal component method.

*Thefactor analysis.* The matrix for the factor analysis included the data on the water chemical composition, geographic and climatic characteristics. The method of factor analysis enables us to estimate the water elements grouping and to identify the factors influencing on the formation of the chemical composition in the lake waters. The results of the factor analysis of the concentrations of macro- and microelements in the waters ofsmall lakes in West Siberia are presented in Table 1. According to the results of the analysis, four main factors were identified with the following percentages of the explained variance:  $1 - 33.4$ ;  $2 - 22.5$ ;  $3 - 6.79$ ;  $4 - 5.38$ .

According to the data of the factor analysis, *the first factor* united the contents of sodium, chlorine, and sulphates relating to the basic mineralization ions, and the following microelements (in the descending order of the coefficients): V, La (and lanthanides), Al, Be, Fe, Pb, Ti, and B. Besides, there is the correlation with color index and the less significant one with total salt content (SEC). This factor having the highest percentage of explained variance does not take into account the natural zoning since it does not include either climatic or geographic indicators; it apparently characterizes the common features of the water composition formation. According to the factor analysis data, there is a significant similarity in the distribution between typomorphic elements (iron and aluminum) and lanthanides in the lakes composition. This fact is also confirmed by the results of the correlation analysis.

Table <sup>1</sup>



#### **The results ofthe factor analysis on the maximum parameter set**

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Table <sup>1</sup>





Table <sup>1</sup>

The second factor correlated the total salt content (SEC), pH, the contents of main mineralization ions (all main cations, carbonates, chlorides and nitrates - to a lesser extent), and TOC with the annual runoff (the factor has a minus sign, i.e. the SEC value decreases while the annual runoff increases) and the sum of active temperatures. The sum of active temperatures increases while the latitude (from north to south) decreases; it affects the process of the ion leaching from the bedrock of the waterproducing area. This factor includes the following indicators: the contents of Si, Sr, As, B, Ba, Li, Rb, Re, and U.

*The thirdfactor* correlated the climatic parameters (precipitation, evaporation,  $C_{\text{hum}}$ , the sum of active temperatures) and one of the geographical parameters (the bogginess degree  $(C_{\text{box}})$  with the content of ammonium and the color index (0.44). Actually, in swamps, the content of ammonium and color index may increase. This factor also includes the contents of microelements (Cu, Bi, and F, -0.40; -0.47, and 0.46, respectively) with the coefficients of about 0.4 according to the analysis results.

*Thefourthfactor* having the lowest percentage of explainable variance indicates the correlation of the forest coverage coefficient  $(C_f)$  with the content of nitrates, Mn (the positive coefficients of 0.52, 0.45), Cl and Br (the negative coefficients of  $-0.51$ , -0.485). Such a correlation may be the proof of the Mn input into the water by the leaf fall decomposition. The correlation of the forest coverage with the content of nitrates can be explained by their active participation in the biochemical processes. The lake coverage coefficient  $(C<sub>1</sub>)$  was not included in any of the factors.

The results of the factor analysis with the maximum data set did not reveal a clear dependence ofthe water composition on the latitude zoning and natural features, since the most numerous data (the large number of microelements) were the first as to the percentage of explained variance. Therefore, to reveal the general regularities of forming the chemical composition of water, the data set was reduced. The results are presented in Table. 2.

Table 2

Parameters	Factor 1	Factor 2	Factor 3
$C_{\rm f}$	$-0.154$	$-0.740$	0.093
$C_{\underline{w}l}$	0.520	$-0.501$	$-0.117$
Precipitation	0.255	$-0.849$	$-0.154$
Evaporation	0.115	$-0.898$	$-0.149$
$\Sigma t > 10$ °C	$-0.605$	$-0.647$	$-0.203$
pH	$-0.706$	0.295	0.022
X	$-0.919$	0.074	$-0.223$
Ca	$-0.839$	$-0.110$	0.028
Mg	$-0.884$	0.121	$-0.220$
Na	$-0.824$	0.106	$-0.344$
K	$-0.826$	0.181	$-0.263$
Alk	$-0.939$	0.049	$-0.088$
SO <sub>4</sub>	$-0.351$	0.014	0.218
<b>Cl</b>	$-0.648$	0.088	$-0.297$
Col	$-0.027$	$-0.658$	0.075
TOC	$-0.743$	$-0.402$	$-0.057$
NO <sub>3</sub>	$-0.368$	$-0.255$	0.551
NH <sub>4</sub>	0.033	$-0.340$	$-0.242$
TN	$-0.767$	$-0.325$	0.282
PO <sub>4</sub>	$-0.234$	$-0.262$	0.485

**The results of the factor analysis on the limited set of parameters**

Parameters	Factor 1	Factor 2	Factor 3
TP	0.083	$-0.044$	0.410
Si	$-0.705$	$-0.099$	0.168
Sr	$-0.547$	0.149	$-0.010$
Al	0.122	$-0.102$	0.099
Fe	0.286	0.075	0.411
Mn	$-0.243$	$-0.478$	0.474
Cr	$-0.428$	0.018	0.571
Cu	$-0.342$	0.120	0.543
Ni	0.026	$-0.036$	0.477
Zn	$-0.185$	0.348	0.509
C <sub>d</sub>	0.089	$-0.180$	$-0.054$
Pb	0.087	0.257	0.254
% of explained variance	27.3	13.3	9.1

Table 2



Root <sup>1</sup>

Fig.1. The scatter plot of the canonical function values discriminating the natural zones. G\_1:1 — tundra; G\_1:2 — northern taiga; G\_1:3 — middle taiga; G\_1:4 — southern taiga; G\_1:5 — forest-steppe

The results of the factor analysis on the reduced data set revealed three factors with the value of explained variance higher than 5%. The first factor determines the zonal conditions of forming the chemical composition of waters, since it is conjugated with the bogginess  $(C_{box})$  of water-producing areas, which is common for West Siberia. Factor 2 also characterizes the regional features, such as the forest coverage in natural

zones or the bogginess degree of water-producing areas (including the organic matter and Mn enrichment and the color index increase caused by it). The local occurrence (factor 3) is expressed in the eutrophication ofthe large number oflakes and the lake water enrichment in Fe, Mn, Cr, Cu, Ni, and Zn. Thus, basing on the factor analysis on the limited data set, the factors and processes can be ranged according to the extent of their impact on the chemical composition of water: 1) geographical zoning, 2) regional features (marine influence, humification, salinity), and 3) local factors both of natural (bogginess, eutrophication) and anthropogenic (man-induced acidification) types.

For the same source data, the discriminant analysis was carried out and the generalized Mahalanobis distances were calculated. The results of the discriminant analysis are presented in Fig. 1, the Mahalanobis distances are presented in Table 3. Zoning was used as the discriminating parameter (G\_1:1 - tundra; G\_1:2 - northern taiga; G\_1: 3 - middle taiga; G\_1: 4 - southern taiga; G\_1: 5 - forest-steppe).

Table 3



**Generalized Mahalanobis distances between natural zones**

The generalized Mahalanobis distances presented in Table 3 demonstrate the measure of discrimination in the chemical composition of waters between the natural zones. According to them, the waters composition in the tundra and taiga zones differs less; there is a smooth variation and overlap of the lake locations in these areas. The forest-steppe zone significantly differs from other natural zones in West Siberia.

*The correlation analysis.* The contents ofsome microelements in rocks are known to correlate. The data of statistical analysis on the microelements correlations in the soil-forming rocks of West Siberia are presented in the study by A.I. Syso [5]. According to these data, significant correlations are established between the following elements: in rocks, arsenic correlates with barium and phosphorus. Rare-earth elements (Be, Bi, Ce, La, Nb, Sc, Y, Yb) tightly correlate; moreover, a strong correlation with the Cu, Mo, Pb, Sn, Sr, Zn contents is registered for many elements of this group. A strong correlation is typical for the following group of elements: Co, Cr, Ni, Ti, V.

The properties of water as the migration environment are determined by several basic and typomorphic elements or ions  $(O_2, CO_2, H_2S, H^+, OH, Cl^-, SO_4^-, HCO_3^-)$  $CO_3^2$ ,  $Ca^{2+}$ , Mg<sup>2</sup>, Na<sup>+</sup>, Fe<sup>3+</sup>, etc.) [6]. Moreover, microelements can correlate with each other, as it occurs in rocks, thus they can be grouped. The method of correlation analysis allows establishing correlations between the contents of macro-components ofnatural waters, some general parameters and the contents of other elements. Table

3 presents the correlation analysis results for the element composition of the lake waters in West Siberia *(Statistika 6* software). The boldfaced correlation coefficients are greater than 0.5.

Consider the relations between the contents of the basic water components and the correlated elements. The *main cations* predominantly correlate with anions: Ca tightly correlates with alkalinity  $(0.79)$ ; Na and K correlate with the alkalinity and chlorides (0.70-0.72). Calcium is in good correlation with other alkaline-earth elements (magnesium (0.80), strontium (0.73), barium (0.89)), as well as with manganese  $(0.75)$ , rubidium  $(0.66)$ , uranium  $(0.59)$ , silicon  $(0.73)$ , and arsenic  $(0.64)$ . The content of*total organic carbon* (TOC) has correlations greater than 0.5 with the contents of main ions (Ca, Na, Mg, K), as well as with some microelements (Ba, Rb, U) and arsenic. The contents of total Fe, Al, lanthanides, Be, and Ti correlate with color index. The pH value correlates with the contents of main cations, Ba, Sr, Rb, and Si. Such regularities may be caused by the processes of the complex formation in metals with water organic components [7], [8].

In the water composition of small lakes in West Siberia, Al and Fe are typomorphic elements [9]. Siderophile Ti, V, as well as Be, Al, and lanthanides correlate with iron, the same elements and Pb correlate with aluminum. There are no obvious correlations ofFe with other siderophile elements (Ni, Cr). The correlations in the microelement compositions are as follows: in addition to iron and aluminum, lanthanides correlate with Be, Pb, Ti, and V; arsenic correlates with Ba, Sr, Rb, Re, and U. Chalcophilic elements (zinc and copper) do not have the correlation coefficients greater than 0.5 with any component of natural waters; they poorly correlate with each other (0.475).

The comparative analysis of the microelement correlations in the soils and soilforming rocks of West Siberia [5] and the data from Table <sup>1</sup> demonstrate that the correlations between the elements in the soil-forming rocks and waters significantly differ. For example, iron in soil-forming rocks correlates better with siderophile elements (Ni, Co) and Cr. There are no correlations with Be, and there is a poor correlation with lanthanum (0.3). In the water composition, it is Fe that correlates best with La and lanthanides; Ni has no correlation coefficients greater than 0.5 with any water component. There are other metals for which the correlations with all other water components are negligible (all coefficients <0.5). They are Mo, W, Bi, Ag, Sn, Zn, and Cd.

**Conclusion.** The statistical analysis of the data on the chemical composition of natural waters ofsmall lakes in West Siberia was carried out. According to the results of the factor analysis, the main factors and processes are determined taking into consideration the extent of their impact on the chemical composition of waters:  $1$ ) geographical zoning, 2) regional features (marine influence, humification, salinity), 3) local factors, both natural (degree ofbogginess, eutrophication) and anthropogenic (man-induced acidification) ones. The results of the discriminant analysis imply that the water composition in the tundra and taiga zones slightly varies, and a sharp difference in the water composition of the forest-steppe lakes is registered.

The correlation analysis revealed the existence of correlations in the waters of small lakes in West Siberia between the basic components (main ions), generalized indicators (TOC, color index), typomorphic elements (Fe, Al), and microelements.

Table 4



### **The table of pair correlations of natural waters components in the small lakes ofWest Siberia**

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## Table 4 continued

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