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RECONSTRUCTION OF IONIC COMPOSITION OF NATURAL WATERS, FORMED WITHIN THE KHIBINY MASSIF

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Assessment of anthropogenic load on water systems is one of the major problems of present-day ecology. This assessment should reside in the knowledge of the ionic composition of natural waters and their formation conditions without anthropogenic factors. Many of the subarctic mountainous water bodies of the Kola Peninsula belong to so-called "reference areas" due to their remoteness from the sources of pollution, hence their study provides necessary information on natural formation of water quality and living environment of aquatic organisms. Such studies raise the effectiveness of water transformation assessment under pollution impact.

Subjects of inquiry of the present paper became surface waters – the Poachvumjok stream, falling down the Khibiny massif, and lake Goltsovoe (Table2). The latter is located at the outlet of the Kunijok river valley in the northern part of the Khibiny massif, in a landscape zone of northern taiga. The bathymetry is characterized by deep canyon (up to 20.8 m) in the southern part of the water body. Numerous mountainous streams flow into the water body from neighboring slopes; many springs also appear in it. Ichtyofauna of the lake consists of grayling and char, which are pollution-sensitive species.

A paleoecological approach was applied for assessment of long-term changes in the lake ecosystem, which is based on stratigraphical study of diatoms complexes in ground sediments. The frustules of diatoms, consisting of amorphous silica, keep well in ground sediments and are widely used for reconstruction of water development (Smol, 1988; Moiseenko et al., 1997). A column of ground sediments with the thickness of 7 cm, taken at a maximum depth (accumulation zone) provided data for the study. Such thickness is sufficient for paleoecological reconstruction in the Arctic, where the sedimentation level is low (about 0.2 mm per year) (Dauvalter, 2002). Besides, an assessment of contemporary littoral diatom flora was performed (July, 2003). The diatom analysis was carried out with the aid of standard methods (Diatom analysis, 1949). In the course of analysis a total of 102 diatomic taxa were observed. Through the whole column diatomic species were found, typical for ultra-oligotrophic water bodies, which are rich in oxygen. Many of the found species are typical for cold mountainous streams. On the whole diatoms complexes are comprised by typical arctoalpine, mountainous and cold-water species, which prefer sub-neutral pH values. The abundance and species variety have slightly changed during the last period and reflect now the natural dynamics of these parameters (Denisov, Kashulin, 2004). Accordingly, no changes, related to recent industrial development of the Kola North, were registered throughout the whole period of column formation. No essential consequences of air borne industrial pollution were registered either; the fact confirmed by data on contemporary littoral diatom communities.

These facts suggest an assumption that the water of this lake was formed naturally in the result of "water-rock-atmosphere" interaction. Such problems are solved via equilibrium thermodynamic method (software system "Selector") (Karpov, 1981).

A system created for the study of chemical composition of freshwater bodies at temperatures +1-+25 oC, over a wide range of pH (from 1 to 12) and Eh values (from 1.2 to -0.8) was employed as an initial multisystem. On the whole the basic multisystem included 225 individual materials (95 in the initial solution, 13 in the gaseous phase and 117 in solid phase). Independent components of the basic multisystem are: Al-Ar-C-Ca-Cl-F-K-Mg-Mn-N-Na-P-S-Si-Sr-H-O-e (e-electron).The chemical composition of the Khibiny massif (Kukharenko et al., 1968) after 100% normalizing is true to the following composition (mass.%): SiO_2 – 53.1164; Al_2O_3 – 21.218; Fe_2O_3 – 2.585; FeO – 1.577; MgO – 0.649; CaO – 1.797; Na_2O – 9.791; K_2O – 6.507; P_2O_5 -0.288; MnO – 0.18; TiO_2 – 1.048; SrO – 0.126; SO_3 – 0.023; F – 0.123; Cl – 0.036; CO_2 – 0.14; H_2O – 0.798. The interaction model "water-rock-atmosphere" took into consideration clarke composition of C (0.038%), S (0.021%), Cl (0.036%), F (0.12%), their migration capacity and accumulation ability. Water migration coefficients of S and Cl exceed by 1-2 orders the water migration coefficients of Ca, Na and F, this being simulated by different degrees of component interaction. All calculations were performed per 1000 kg of water. The system was studied in open conditions (100 kg of atmosphere) (Mazukhina, Sandimirov, 2005). Table 1 shows the simulation results for the system "water-rock-atmosphere". Thermodynamic models of natural waters were made basing on analytical data on chemical composition of waters of lake Goltsovoe (surface and near-bottom horizons) and the stream Poachvumjok through calculation of equilibrium state of the system "aqueous solution-atmosphere".

Table1. Computer-based prototype of ionic composition of surface water as a result of water-rock-atmosphere interaction (T = 5°C, P=1 bar), mg/l

Rock, g	Ca^{+2}	Cl^{-}	K^{+}	Mg^{+2}	Na^{+}	F^{-}	SO_4^{-2}	SiO_2	HCO_3^{-}	pH
10	0.129	0.184	0.212	0.039	0.674	0.132	0.321	2.248	1.587	6.64
15.84	0.204	0.291	0.385	0.062	1.058	0.139	0.509	3.431	2.764	6.87
25.11	0.277	0.461	0.457	0.098	1.713	0.146	0.806	3.93	4.387	7.09
39.81	0.401	0.731	0.431	0.156	2.787	0.159	1.277	3.9 3	6.862	7.29
63.1	0.640	1.159	0.401	0.247	4.488	0.181	2.023	3.93	10.825	7.50
100	1.011	1.837	0.368	0.391	7.180	0.217	3.202	3.93	17.110	7.71

Mineral composition of newly-formed phases, mole

	Msc	Apt	FeOOH	Mnt	SiO_2
10	0,0084	0	0,005	0,0070	0
15.84	0,0120	0	0,0086	0,0128	0
25.11	0,0230	0,0002	0,0136	0,0152	0,0318
39.81	0,0440	0,0005	0,0216	0,0145	0,1016
63.1	0,0770	0,0008	0,0343	0,0137	0,2117
100	0,1289	0,0013	0,0544	0,0128	0,3856

NOTE: Msc- muscovite, Apt- apatite, FeOOH- goethite, Mnt- montrmorilonite

However, only the content of cation elements (Na, K, Ca, Mg, and Fe) was determined in the solution and the content of some anion elements (P, Cl, N, S, Si), which concentrations correspond with analytical ones. The content of atmophyl anion elements (C-H-O) was determined during the calculation of the thermodynamic model. Through varying of CO_2 and O_2 the correspondence of analytical pH values to calculated ones was achieved. Thus, full coherence of calculated and analytical values of chemical parameters of natural water was obtained to evaluate real rate of water saturation with air gaseous components (Krainov et al., 1988). The computer prototypes of natural waters were at first calculated at temperature 25oC, this being the temperature of analytical work, and then they were brought to the sampling temperature (Table 2). Analytical data of the lake and stream didn't contain F, so, comparing it to simulation results, it is safe to assume that natural water contains from 0.15 to 0.2 mg/l of fluorine. Besides, the analysis of high Al content (stream) suggests the conclusion about its natural mobility. At the next stage the mineral saturation rate of natural water of lake Golsovoe was determined at various temperatures. The simulation results are given in Table 3.

Table 2. The results of analysis and simulation of water chemical composition.

		Lake Goltsovoe, 4.07.2001				Stream
		surface			bottom	06.06.2001
ToC			25	15	10	10
PH	7,12		7,11108	7,1229	7,13727	7,19211
Eh, B			0,79627	0,81178	0,81906	0,81601
P, бар			1	1	2,5	
analysis, mg/l		Simulation , mg/l				
		Ar	0,5086	0,6085	0,6752	0,676
Al	0,0228	AlO_2^-	0,0231	0,0197	0,014	0,2453
		$HAlO_2$	0,005	0,007	0,0065	0,0997
		$Al(OH)^{+2}$	0	0	0,0001	0,0007
		$Al(OH)_2+$	0,0003	0,0007	0,0009	0,0123
		$Al(OH)_3$	0,0046	0,0058	0,005	0,0768
		$Al(OH)_4-$	0,0291	0,0292	0,0223	0,3891
		$CaCO_3$	0,0003	0,0002	0,0001	0,0002
		$Ca(HCO_3)^+$	0,0028	0,0028	0,0025	0,0033
Ca	0,5	Ca^{+2}	0,4975	0,4976	0,4383	0,6272
		$CaSO_4$*	0,0043	0,004	0,0022	0,0046
Cl	0,9	Cl-	0,9	0,9	0,75	0,52
		$Fe(OH)_4^-$	0,0012	0,0007	0,0006	0,0017
Fe	0,0087	$Fe(OH)_2^+$	0,0017	0,0029	0,0044	0,0098
		$Fe(OH)_3$	0,0135	0,0125	0,0137	0,0347
K	1,32	K^+	1,3198	1,3198	1,2699	1,1698
		KSO_4-	0,0007	0,0007	0,0004	0,0006
		$Mg(HCO_3)+$	0,0005	0,0005	0,0005	0,0005
Mg	0,07	Mg^{+2}	0,0698	0,0698	0,0599	0,0699
Mn	0,0005	Mn^{+2}	0,0005	0,0005	0,0004	0,003
		Na+	5,0999	5,0999	4,6684	4,4999
Na	5,1	$NaAlO_2$	0	0	0,0052	0
		$NaHSiO_3$	0,0002	0,0001	0,0001	0,0001
		NO_3^-eq.	0,0069	0,0067	0,0067	0,0077
NO_3-	0,054	NO_3-	0,054	0,054	0,036	
		CO_2	1,5629	1,7909	1,8992	1,5627
		CO_3^{-2}	0,0083	0,0068	0,0061	0,0064
		N_2	14,4011	16,923	18,617	18,6455
		Ne	0,0002	0,0002	0,0002	0,0002
		O_2	8,0906	9,7047	10,7909	10,8451
		$H_2PO_4^-$	0,0017	0,0017	0,0035	0,0005
		HPO_4^{-2}	0,0014	0,0014	0,0027	0,0005
		$HSiO_3-$	0,0136	0,0098	0,0065	0,0038
NH_4+		NH_4+	0,017	0,017	0,017	
SO4	2,2	SO_4^{-2}	2,1965	2,1967	1,3981	2,0463
Si	3,33	SiO2*	7,1133	7,1163	5,4075	2,7781
Sr	0,0545	Sr^{+2}	0,0545	0,0545	0,054	0,05
		HCO_3-	13,122	13,1379	12,9875	12,1065

Table 3. Composition and content of minerals, with which the water of the Goltsovoe lake is saturated, mole.

ToC	25	15	10
FeOOH	1.55e-04	1.55e-04	1.55e-04
Mnt	3.6e-04	3.6e-04	-
Msc			2.8e-04
SiO2		3.00e-04	2.86e-02

NOTE: Msc- muscovite, FeOOH- goethite, Mnt- montrmorilonite

The analysis of the given data prooves low content of suspended matters in the lake and formation of amorphous silica at low temperatures, which was subsequently confirmed by monitoring.
A conclusion can be drawn based on the research data that the water of lake Goltsovoe can serve as reference water during the comparison with the lake and streams formed in the Khibiny massif and subjected to industrial pollution.

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