

UDC 536-12:579.222.4

## Study on the Condition of the Bolshoy Vudyavr Lake Waters after the Ecocatastrophe of 1930ths by Physicochemical Simulation Methods

S. I. MAZUKHINA<sup>1</sup>, V. A. MASLOBOEV<sup>1</sup>, K. V. CHUDNENKO<sup>2</sup>, V. A. BYCHINSKIY<sup>2</sup> and S. S. SANDIMIROV<sup>1</sup>

<sup>1</sup>*Institute of North Industrial Ecology, Kola Science Centre of the Russian Academy of Sciences, Ul. Fersmana 14a, Apatity 184209 (Russia)*

*E-mail: mazukhina@inep.ksc.ru*

<sup>2</sup>*Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Favorskogo 1a, Irkutsk 664033 (Russia)*

(Received May 20, 2008; revised October 31, 2008)

### Abstract

Basing on the data of the hydrochemical analysis carried out within 1938–1939, changes in water composition of the Bolshoy Vudyavr Lake due to mining manufacture wastewater impact were investigated. With the use of thermodynamic methods an overall chemical composition of natural water was reconstructed as well as ecological condition was estimated for the B. Vudyavr Lake. The results obtained are of practical and methodical value for forecasting long-term man-caused impact on aquatic ecosystems or the Subarctic region.

**Key words:** oil, hydrocarbons, atmosphere, natural waters, computer modeling

### INTRODUCTION

The contamination of water in the Bolshoy Vudyavr Lake began from industrial development of the Khibiny. Earlier the estimation of aquatic ecosystem condition for the Kola Peninsula was carried out basing on hydrobiological and hydrochemical parameters only. However, due to the introduction of physicochemical simulation methods into environmental research practice nowadays it is possible to obtain qualitatively new data concerning the processes occurring in aquatic ecosystems exposed to a man-caused impact to influence at present time, as well as to reconstruct the features of man-caused ecocatastrophes those took place in the past. As demonstrated in [1, 2], the studies on changing the chemical composition of lake and river waters under the influence of natural and anthropogenous factors can be performed with the help of modern physicochemical simulation methods [3].

In environmental research whose realization technique differs from the technique of per-

forming hydrochemical work, one should take into account the fact that no standard analytical procedures provide reliable correspondence between the results of the laboratory chemical analysis and the hydrochemical composition of natural waters at the moment of sampling. In the most of cases the temperature and gas conditions change vary since the moment of sampling till the moment performing laboratory analyses.

In this connection the major part of the present research consisted in bringing the analytical data into conformity with temperature, pressure, gas conditions and hydrodynamical circumstances of the natural system that is presented by the samples of natural waters as well as in estimating the influence of industrial wastewaters upon the chemical condition of the B. Vudyavr Lake waters. Moreover, it is rather problematic to estimate the prevalence of elements in natural waters having no information concerning the forms of their existence, whereas to determine them with the help of analytical procedures is not always pos-

sible. Physicochemical simulation of a complex hydrochemical system allows one to establish logic connection between man-caused impact and changes in the composition of natural waters, to determine forms of micro- and macro-components existence as well as to reveal environmental parameters determining the direction and character of these changes.

#### MAN-CAUSED IMPACT ON THE B. VUDYAVR LAKE

The first studies concerning the hydrochemistry and biology of Bolshoy and Maly Vudyavr lakes. Big were performed by the USSR Academy of Sciences expedition in 1930, before the construction of large-scale industrial enterprises in neighboring territories and, correspondingly, before the contamination of the B. Vudyavr Lake. In 1931 an experimental plant has been placed into operation in the valley of the Yuksporyok River flowing into the B. Vudyavr Lake, and in 1933 a factory for enriching and processing lovchorrite and rare-earth elements for the defence industry had been begun to build nearby [4–6]. From that moment on, the Yuksporyok River has become a sewage collector. So, as the result of the work performed by the second expedition of the USSR Academy of Sciences (1938–1939), it had been established, that volumes of wastewater discharge into sewage from the experimental plant and the lovchorrite factory amounted to 31 363 and 29 295 m<sup>3</sup>/month, respectively.

Table 1 demonstrates data concerning the amount of pollutants entering the Yuksporyok River with wastewaters from and the lovchorrite factory experimental plant. The wastewaters entering the B. Vudyavr Lake together with the Yuksporyok River water had resulted in a considerable changing of the lake water chemical composition as well as of species composition with respect to aquatic organisms therein [7].

Generalized results of the studies on the B. Vudyavr Lake performed during 1938–1939 indicate environmentally unfavourable condition of the lake:

– During the winter period the amount of dissolved oxygen in the surface layer of water varied from 81 to 89 %. From February to May the amount of oxygen in water at the depth more than 27 m was 18 % reduced, whereas from January to May at the depths more than 30 m this parameter was 37.5 % reduced.

– The reduction processes occurring in sludge sediments under the action of organic matter of wastewaters, had resulted in the fact that at the depth more than 30 m the content of ammonia during the winter period reached 5 mg/L, the total content of iron reached 5 mg/L, that of manganese amounted up to 2 mg/L.

– During the summer time the enrichment of the lake waters by nitrogen and phosphates caused mass development of weed, so-called “bloom” of water.

– At the majority of lake observation posts no bottom organisms were revealed, whereas at the depth more than 30 m they were observed to be absolutely absent.

The major environmental factors those determine the habitation conditions required for aquatic organisms and their reproduction consist in water composition and mineralization level. For normal survival, aquatic organisms need for a constant ratio between the total content of one- and bivalent ions [8]. Basing on chemical analyses it was established that the ratio between the concentrations of main ions ( $k = C_{(Na + K)}/C_{(Ca+Mg)}$ ) in the B. Vudyavr Lake waters, the Yuksporyok River outlet, the M. Vudyavr Lake and the Vudyavryok River amount to 1.80, 0.95, 3.80, 3.70, respectively [7, 9]. According to data from [7], the M. Vudyavr Lake and the Vudyavryok River were considered to be non-contaminated objects, therefore one may

TABLE 1

Data concerning pollutants entering the Yuksporyok River, kg/month

Wastewater	Al	Ca	Na	Mg	Fe	SiO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>
Lovchorrite factory	46.58	285.04	–	21.09	1.46	234.36	216.78	339.24	17.58	45.41	11.72	1624.11
Experimental plant	205.11	2465.13	1154.15	46.42	3.14	1599.51	227.28	4.05	3261.75	831.75	658.62	1103.98

consider that the concentration ratio between the main ions ranging within  $3.7 < k < 3.8$  to be corresponding to the ratio between the major ions in naturally occurring waters. For the wastewaters of the Yuksporyok River ( $k = 0.95$ ) the content of alkali earth elements exceeds the content of alkali elements. The influence of these wastewaters on the B. Vudyavr Lake water during 10 years had resulted in changing the ratio between the major ions therein ( $k = 1.80$ ).

A considerable increase in the content of calcium, phosphorus and other elements present in the wastewater of the lovchorrite factory and the experimental plant and in the bottom sediment of the B. Vudyavr Lake with the beginning of the industrialization of the Khibiny region is confirmed by the investigation of bottom sediments in the lakes formed within the Khibiny mountain range territory [10].

The investigation of natural waters of the B. Vudyavr Lake, the Yuksporyok and Vudyavryok river outlet as well as the lovchorrite factory wastewaters according the model proposed by the authors of [2] basing on the chemical composition of the waters [7] has allowed the researchers to reveal that the wastewaters do not contain oxygen, whereas the content of organic compounds therein is three to four times higher than the content in naturally occurring water (for example, in non-contaminated wa-

ter of the Vudyavryok River) [9]. In order to determine the composition of these organic compounds we have developed new models and approaches.

#### INVESTIGATION TECHNIQUE

We have constructed a thermodynamic model allowing us to reconstruct physicochemical conditions those had been established within the ecosystem of B. Vudyavr Lake (Fig. 1) as the result of the ecocatastrophe happened in the beginning of 1930ths. The investigation was carried out with the help of last version of Selector software package (SP) [11]. The principle of model construction realized in the SP basing on the decomposition of the objects under investigated with the conservation of all the interrelations between the systems allows researchers to consider any naturally occurring process in the form of interacting conjugated reservoirs combined into megasystems [12–16]. The list the basic model of a multi-system contained 24 independent components (Al–B–Br–Ar–He–Ne–C–Ca–Cl–F–K–Mg–Mn–N–Na–P–S–Si–Sr–Cu–Zn–H–O–e), 872 dependent components, including 295 those in aqueous solution, 76 in the gas phase, 111 liquid hydrocarbons, 390 solid phases, organic

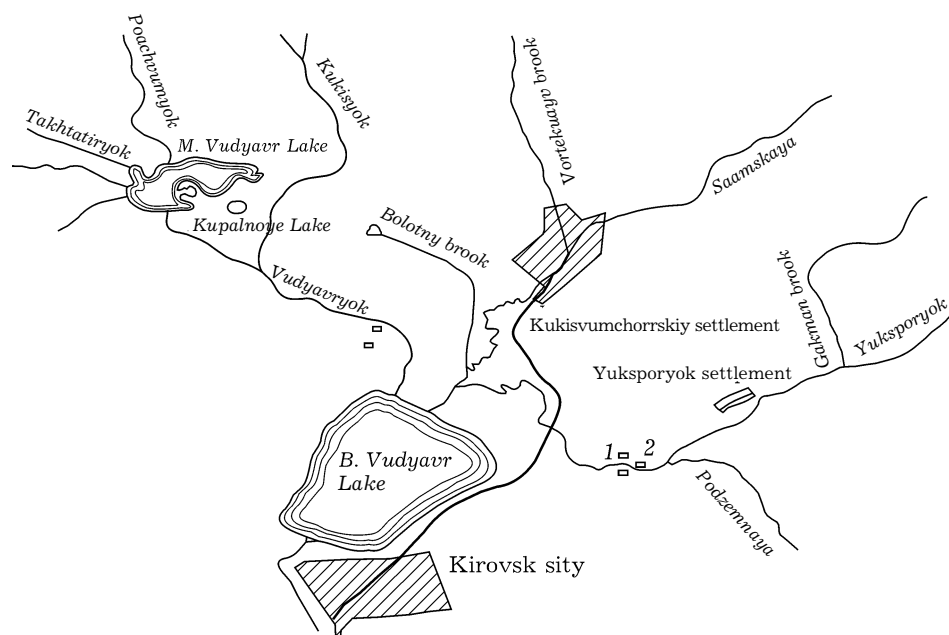


Fig. 1. Schematic map of the drainage network within the region of the Kirovsk city (1939): 1 – the lovchorrite factory, 2 – the experimental plant.

and mineral substances. The following problems have been set in this work:

1. To calculate the componential composition of the lovchorrite factory and experimental plant wastewaters employing physicochemical simulation.

2. To estimate the influence of industrial wastewaters upon the B. Vudyavr Lake water with the help of a dynamic model. To study the influence of annual the lovchorrite factory and experimental plant wastewaters upon the aquatic object under the conditions open with respect to the atmosphere and bottom sediments. To take into account the content of a "fixed" quantity of organic matter in the lovchorrite factory wastewater containing oleic acid [7, 17].

The model includes five interacting reservoirs; three of those represent surface waters, bottom waters and bottom sediments of the lake. The volume of surface waters (0–15 m) amounted to  $0.02385 \text{ km}^3$ , the volume of bottom waters (at the depth of 30–38 m) was  $0.00395 \text{ km}^3$ , the layer of bottom sediments contacting with bottom waters (up to 0.05 m) is equal to  $0.000025 \text{ km}^3$ . In order to simplify the thermodynamic calculations, the volumes of reservoirs have been normalized with respect to the volumes occupied: the first reservoir (surface waters) corresponded to 1 kg of the lake water, the second reservoir (bottom waters) corresponded to 0.16 kg of that, and the third reservoir (bottom sediments) corresponded to 0.001 kg of water.

A generalized schematic diagram of the dynamic model is presented in Fig. 2. Main characteristics of the model constructed are presented below:

**The first reservoir** represents the atmosphere (external environment,  $T = 10 \text{ }^\circ\text{C}$ ,  $P = 1 \text{ bar}$ ) with respect to which all the other reservoirs are open. **The second reservoir** represents surface waters including an aqueous solution, gas phase, as well as solid mineral and organic components ( $T = 6.7 \text{ }^\circ\text{C}$ ,  $P = 1 \text{ bar}$ ). **The third reservoir** represents organic matter in the form of a film or an emulsion, presented by liquid hydrocarbons, gases and the solid (restite); the system is metastable ( $T = 6.7 \text{ }^\circ\text{C}$ ,  $P = 1 \text{ bar}$ ). **The fourth reservoir** represents bottom water in metastable equilibrium with the surface water and the bottom sediments presented by

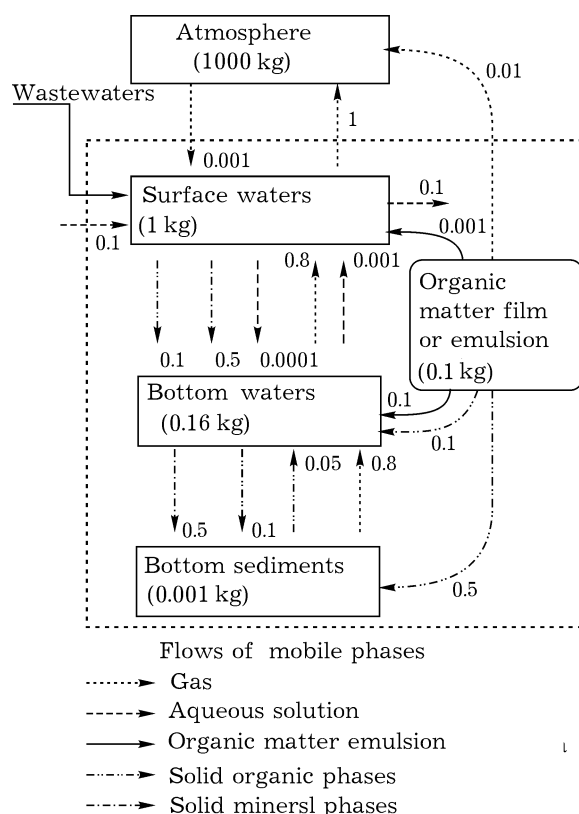


Fig. 2. Schematic diagram of the dynamic model for the B. Vudyavr Lake. The numbers at the arrows denote a mobile phase part passed from a reservoir to another reservoir during unit time.

an aqueous solution, gases, solid hydrocarbons and mineral phases ( $T = 6.7 \text{ }^\circ\text{C}$ ,  $P = 2 \text{ bar}$ ). **The fifth reservoir** represents bottom sediments of the lake presented by aluminosilicates, carbonates and other mineral and organic compounds ( $T = 6.7 \text{ }^\circ\text{C}$ ,  $P = 3 \text{ bar}$ ).

The numerical values of macrokinetic transport coefficients for mobile phases transfer between the reservoirs were set basing on empirically determined relationships for the rates of the processes such as evaporation, dissolution, sedimentation, redeposition under the conditions of hydrodynamic water mass circulation [18].

As the controlling parameter, the reservoir is entered with industrial wastewaters (from the factory or from the plant), whose annual volume is normalized with respect to the volume of the 2nd reservoir. The outflow rate of the Belaya River, the only river running out of the B. Vudyavr Lake is equal to  $969 \text{ L/s}$  [7], thus, for maintaining the balance the same amount of lake water from the external environment should enter the 2nd reservoir. An

exchange flow of aqueous phase is taken into account for the transfer between the lake water thickness and bottom waters with corresponding normalizing the transport coefficients with respect to the bases of the reservoirs.

The gas phase streams provide a dynamic equilibrium between the waters of lake and the atmosphere. A partial degassing of bottom waters and bottom sediments is provided. In the case of organic matter emulsion formation (the 3rd reservoir), it is subject to a consecutive destruction with the possibility of evaporating and transporting a part of liquid hydrocarbons to the surface and bottom waters of the lake.

At each time step, a partial transport (sedimentation) is performed from the aqueous solution to bottom waters and bottom sediments of solid mineral and organic phases with the subsequent burial the possibility of returning their certain fraction to the bottom waters. Thus, the exchange processes occurring at the interface of the lake water and bottom sediments are taken into account.

## RESULTS AND DISCUSSION

The results of physicochemical simulation of the wastewater composition from the lovchorrite processing and enrichment factory indicate the absence of oxygen therein ( $\text{pH } 7.70$ ,  $E_h = -0.30 \text{ V}$ ) and the presence of metastable organic and organometallic compounds (Table 2).

The values calculated for  $\text{pH}$  and  $\text{HCO}_3^-$  concentration in the experimental plant the wastewaters differ from the corresponding data presented in [7]. It is connected with the accuracy of chemical analyses performed within 1938–1939. As known, thermophosphates use to be obtained by introduction soda in the process; therefore there should be sodium in the wastewaters. However, when chemical analysis carried out in 1939, this chemical element was not determined. The introduction of sodium in our model and fitting its concentration have allowed us to reconstruct adequately the composition of apatite manufacturing wastewaters, wherewith the calculated data concerning  $\text{pH}$

TABLE 2

Analytical data [7] and data obtained from the simulation the lovchorrite factory wastewaters,  $\text{mg/L}$  ( $T = 25 \text{ }^\circ\text{C}$ ,  $P = 1 \text{ bar}$ )

Components	Analysis	Model	Components	Analysis	Model	Components	Analysis	Model
$E_h$	–	–0.29694	$\text{Fe(OH)}_3$		$3.47 \cdot 10^{-9}$	$\text{PO}_4^{3-}$		$8.97 \cdot 10^{-6}$
$\text{pH}$	7.7	7.70354	$\text{FeOH}^+$		$5.66 \cdot 10^{-3}$	$\text{H}_2\text{PO}_4^-$		$9.07 \cdot 10^{-2}$
$\text{Al}$	1.59	1.59	$\text{FeO}^+$		$1.19 \cdot 10^{-9}$	$\text{H}_3\text{PO}_4$		$2.59 \cdot 10^{-7}$
$\text{Al(OH)}_2^+$		$6.52 \cdot 10^{-4}$	$\text{FeO}$		$2.21 \cdot 10^{-6}$	$\text{HPO}_4^{2-}$		$3.15 \cdot 10^{-1}$
$\text{AlO}_2^-$		1.85	$\text{HFeO}_2$		$3.12 \cdot 10^{-8}$	$\text{HP}_2\text{O}_7^{3-}$		$1.13 \cdot 10^{-8}$
$\text{HAlO}_2$		0.10	$\text{FeCl}^+$		$3.22 \cdot 10^{-6}$	$\text{Cl (total)}$	0.6	–
$\text{Al(OH)}_2^{2+}$		$9.92 \cdot 10^{-6}$	$\text{FeCHO}_2^+$		$1.30 \cdot 10^{-7}$	$\text{HCl}$		$2.3 \cdot 10^{-9}$
$\text{Al(OH)}_2^+$		$1.46 \cdot 10^{-3}$	$\text{HCO}_3^-$ (total)	55.44	–	$\text{Cl}^-$		$6.0 \cdot 10^{-1}$
$\text{Al(OH)}_3$		$9.29 \cdot 10^{-2}$	$\text{CO}_3^{2-}$		$1.45 \cdot 10^{-1}$	$\text{Mg}$	0.72	0.72
$\text{Al(OH)}_4^-$		2.34	$\text{HCO}_3^-$		55.8	$\text{Mg}^{2+}$		$7.06 \cdot 10^{-1}$
$\text{Ca}$	9.73	9.73	$\text{HCO}_2^-$		$2.86 \cdot 10^{-4}$	$\text{MgOH}^+$		$1.15 \cdot 10^{-4}$
$\text{Ca}^{2+}$		9.54	$\text{H}_2\text{CO}_2$		$3.16 \cdot 10^{-8}$	$\text{MgCO}_3$		$4.22 \cdot 10^{-3}$
$\text{CaOH}^+$		$9.18 \cdot 10^{-5}$	$\text{CH}_4$		$7.94 \cdot 10^{-1}$	$\text{Mg(HCO}_3)^+$		$2.13 \cdot 10^{-2}$
$\text{CaCO}_3$		$9.16 \cdot 10^{-2}$	$\text{NO}_3^-$ (total)	1.55	–	$\text{MgCl}^+$		$1.86 \cdot 10^{-5}$
$\text{Ca(HCO}_3)^+$		$2.12 \cdot 10^{-1}$	$\text{HNO}_2$		$8.07 \cdot 10^{-6}$	$\text{MgCH}_3\text{COO}^+$		$4.38 \cdot 10^{-9}$
$\text{CaHSiO}_3^+$		$1.57 \cdot 10^{-4}$	$\text{NO}_3^-$		1.55	$\text{MgSO}_4$		$3.41 \cdot 10^{-2}$
$\text{CaCl}^+$		$1.34 \cdot 10^{-4}$	$\text{NO}_2^-$		$2.46 \cdot 10^{-1}$	$\text{MgHSiO}_3^+$		$2.95 \cdot 10^{-5}$
$\text{CaCl}_2$		$1.39 \cdot 10^{-9}$	$\text{HNO}_3$		$1.12 \cdot 10^{-9}$	$\text{SO}_4^-$ (total)	7.4	–
$\text{CaSO}_4$		$2.41 \cdot 10^{-1}$	$\text{NH}_4^-$ (total)	11.58	–	$\text{SO}_4^{2-}$		7.37
$\text{CaCH}_3\text{COO}^+$		$1.91 \cdot 10^{-8}$	$\text{NH}_4^+$		11.6	$\text{SiO}_2^-$ (total)	8.0	–
$\text{Fe}$	0.05	0.05	$\text{CO}_2$		1.68	$\text{SiO}_2$		2.77
$\text{Fe}^{2+}$		$1.95 \cdot 10^{-1}$	$\text{H}_2$		$7.1 \cdot 10^{-6}$	$\text{HSiO}_3^-$		$4.91 \cdot 10^{-2}$
$\text{FeSO}_4$		$2.60 \cdot 10^{-3}$	$\text{PO}_4^-$ (total)	0.4	–	$\text{H}_4\text{SiO}_4$		8.31

TABLE 3

Analytical data [7] and data obtained from the simulation the experimental plant wastewaters, mg/L ( $T = 20\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$ )

Components	Analysis	Model	Components	Analysis	Model	Components	Analysis	Model
$E_h$	–	–0.431182	$\text{FeO}^+$		$5.55 \cdot 10^{-9}$	Mg	148	148
pH	>9.75	9.76976	FeO		$2.37 \cdot 10^{-3}$	$\text{Mg}^{2+}$		136
Al	6.54	6.54	$\text{HFeO}_2$		$1.13 \cdot 10^{-5}$	$\text{MgOH}^+$		$1.61 \cdot 10^{-2}$
$\text{Al(OH)}_2^+$		$3.20 \cdot 10^{-7}$	$\text{FeO}_2^-$		$1.30 \cdot 10^{-5}$	$\text{MgCO}_3$		$3.13 \cdot 10^{-1}$
$\text{AlO}_2^-$		7.72	$\text{FeCl}^+$		$9.58 \cdot 10^{-5}$	$\text{Mg(HCO}_3)^+$		$1.60 \cdot 10^{-2}$
$\text{HAlO}_2$		$4.6 \cdot 10^{-3}$	$\text{FeCHO}_2^+$		$4.12 \cdot 10^{-8}$	$\text{MgCl}^+$		$5.92 \cdot 10^{-3}$
$\text{Al(OH)}_2^+$		$7.95 \cdot 10^{-7}$	Na	36.8	36.8	$\text{MgCH}_3\text{COO}^+$		$1.08 \cdot 10^{-8}$
$\text{Al(OH)}_3$		$4.02 \cdot 10^{-3}$	$\text{Na}^+$		36.1	$\text{MgSO}_4$		$5.69 \cdot 10^{-2}$
$\text{Al(OH)}_4^-$		10.6	NaOH		$1.51 \cdot 10^{-3}$	$\text{MgHSiO}_3^+$		$2.30 \cdot 10^{-2}$
Ca	78.6	78.6	$\text{NaAlO}_2$		$2.61 \cdot 10^{-3}$	$\text{SO}_4$ (total)	7.25	–
$\text{Ca}^{2+}$		68.0	NaCl		$3.97 \cdot 10^{-2}$	$\text{SO}_4^{2-}$		7.25
$\text{CaOH}^+$		$4.32 \cdot 10^{-2}$	$\text{NaSO}_4^-$		$5.69 \cdot 10^{-2}$	$\text{SiO}_2$ (total)	51	–
$\text{CaCO}_3$		24.1	$\text{NaHSiO}_3$		2.98	$\text{SiO}_2$		11.0
$\text{Ca(HCO}_3)^+$		$5.95 \cdot 10^{-1}$	$\text{NaCH}_3\text{COO}$		$1.28 \cdot 10^{-8}$	$\text{HSiO}_3^-$		20.4
$\text{CaHSiO}_3^+$		$4.41 \cdot 10^{-1}$	$\text{HCO}_3^-$ (total)	35.2	–	$\text{H}_4\text{SiO}_4$		35.4
$\text{CaCl}^+$		$1.52 \cdot 10^{-1}$	$\text{CO}_3^{2-}$		6.46	$\text{PO}_4$ (total)	21	–
$\text{CaCl}_2$		$2.92 \cdot 10^{-4}$	$\text{HCO}_3^-$		23.0	$\text{PO}_4^{3-}$		$6.67 \cdot 10^{-2}$
$\text{CaSO}_4$		1.49	$\text{HCO}_2^-$		$4.82 \cdot 10^{-4}$	$\text{H}_2\text{PO}_4^-$		$5.23 \cdot 10^{-2}$
$\text{CaCH}_3\text{COO}^+$		$1.64 \cdot 10^{-7}$	$\text{CO}_2$		$6.31 \cdot 10^{-3}$	$\text{H}_3\text{PO}_4$		$1.20 \cdot 10^{-9}$
Fe	0.1	0.1	$\text{NO}_3$ (total)	26.52	–	$\text{HPO}_4^{2-}$		21.1
$\text{Fe}^{2+}$		$3.54 \cdot 10^{-2}$	$\text{NO}_3^-$		26.5	$\text{P}_2\text{O}_7^{4-}$		$1.46 \cdot 10^{-6}$
$\text{FeSO}_4$		$4.17 \cdot 10^{-4}$	$\text{NH}_4$ (total)	0.129	–	$\text{HP}_2\text{O}_7^{3-}$		$3.81 \cdot 10^{-7}$
$\text{Fe(OH)}_3$		$1.20 \cdot 10^{-6}$	$\text{NH}_4^+$		$1.29 \cdot 10^{-1}$	$\text{CH}_4$		2.53
$\text{Fe(OH)}_4^-$		$4.00 \cdot 10^{-5}$	Cl (total)	104	–	$\text{H}_2$		$2.58 \cdot 10^{-5}$
$\text{FeOH}^+$		$8.15 \cdot 10^{-2}$	$\text{Cl}^-$	104				

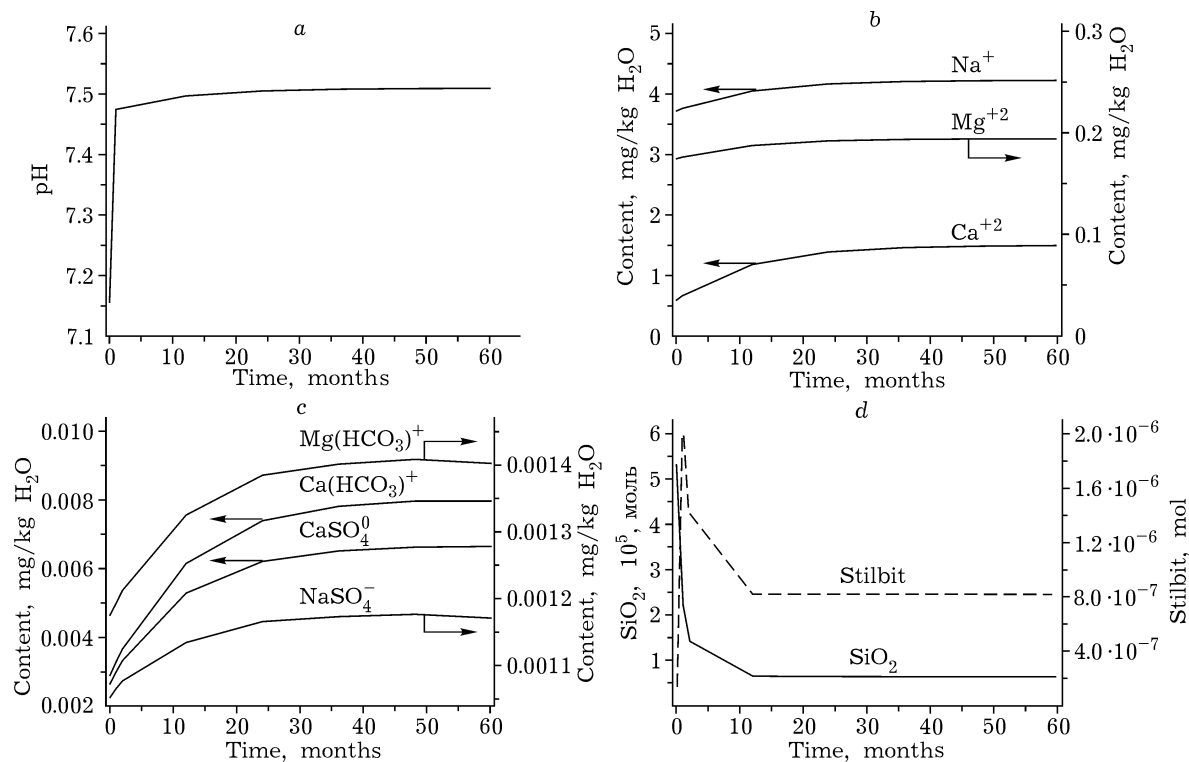


Fig. 3. B. Vudyavr Lake water interaction with the wastewaters of the experimental plant and lovchorrite factory (the 2nd reservoir): *a* – pH change; *b, c* – change in the content of main cations and anions; *d* – precipitation of solids.  $T = 6.7\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$ .

and  $\text{HCO}_3^-$  concentration were managed to bring into accordance with the analytical data from [7]. The wastewaters of the experimental plant are characterized by strong alkalinity, high negative values of the oxidation-reduction potential (pH 9.76,  $E_h = -0.43$  V) and a high concentration of organic compounds (Table 3).

At the following stage of the studies we have performed the modelling of joint influence of wastewaters from the experimental plant and the factory upon the B. Vudyavr Lake waters (Figs. 3–5). In the model we studied the lake

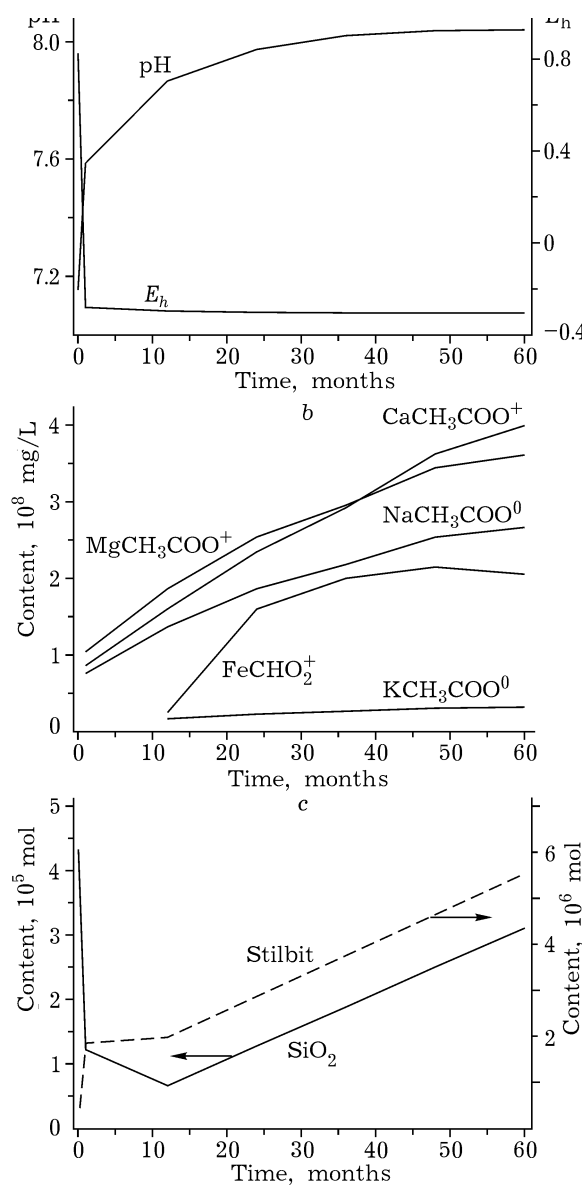


Fig. 4. Changing in the properties and composition of the bottom waters (the 4th reservoir): a – parameters pH– $E_h$ , b – organometallic compounds, c – the formation of solid phases.

water transformation during 60 months (five years). A significant change in the ratio) between main cations ( $k = 2.17$ ) have been obtained.

In Figs. 3–5 zero mark corresponds to the chemical composition of the B. Vudyavr Lake waters before its industrial pollution (1930). The variation of the content of components for the period of time under investigation is characterized by the following features. Already for the second year (15–20 months) the change of naturally occurring waters decelerates, whereas the wastewater–natural water–atmosphere system comes into metastable equilibrium. With the increase in the volume of wastewaters, only the content of solid phases grows. Just for this reason such parameters as the content of dissolved components, pH,  $E_h$ , are stabilized under model conditions by the third year. Under low-temperature and open-atmosphere conditions a significant part of wastewater components either passes into a sediment, or enters the gas phase.

The results obtained are of important value, since basing only on data concerning hydrochemical composition of waters it is impossible to estimate the amount of inflowing wastewaters and their influence upon the system as a whole. Physicochemical simulation and complex hydrogeochemical research allow one to determine the pathways of wastewater transformation as well as to evaluate these processes more adequately. With use of this approach it appears possible to determine the amount of matter that would enter a deposit, pass to the gas phase or remain in the dissolved form. So, in case that surface water acidity amounts up to pH 7.5 (see Fig. 3) a much more abrupt increase in this parameter, change in oxida-

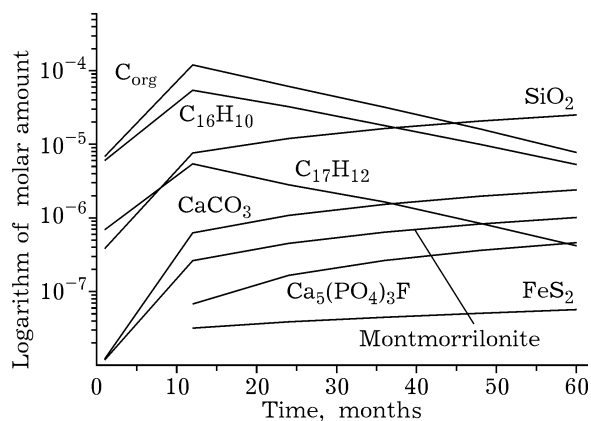


Fig. 5. Precipitation of solid phases into the bottom sediment (the 5th reservoir).

TABLE 4

Comparative characteristics for the chemical composition of the B. Vudyavr Lake water, mg/L

Components	Non-polluted condition [2, 7], total	During ecocatastrophe [7]		Contemporary condition [10], surface
		Surface	Depth 33 m	
pH	6.6–7.3	6.5–7.1	6.5–7.1	7.6–9.0
Al	0.02–0.2	0.19	0.19	0.09
K	1.1–1.3	1.10	–	6.2–6.45
Na	3.6–3.7	4.10	–	19.3–21.3
NH <sub>4</sub>	–	0.24	0.24	0.19–0.37
Ca	0.5–0.8	2.00	1.93	3.78–4.11
Mg	0.07–0.17	0.24	0.22	0.4
Mn	0–0.0005	–	–	0.004
Fe	0–0.01	0.1	0.10	0–0.06
Cl	0.5–1	1.35	1.36	0.74
NO <sub>3</sub>	–	0.66	0.66	1.44–2.02
HCO <sub>3</sub> <sup>–</sup>	11–12	12.42	12.42	39–40
SO <sub>4</sub> <sup>2–</sup>	1.17–2.2	1.52	1.56	20
PO <sub>4</sub> <sup>3–</sup>	0–0.001	0.25	0.25	0.19–0.25
SiO <sub>2</sub>	8	8	8	–
Si	1.3–3	–	–	1.30–2.83
O <sub>2</sub>	10–13	10.80	10.76	–
Sr	0–0.05	–	–	0.19
F	0.15–0.20	–	–	–

tion-reduction conditions, as well as organic and organometallic complexes formation are observed for bottom water (see Fig. 4).

The effect of industrial wastewaters on naturally occurring waters is well traced by the example of the comparative characteristics of changing the composition of B. Vudyavr Lake water. It is obvious, that the changes in pH, the content of sodium, potassium, nitrates and bicarbonates within the given time interval are of irreversible character (Table 4). This is connected with the fact that there are evolution of gases (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S) and burial of solids (see Fig. 5) occurring in the course of organic matter transformation.

## CONCLUSION

In the course of the investigation carried out we have reconstructed the hydrochemical circumstances developed during the ecocatastrophe within the lake-river system the Bolshoy Vudyavr Lake–the Yuksoryok River in 1930ths. Modern studies [10, 19] have demonstrated cle-

arly that the processes of alkalization, the increase in the total water mineralization level, the eutrophication and the increase in the content of toxic components are still inherent in these water reservoirs.

The generalized results of physicochemical simulation obtained for a multi-reservoir dynamic system such as atmosphere–lake–industrial wastewaters–near-bottom waters–bottom sediment allow us to draw the following conclusions.

1. The inflow of wastewaters with high concentration of Ca, P, N, Fe, Na and oleic acid resulted in changing the chemical composition of the Bolshoy Vudyavr Lake waters and their gas condition.

2. Under the wastewater influence there is a change in total content proportion for main cations occurring in surface water open with respect to the atmosphere. For the near-bottom waters partly isolated from the atmosphere, reducing conditions are observed to form in the presence of organic matter. As far as the gas phase being in equilibrium with respect to aqueous solution is concerned, there



are methane prevalence and hydrogen sulphide evolution observed. The aqueous solution exhibits an increase in the content of organometallic complexes, as well as the formation of carbonates is observed therein. Metastable organic compounds, in spite of their short lifetime, exert a considerable effect on physicochemical processes in the systems “aqueous solution–gas–carbon” determining the dissolution, transport and sedimentation of such hypergene elements as Al, Ca, Mg, and Na.

3. Methane entering the B. Vudyavr Lake water makes an essential impact upon the processes occurring in the lake during the winter time, particularly taking into account the fact, that within approximately half a year the lake is covered with ice. First of all, this fact concerns the accumulation and putrefaction of organic matter, whereupon the content of dissolved oxygen in waters decreases [20], the composition of the waters as well as that of the suspensions present therein are observed to vary. These processes have resulted in changing the species composition of aquatic organisms and in fish disappearance in the B. Vudyavr Lake [7].

4. The consequences of the B. Vudyavr Lake water contamination by industrial wastewaters are similar to the situation observed for the Black Sea shoaling water in 1950ths. With the development of industries and the application of fertilizers in the agriculture the Black Sea waters were entered with wastewaters containing nitrogen and phosphorus, which stimulated the development of phytoplankton. A significant part of primary products had not time to decompose in water thickness and thus underwent sedimentation onto the bottom. The appeared aerobic conditions promoted hydrogen sulphide formation and evolution, which hydrogen sulphide has brought to the death of living organisms [21].

The model proposed allows one to obtain a qualitative picture of natural object functioning in the mode of successive events changing in real (annual) time units.

## REFERENCES

- 1 S. R. Kraynov, Yu. V. Shvarov, D. V. Grichuk *et al.*, *Metody Geokhimicheskogo Modelirovaniya i Prognozirovaniya v Gidrogeologii*, Nedra, Moscow, 1988.
- 2 S. I. Mazukhina, S. S. Sandimirov, *Primeneniye Fiziko-Khimicheskogo Modelirovaniya dlya Resheniya Ekologicheskikh Zadach Kolskogo Severa*, Apatity, 2005.
- 3 S. L. Shvartsev, B. N. Ryzhenko, V. A. Alekseev *et al.*, *Geologicheskaya Evolyutsiya i Samoorganizatsiya Sistemy Voda–Poroda*, vol. 2, Izd-vo SO RAN, Novosibirsk, 2007.
- 4 *Mineralogiya Khibinskikh i Levozerskikh Tundr*, Izd-vo AN SSSR, Moscow–Leningrad, 1937.
- 5 *Khibinskiye Redkiye Elementy i Pirrotiny*, Goskhimtekhnizdat, Leningrad, 1933.
- 6 *Khibinskiye Apatity: Itogi Nauchno-Izdatelskikh i Poiskovykh Rabot*, Leningrad, 1933.
- 7 A. V. Kanygina, *Gidrobiologicheskoye i Gidrokhimicheskoye Issledovaniye Ozer Bolshoy i Maly Vudyavr*, Materialy k izucheniyu vod Kolskogo Poluostrova, Kolskaya baza AN SSSR, sb. 1, 1940.
- 8 P. A. Lozovik, L. V. Dubrovina, *Ekol. Khim.*, 7, 4 (1998) 243.
- 9 S. I. Mazukhina, *Budushcheye Gidrogeologii: Sovremennye Tendentsii i Perspektivy* (A Collection of Papers), St. Petersburg, 2008, pp. 164–173.
- 10 D. B. Denisov, *Vod. Res.*, 14, 6 (2007) 719.
- 11 K. V. Chudnenko, *Teoriya i Programmnoye Obespecheniye Metoda Minimizatsii Termodinamicheskikh Potentsialov dlya Resheniya Geokhimicheskikh Zadach* (Doctoral Dissertation in Geology and Mineralogy), Irkutsk, 2007.
- 12 I. K. Karpov, *Fiziko-Khimicheskoye Modelirovaniye na EVM v Geokhimii*, Nauka, Novosibirsk, 1981.
- 13 S. Kh. Pavlov, I. K. Karpov, K. V. Chudnenko, *Geokhim.*, 7 (2006) 797.
- 14 K. V. Chudnenko, I. K. Karpov, S. I. Mazukhina, *Geol. i Geofiz.*, 40, 1 (1999) 44.
- 15 H. C. Helgeson, A. M. Knox, C. E. Owens, E. L. Shock, *Geochem. Cosmochim. Acta*, 57, 14 (1993) 3295.
- 16 L. C. Price and DeWitt Ed, *Ibid.*, 65, 21 (2001) 3791.
- 17 N. S. Aleynikova, G. A. Golovanova, V. M. Sintsova, A. M. Zhelnina, *Osnovnyye Problemy Razvitiya Kombinata “Apatit”* (A Collection of Papers), Apatity, 1971, part 2, pp. 177–182.
- 18 K. V. Chudnenko, V. A. Bychinskiy, S. I. Mazukhina *et al.*, *Vseros. Nauch. Konf. (Proceedings)*, Apatity, 2008, part 1, pp. 36–40.
- 19 S. I. Mazukhina, D. B. Denisov, O. I. Vandysh, V. A. Masloboev, *Mezhdunar. Nauch. Konf. (Proceedings)*, Apatity, 2006, part 1, pp. 188–191.
- 20 A. S. Konstantinov, *Obshchaya Gidrobiologiya* (High School Textbook), Vyssh. Shk., Moscow, 1972.
- 21 V. S. Gubarev, *XXI Vek. Rassvet. Sud’ba Uchenykh i Nauki Rossii*, Nauka/Interperiodika, Moscow, 2001.