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Distribution of Inorganic Pollutants over the Depth of Upper Peat Deposit

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Abstract—A model of distribution of inorganic substances in the polluted waters of an oligotrophic bog has been developed and geomigratory calculations have been carried out on the example of Vasyugan Bog. It is shown that the most significant changes of mineralization of bog waters caused by the inflow of industrial waste waters from oil and gas production enterprises are referred to the high layer with a thickness of approximately 0.5–1.0 m. The creation of loam as an insulating barrier in the active layer of the bog helps reduce the negative impact on the waters, but does not preserve their baseline state on the lower layer.

Keywords: bog waters, pollutants, geomigratory calculations

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INTRODUCTION

Pollution of water bodies due to oil and gas recovery is a serious problem that considerably slows down the economic development of the central and northern regions of Western Siberia. One peculiar feature of this territory is the wide prevalence of bogs performing complex ecological functions during the functioning of natural and man-made complexes referred (in accordance with the applicable environment protection legislation of the Russian Federation) to the surface water bodies. The last circumstance imposes a number of restrictions with respect to the construction and operation of sludge pits, solid-waste landfills, and wastewater outlets on the bogs, which determines the relevance of studying conditions for the distribution of pollutants in bog waters.

We have considered this task with respect to conditions of migration of principal ions with respect to the depth of the upper peat deposit in the South Taiga subzone of Western Siberia within the framework of a theoretical justification of environmental protection measures to prevent and liquidate the consequences of pollution of peat bogs in the process of recovery of oil and gas (due to the disposal of drilling wastes and accidents in the reservoir pressure-maintenance system). The oligotrophic area of the Vasyugan bog at the watershed of the Bakchar and Iksa rivers located 160 km from the city of Tomsk and 140–160 km from the nearest operating oil-and-gas production enterprises served as the key object of study (Fig. 1). The prevailing phytocenosis within the area and on the adjacent territory is pine sphagnum–dwarf (“low riam”). The base peat deposit is represented by transition-type peats and highbog peats (fuscum and magellanicum) at the top of the section. A more detailed description of the area is given in the paper (Savichev et al., 2011).

The research included the development of the mathematical model of migration of principal ions (the total content of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-} ions) in the bog waters with respect to the depth of peat deposit, as well as modeling conditions of their pollution and interpretation of results.

MATERIALS AND METHODS

Structure of Mathematical Model

The basis of the analyzed model is a one-dimensional transfer equation in the form of

$$n_a\frac{\partial C}{\partial t}+\frac{\partial(V_zC)}{\partial z} = \frac{\partial}{\partial z}\left(D_z\frac{\partial C}{\partial z}\right)+S, \quad (1)$$

$$V_z = k_wI \approx k_w\left(1+\frac{h_s}{L}\right), \quad (2)$$

$$k_w = k_f\left(\frac{w-w_0}{w_1-w_0}\right)^{k_1}, \quad (3)$$

$$k_f = \frac{k_2k_a}{(z+k_3)^{k_4}}, \quad (4)$$

$$D_z = D_m+k_5V_z, \quad (5)$$

where C is the value of hydrochemical indicator (concentration of the analyzed substance or the sum of principal ions); z and t are the spatial (from the middle bog surface) and temporal coordinates; n_a is active porosity; V_z is the rate of filtration; I is head gradient; k_f is filtration coefficient; k_w is moisture transfer coefficient (filtration in case of full saturation); k_a is the coefficient taking into account the anisotropic behavior of peats; L is the length of the zone of capilarity; h_s is the height of the layer waste (atmospheric) waters flowing on the bog surface; w is peat moisture at a depth of z; w_0 is the content of bound moisture; w_1 is the moisture at full saturation; D_z is the coefficient of hydrodynamic dispersion; D_m is the coefficient of molecular diffusion; S is the function characterizing the inflow of the substance, organo-mineral deposits, and suspended substances from peats into bog waters and processes of its extraction from the solution; and k_1, k_2, k_3, k_4, and k_5 are empirical coefficients (Lishtvan et al., 1989; Loucks and van Beek, 2005; Permyakov, et al., 2009).

The coefficient k_1 is assumed to be 3.5, according to S.F. Averianov; the coefficient k_5 (0.0025) and n_a value (85.4%) is assumed taking into consideration the density of peat skeleton p_s (113.1 kg/m^3) according to (Lishtvan et al., 1989); and the peat moisture at a height of z^* (cm) above the level of bog waters is determined according to the dependence described in (Ivanov, 1975):

$$w = \rho_p \exp(k_6 - k_7 \ln z^*), \quad (6)$$

where ρ_p is the volume weight of absolute dry peat (80 kg/m^3); k_6 (0.119) and k_7 (0.024) are the empirical coefficients calculated on the basis of the measured value of peat moisture at a depth of 0.1 m from the bog surface (85%); k_2 (82.659), k_3, and k_4 values are determined according to the materials (Ivanov, 1975); and k_a (0.626) are determined according to the data on filtration properties of peats of the Tomsk oblast (Emel'yanova and Kramarenko, 2001). Below the level of bog waters, peat moisture is approximately assumed to be equal to the average moisture of peat $\overline{W}$ (90.1%) in the Vasuygan peat bog (area no. 5) (*Peat resources*, 1998). The values of ρ_p and porosity n (94.8 %), which is used as an approximation for w_1, are assumed in accordance with (*Torfyanye resursy*..., 1977); the coefficient of molecular diffusion of principal ions is assumed to be equal 0.85×10^{-5} cm^2 (Krainov et al., 2004). The value of w_0 (69.8 %) was estimated on the basis of porosity n according to the data (*Melioratsiya*..., 1985). The average value of peat skeleton density p_s is calculated according to (Lishtvan et al., 1989) using the equation

$$\rho_s = 924 - 9W. \quad (7)$$

The function of S source was determined in two ways: (1) by back calculation using Eq. (1) for each calculated interval assuming the invariability of the resulted values in time and (2) as functions of peat moisture: the coefficient of moisture conductivity and concentration of substance in bog waters. In the latter case, the formula for the S function was determined taking into account the suggestions on the calculation of the rate of dissolution of minerals and organic mineral compounds V_{md} and the water and mineral contact area A (White, 1995):

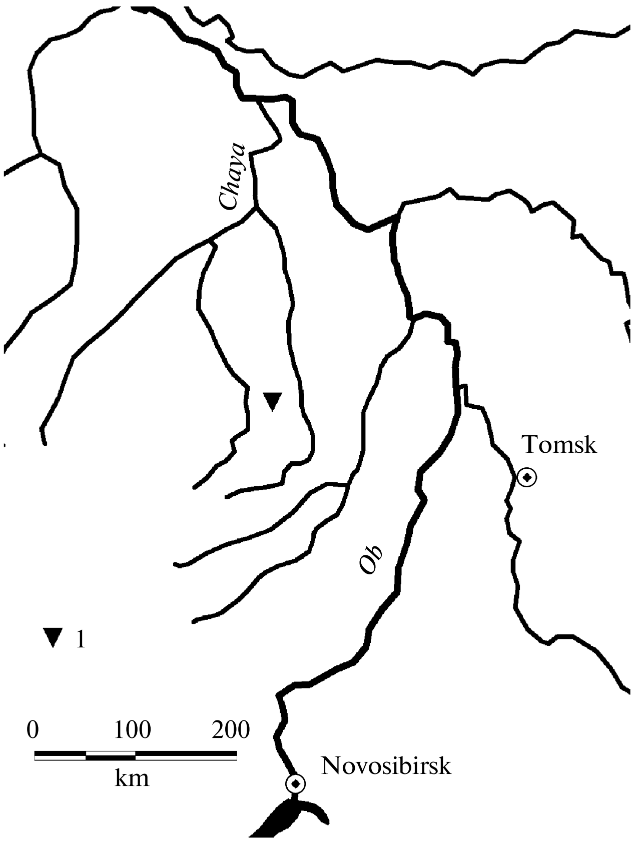

Fig. 1. Layout of the research area (1).

$$V_{md} = V_0 A f_{\mathrm{pH}} f_E f_J f_{\Delta G} f_C, \quad (8)$$

$$A_0 = \frac{6\lambda}{\rho_m d}, \quad (9)$$

where V_0 is the mineral dissolution rate constant; f_{pH}, f_E, f_J, $f_{\Delta G}$, and f_C are functions reflecting the dependence of the dissolution rate from pH, energy of chemical reaction activation E, ionic strength of solution J, deviation from equilibrium state, and concentration of the substance in the solution (in the latter case, f_C is usually the product of the activities of the components participating in the reaction); d is the diameter of mineral grains; ρ_m is the density of the substance interacting with water; and L is the coefficient reflecting the ratio of actual and estimated areas of the contact of particles with water.

Since it is difficult to reliably estimate the value of most of the parameters of equations (8) and (9) for peats on the one hand, and there are semiempirical dependencies of moisture values and moisture conductivity coefficients from the depth of the reference point (as indirect features of peat porosity and density)

Table 1. Initial data for geomigration calculations

Indicator	Units of measurement	Sampling point in the Vasuygan Bog; May 27, 2010; sampling depth, m				Mean values*	
		0.3	1.2	1.8	2.3	pit waters	rain waters
Σ_{mi}	mg/dm^3	8.0	11.6	35.5	55.6	7211.8	50.9
Ca^{2+}	Same	2.4	4.0	9.0	10.4	248.4	5.4
Mg^{2+}	"	0.1	0.6	1.6	1.0	31.8	2.0
Na^+	"	0.6	0.4	0.6	0.9	2124.8	3.2
K^+	"	0.1	2.0	2.9	2.9	202.2	
HCO_3^-	"	<3	<3	17.7	35.4	338.3	29.1
SO_4^{2-}	"	1.0	0.5	1.1	0.6	388.1	8.0
Cl^-	"	2.3	2.6	2.6	4.4	3874.4	3.2
DO	mgO/dm^3	124.0	124.0	108.0	99.0	364.0	4
pH	–	3.90	4.18	5.49	6.12	8.00	6.50

* According to data of (Savichev and Ivanov, 2010; Savichev et al., 2013); Σ_{mi} is the sum of principal ions and DO is dichromate oxidability.

on the other hand, the expression for a description of S can be presented as follows:

$$S = k_8 k_w^{k_9} (\overline{W} - w + 0.1)^{k_{10}} C^{k_{11}} - S_{\min} - 0.01, \quad (10)$$

$S_{\min}$ (0.53) is the minimum value of S; k_8 (0.388), k_9 (–0.118), k_{10} (0.074), k_{11} (–0.221) are the empirical coefficients determined by the least-squares method using the known values of S, $\overline{W}$, w, C, and $S_{\min}$ (the S values are preliminarily calculated using the first method for $t = 0$; the correlation squared ratio R^2 of regression equation (10), with the above-specified values of k_8, k_9, k_{10}, and k_{11}, is 0.52 at critical value 0.36).

The implicit finite-difference scheme is used for approximation of Eq. (1):

$$f_1 = \frac{\partial C}{\partial t} \approx \frac{C_{t+1,z} - C_{t,z}}{\Delta t}, \quad (11)$$

$$f_2 = \frac{\partial C}{\partial z} \approx \frac{C_{t+1,z+1} - C_{t+1,z-1}}{2\Delta z}, \quad (12)$$

$$f_3 = \frac{\partial^2 C}{\partial z^2} \approx \frac{C_{t+1,z+1} - 2C_{t+1,z} + C_{t+1,z+1}}{\Delta z^2}, \quad (13)$$

where Δt is time increment; Δz is peat deposit depth increment (Benedini and Tsakiris, 2013). A search for a solution of the resulting equation system was carried out on the basis of the iterative method (method of golden section) using the objective function

$$F = \sum_{i=1}^{N} (f_{1,i,t} + f_{2,i,t} - f_{3,i,t} - S_{i,t})^2 + (\Phi_t - \Phi_{t-1})^2 \longrightarrow 0, \quad (14)$$

where N is the number of estimated intervals Δz with respect to the depth of peat deposit; Φ_t is the weight of substance in the column with a 1 m base and a height equal to the peat deposit depth taking into account the inflow of substances from the solution (S) for the time period from 0 to t. The increment on time ($\Delta t = 2$ s) and on depth ($\Delta z = 0.0025$ m) was chosen proceeding from observing condition $\frac{V_z \Delta z}{D_z} \le 2$ (Benedini and Tsakiris, 2013).

Modeling Options

The data of the research conducted at Tomsk Polytechnic University (TPU) in 2010 were used for testing the model. The sampling was carried out on the oligotrophic area of the Vasyugan bog at a distance of 300 m from the waterless valley (one sampling point) jointly with M.A. Zdvizhkov and A.V. Shmakov using the vacuum pump according to the Russian Hydrometeorology and Environmental Monitoring; the laboratory works were carried out at the accredited hydrochemical laboratory of TPU according to the tested methods. Materials on the total content of principal ions (Σ_{mi}) at a depth of 0.3, 1.2, 1.8, and 2.3 m were used for modeling as of May 27, 2010 (Table 1). The values of Σ_{mi} in all rest points of the section were determined by linear interpolation (in the layer with depths from 0 to 0.3 m, the constant value Σ_{mi} is assumed to be equal 8.0 mg/dm^3). The level of bog waters was 0.2 m from the bog surface; the depth of peat deposit was 2.3 m.

Three main options are considered when modeling the distribution of pollutants in the peat deposit: (1) one-time discharge of pollutants to the surface of

Table 2. Options of geomigration calculations

Calculation option	Method of calculation of S source function	Nature of inflow of waste waters
I	Back calculation according to Eq. (1)	Inflow of waste waters at moment $t = 0$ s; 0.0025-m layer; $\Sigma_{mi} = 7211.8$ mg/dm^3; initial state at moment $t = 0$
II	Back calculation according to Eq. (1)	Inflow of waste waters at moment $t = 0$ s; 0.0025-m layer; $\Sigma_{mi} = 7211.8$ mg/dm^3; estimated time $t = 60$ s
III	Calculation according to Eq. (10)	Inflow of waste waters at moment $t = 0$; 0.0025-m layer; $\Sigma_{mi} = 7211.8$ mg/dm^3; estimated time $t = 60$ s
IV	Calculation according to Eq. (10)	Continuous inflow of waste waters at any specific time t; 0.0025-m layer; $\Sigma_{mi} = 7211.8$ mg/dm^3; estimated time $t = 60$ s
V	Calculation according to Eq. (10)	Continuous inflow of waste waters; 0.0025-m layer; $\Sigma_{mi} = 7211.8$ mg/dm^3; presence of insulating layer of loams with thickness of 0.1–0.2 m, 10% porosity, and $k_f = 10^{-6}$ m/s; estimated time $t = 60$ s
VI	Calculation according to Eq. (10)	Continuous inflow of atmospheric precipitations; 0.0025-m layer; $\Sigma_{mi} = 50.9$ mg/dm^3; the peat deposit is polluted at constant value $\Sigma_{mi} = 7211.8$ mg/dm^3; estimated time $t = 60$ s

nonpolluted bog at moment $t = 0$; (2) the continuous inflow of pollutants to the surface of nonpolluted bog; and (3) the continuous inflow of atmospheric waters to the surface of polluted bog (uniformly with respect to the whole depth of peat deposit). The peculiarities of change of the total content of principal ions in bog waters were additionally studied, taking into account the presence of the low permeable layer and atmospheric precipitation. The macrocomponent composition of bog, waste, and atmospheric waters and the values of pH, Σ_{mi}, and dichromate oxidizability (DO) is given in Table 1; the modeling options are shown in Table 2. The estimated layer of waste waters is 0.0025 m.

RESULTS AND DISCUSSION

Research into the estimated distribution of Σ_{mi} value with respect to the depth of peat deposit showed that, within the active layer (under natural conditions), there was a quite intensive extraction of salts from the solution in the range up to 0.35 m from the bog surface, the minimum value of S function being referred to the layer of bog waters (Fig. 2). This is due to the increase in the contact area of water and organic and mineral substances in the lower active layer, which leads to an increase in the weight of low-soluble metal compounds with huminic acids which are extracted from the solution even in the case of a relatively low content of principal ions. In addition, the codeposition and sorption of a number of other compounds on the peat particles presumably take place, which leads to the formation of a layer with elevated concentrations of Ca, Mg, Fe, Th, U, Hg, and many other elements in peat.

The levels of bog waters of the given oligotrophic bog vary within the range from 0.15 to 0.30 m. Also, in dry years, the pit deposit may be potentially settled and, in the years which are optimal with respect to air moisture and temperature, there is an increase; the maximum value of this increase in the research area reaches 2.62 mm/year according to the assessments (Pologova and Lapshina, 2002). Due to this, a certain scatter of depths is observed which the elevated concentrations of macro- and microelements in the peats were referred to. Nonetheless, on the whole, we can assume that, if during the whole period of formation and evolution of oligotrophic bog (at least in the South Taiga subzone of Western Siberia) the hydroclimatic conditions did not change significantly, then, first, the general trend of lowering the total content of dissolved salts is observed in the bog waters from the bog surface, where there is a maximum influence of atmospheric ultrafresh precipitation to the border of bog deposits and mineral grounds, characterized by the inflow of more mineralized underground waters to a particular

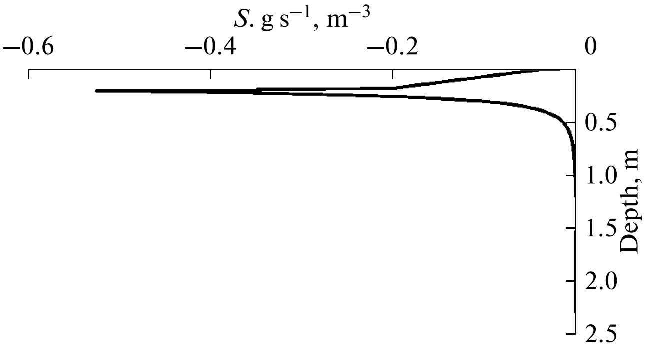

Fig. 2. Change of S function with respect to the depth of peat deposit in the waters of the analyzed area of the Vasyugan Bog as of May 27, 2010.

Table 3. Distribution of the sum of principal ions in bog waters at different geomigration calculation options

Depth, m	Calculation option*, calculated time 60 s					
	I, $t = 0$ s	II	III	IV	V	VI
0.0	7211.8	125.7	125.6	7211.8	7211.8	50.9
0.1	8.0	35.0	35.0	7211.8	7211.8	7160.8
0.2	8.0	8.2	8.2	211.5	8.1	7211.8
0.3	8.0	8.0	8.0	8.0	8.0	7211.8
0.4	8.4	8.4	8.4	8.4	8.4	7211.8
0.5	8.8	8.8	8.8	8.8	8.8	7211.8
0.6	9.2	9.2	9.2	9.2	9.2	7211.8
0.7	9.6	9.6	9.6	9.6	9.6	7211.8
0.8	10.0	10.0	10.0	10.0	10.0	7211.8
0.9	10.4	10.4	10.4	10.4	10.4	7211.8
1.0	10.8	10.8	10.8	10.8	10.8	7211.8
1.1	11.2	11.2	11.2	11.2	11.2	7211.8
1.2	11.6	11.6	11.6	11.6	11.6	7211.8
1.3	15.6	15.6	15.6	15.6	15.6	7211.8
1.4	19.6	19.6	19.6	19.6	19.6	7211.8
1.5	23.6	23.6	23.6	23.6	23.6	7211.8
1.6	27.5	27.5	27.5	27.5	27.5	7211.8
1.7	31.5	31.5	31.5	31.5	31.5	7211.8
1.8	35.5	35.5	35.5	35.5	35.5	7211.8
1.9	39.5	39.5	39.5	39.5	39.5	7211.8
2.0	43.5	43.5	43.5	43.5	43.5	7211.8
2.1	47.6	47.6	47.6	47.6	47.6	7211.8
2.2	51.6	51.6	51.6	51.6	51.6	7211.8
2.3	55.6	55.6	55.6	55.6	55.6	7211.8

* The options are given in Table 2.

extent. Second, on the border of layers with significantly different filtration properties controlling the intensity of water exchange (consequently, time and area of contact of water and organic and mineral substances), there is a formation of layers having relatively small thicknesses with high concentrations of a number of substances in peats. It is this nature of change of chemical composition of peats and bog waters that is observed on the analyzed (oligotrophic) area of the Vasyugan Bog, which is confirmed by the data given in (Bakhnov, 2002; Mezhibor, 2009; Arbuzov et al., 2009; Lyapina, 2012).

In other cases (when hydroclimatic conditions and bog processes themselves change in time), a more complicated pattern of distribution of substances in bog waters and peats may be marked which is characterized by the presence of several "peaks" of concentrations of chemical elements in the bog components. Examples of such changes can be found primarily in oligotrophic and mesotrophic bogs at the border of forest-steppe and taiga zones, as well as in near-terrace bogs of different types (Savicheva and Inisheva, 2008; Savichev and Shmakov, 2012; Lyapina, 2012).

The analysis of results showed that a determination of S function using Eq. (10) and back calculation according to Eq. (1) allowed us to get comparable results on the whole (Table 3, options II and III); however, in the first case there is an opportunity to consider changes of filtration properties of peats. For this reason it is this method that was used during modeling according to options IV–VI.

The distribution of dissolved salts with respect to the depth of peat deposit in the case of the one-time (emergency) discharge of brackish waste waters takes place in the active layer (Fig. 3). In this case, an approximation to the "background" state preceding the discharge of waste waters takes place approximately after 5 min.

In the case of the continuous inflow of waste waters to the surface of peat deposit, the content of dissolved salts reaches the value of 7211.8 mg/dm^3 at a depth of 0.2 m (level of bog waters) just after 2 min and at a depth of 0.5 m after 22 min, but further distribution of contamination front slows down dramatically due to the significant deterioration of filtration properties of peats with an increase in depth, which is confirmed by the results of earlier conducted field studies (Bazanov et al., Savichev, Volostnov, et al., 2004; Savichev et al., 2013) on the area of operation of Western Siberian oil and gas production enterprises (Table 4) and materials by other authors concerning the distribution of a number of chemical elements in peats, with peaks mainly in the upper half-meter layer (Mezhibor, 2009; Arbuzov et al., 2009). On the whole, in the case of a continuous inflow of pollutants to the bog surface, their major portion is distributed mainly in the upper layer with a thickness of approximately 1 m.

In practice, sludge pits are often the source of pollution of peats and bog waters in Western Siberia; their construction yields a waterproofing layer made up of clays or loams. Such an activity may also be carried out in other cases (for example, in the case of the construction of domestic waste landfills). Against this background, a calculation of distribution of dissolved salts in bog waters was made assuming that the layer of peat deposit from the surface with thickness of 0.1–0.2 m is filled with loam having 10% porosity and the coefficient of filtration 10^{-6} m/s (option V). Such an advantage provided by the ground properties results in a certain change of the velocity and nature of distribution of the contamination front (Table 3). In particular, compared with option IV, in the first few minutes after waste waters began to inflow the field of high concentrations relative to the "background" of concentrations was more compact and Σ_{mi} in the layer with a thickness of 0–0.2 m is visibly higher (Table 3).

One more calculation option (VI) consisted of the assumption that there was pollution of the peat deposit with respect to the whole depth and later there was gradual washing by atmospheric precipitation (precipitation depth was 0.0025 m; the content of dissolved salts in the precipitation in amount of 50.9 mg/dm^3 was assumed according to (Savichev and Ivanov, 2010). The modeling results indicate that lowering of mineralization of polluted waters to the "background" level is a rather long process (beyond the capabilities of the applied numerical methods), which is confirmed by the research data concerning the polluted areas of bogs in Western Siberia (Fominykh and Shcherbak, 2012; Bleuten et al., 1999).

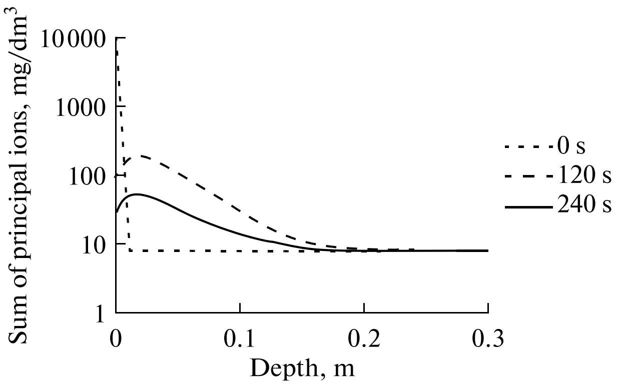

Fig. 3. Distribution of the sum of principal ions in bog waters using calculation according to option III (Table 2); at moment $t = 300$ s for the range of depths from 0.0 to 0.3 m. The Σ_{mi} value is 8.0 mg/dm^3.

CONCLUSIONS

As a result of the conducted research, the model of distribution of mineral salts in polluted waters of an oligotrophic bog was developed. One feature of the model is the assessment of S component characterizing the inflow of substance from peats to bog waters, the inflow of organic mineral deposits, and processes of its extraction from the solution as the functions of moisture, coefficient of peat moisture conductivity, and concentration of substance.

The geomigration calculations using the given model have shown that the short-term inflow of brackish waste waters (with the total content of principal ions 7211.8 mg/dm^3), for instance, due to a local emergency situation during the extraction of minerals, does not significantly influence the ion composition of bog waters and is restricted mainly by the active layer. The continuous discharge of waste waters results in a more significant change in the chemical composition of waters, the most serious pollution being referred to the upper layer with a thickness reaching 0.5–1.0 m. On the whole, the resulting data indicate that there is an opportunity to use planned models for calculations of distribution of pollutants (over the bog substance along and perpendicularly to the waterless valley) for the active layer of peat deposit.

The creation of the insulation layer from loam in the range of depth from 0.1 to 0.2 m from the surface leads to pollutants concentrating in the active layer,

Table 4. Chemical composition of waters of the polluted area of the peat bog on the area of Dvurechensk field*, mg/dm^3

Element	Interval of sampling, m from the surface			
	0.00–0.15	0.15–0.20	0.20–0.25	0.25–0.50
Ca^{2+}	4358.7	14278.5	11573.1	1503.0
Cl^-	286.0	190.0	126.0	128.0

* Bazanov et al., 2004.

but does not preserve the "background" level of the content of dissolved salts in the peat deposit layers located below. Against this background, when building sludge pits and other facilities which are potential sources of pollution of bogs, along with low permeable filters from loams and clays, it is necessary to use materials providing more reliable waterproofing.

The polluted peat deposit is washed by atmospheric precipitation, but it is a rather long process, which demonstrates the need for special measures in reclaiming works in order to enhance water exchange in the peat deposit.

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