

STUDIES OF THE INFLUENCE OF SOIL BIOGENIC ACIDITY ON PODZOL FORMATION

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Abstract: The paper with a review and generalization of data analysis on the principal forms of soil biogenic acidity is based on research into representative podzols and podzoluvisols with combined parent materials and boreal (taiga) ecosystems at the Central Forest Biosphere Reserve (CFBR) (Tver region), Forest Experimental Station of RSAU (FES) (Moscow) and LAMP Experimental plot in Taiga park of Petrozavodsk. Long-term monitoring of acidity forms was performed by the authors during 2002-2012.

Two principal approaches — chemical and soil-ecological — of soil acidity nature can be used in soil acidity studies. The former is to be applied when soils of agricultural ecosystems that determine their acidity regulation methods through liming are studied. Soil-ecological assessment is associated with the diagnosis of biogenic acidity of taiga ecosystems and includes biochemical cycling of organic carbon formed during photosynthetic process and humification of organic acids with low molecular weight, polyphenols and fulvic acids. The quantitative evaluation of the biogenic acidity was made through the study of migration of water soluble organic substances (WOS) with acidic properties. The sorption lysimeter method (SLM) was used in this research. The highest values of hydrolytic acidity and active acidity were fixed in sod-podzoluvi sols in larch and pine mature plantations at the Forest Experimental Station, in mature spruce forest at the Central Forest Biosphere Reserve and in podzols at the LAMP Experimental plot in Taiga park of Petrozavodsk. The above is strongly related with lysimeter data on mobilization of WOS with acidic properties and fulvic acids in solution. Al and Fe compounds leaching from topsoil were observed after considerable Ca and Mg depletion from dominating minerals. The process of surface gleization of sod-podzoluvisols is connected with their inter-profile gleization at the parent material boundary and activates the lateral removal of Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} ions with the participation of WOS. As to sod-podzoluvisols of FES, WOS outflow from the upper horizon A_0 can be up to 24 g/m² C in autumn (one of principal migration peaks), and from the A_0^t horizon of the Petrozavodsky permanent plot - 16-21 g/m².

Key words: acidity, soil acidity nature, podzol, sod-podzoluvi sol, sorption lysimeter method, water soluble organic substances, leaching, lateral migration, boreal (taiga) ecosystems.

Currently, in the study of soil acidity, there are two scientific approaches: chemical and soil-ecological. The first one covers mainly agricultural soil ecosystems by which the regulation of soil acidity is determined through liming. Here experts attribute the leading role in the formation of soil acidity to ions of hydrogen and aluminum. The source of hydrogen ions is considered to be derived from soil humus substances [1, 7, 27, 38]. The soil ecological assessment is associated with the diagnosis of the biogenic acidity in taiga ecosystems. This approach considers the biogeochemical cycle of organic carbon, formed during the processes of photosynthesis and humification of low-molecular organic acids (LMOA), polyphenols and fulvic acids (FA) with acidic and other properties at the ecosystem

level with the participation of mold fungi-acid producers (*Penicillium sp.*) [4]. The acidic adaptation mechanism of the taiga biota is referred to as "biogenic acid production" by researchers [16, 17, 26]. Moreover, as early as in 1989, E. N. Mishustin pointed out the importance of applying a biological approach to the soil research [18]. Despite existing factual data, the connection between the biogenic acidity of the taiga ecosystems and soil acidity has not been fully discovered.

Objects and methods

The permanent area of the Forest Experimental Station (FES) is located in the wooded-park area of the Russian State Agrarian University named after K.A. Timiryazev (RSAU-MTAA) in Moscow. It includes a soil-ecological catena in quarter 7 placor — a gentle hillslope with a southern exposure (Figure 1) — bottom of a hill slope. Catena soils are sod-podzolic sandy clay soils (with binomial deposits) under pine-larch forest with maple undergrowth [35]. Geographically, FES is located within the moraine plain which occupies the area at the altitude of 165-175 m above sea level, with earth coordinates: 55° 82'N and 37° 56'E [9].



Fig. 1. Pine larch forest plot in quarter 7 of FES of RSAU-MTAA (middle of the hillslope): a - Prof. I.M. Yashin studying the podzol profile, May 2006; b - installation of sorption lysimeters by a postgraduate student A. A. Petukhova, July 10th, 2012

Detailed forest resource research of the plantation and the soil mapping in different quarters of FES have been carried out by V.D. Naumov, A.N. Polyakov [19] and V.I. Savich [23]. Research of the soils and plots of FES were conducted in the spring-summer and autumn seasons of 2001-2004, and then in 2008-2012. The data obtained are particularly detailed in this study [34].

The permanent experimental area in CFBR is located in quarter 95, about 4.4 km north-east of the central farm (in the village of B. Fedorovskoe), in the thick green moss-bilberry-spruce forest plot on a ridged placor with pronounced micro-relief (Figure 2). CFBR is located 34 km from the town of Nelidovo in Tver region and 354 km from Moscow. It consists of forested ridges, ranges and hills at the altitude of 230-270 m above sea level, interspersed with massive marshlands, small meadows, little cutting clearings and windbreaks; there are very few arable plots, which is quite attractive for wild animals [13].



a



б

Fig. 2. Thick green moss-bilberry-spruce forest plot - in quarter 95 of CFBR: a - Prof. **1.1.** Vasenev (by the theodolite) while mapping of the experimental plot in quarter 95 (29.09.2011); b - Prof. I.M. Yashin installing sorption lysimeters (SL) in the profile of podzols (30.09.2011)

The river network, e. g., the river Mezha has weakly incised channels, and its flood plains are swamped. The water of the rivers and streams differs by its intensive dark brown colour all year round — it contains various components of WOS [13] - (Figure 3). The ground waters (on the placors) are as close to the surface as 1.7-2.3 m. During the rainy season, in sod-podzol parent layer thin film is quickly formed, intensifying gleization in the soil profile and mobility of WOS, so the border transitions between different horizons become diffuse and blurred, and lateral form of migration activates. The selection of soil samples, plant fallen material and mosses was conducted seasonally in May, July and September 2011, and also from the 16* to the 18* of April 2012 (with snow cover reaching 29-34 cm).



a



б

Fig. 3. CFBR: a - collecting melted water by senior lecturer T. M. Dzhancharov near quarter 95 for diagnosing water quality and the composition of WOS (17.04.2012); b - collecting water samples from the river Mezha done by assistant lecturer A.V. Buzylev (in the background), and postgraduate student D.A. Grachev (21.05.2011)

The permanent experimental plot in the taiga wooded-park of Petrozavodsk is located on a moraine ridge with a smooth slope of southern exposure (Perevalky district, Universitetskaya street). Nearby a major traffic intersection and a petrol station are located and a supermarket is being built. Thus, the plots are exposed to increasing chemical pollution and contamination). The soil and environmental catena of Petrozavodsk includes the following plots: on the placor - spruce dead cover forest with intact podzols in parent layer; in the middle of the sloping ridge (hollow depressions, clearings in the bilberry sphagnum area with transformed gleyey podzols — Figure 4a), and at the lower third of the sloping ridge in the thick green bilberry spruce forest on transformed gleyey podzols. Monitoring of the soil and environment here has been conducted from 2002 to 2012. Sorption lysimeters were installed in the podzol profiles of catena keypoints. The studied taiga wooded park landscape during this period endured cuttings of trees and is actively visited by people: there were marked footpaths, bonfire remains and small debris and garbage. People gather mushrooms and berries there; a holiday cottage settlement is located nearby. In 2012, (in the rainy season), some large anthills were abandoned by ants: they moved from the depth of the forest park to its margins.



Fig. 4. Petrozavodsky permanent experimental plot in Karelia: a - SL installation by postgraduate student A. A. Petukhova: bilberry sphagnum forest plots (facies) (clearings - hollow depression) 14.07.2011; b - for comparison: the podzol profile in 2002, two years after the trees had been cut down: the beginning of the transformation of iron hydroxide hydrogels in the B₁ horizon (podzol evolves into marshy podzolic soil), 26.07.2002

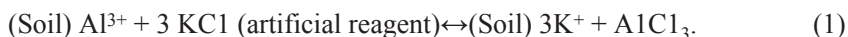
Previously, the composition of humus and the chemical properties of sod-podzoluvisol [33] were studied.

The assessment of the biogenic acidity of taiga ecosystems was done through studying the migration streams of WOS with acidic properties. To achieve this, the sorption lysimeter method (SLM) - [5, 16, 17, 32, 34] was used. The sorption lysimeters were usually placed under the main genetic horizons of the soil, formed on binomial noncarbonate deposits. After the set period, SL were removed from the profile and taken to the laboratory, where the sorbents were dried and weighed. Upon that, the desorption of chemical elements (C_{org} , Fe, Pb, etc.) from the sorbents in statics was performed: from cation KU-2 in the H⁺ form - In. HNO₃ solution and from low-in-mineral activated carbon - O.in. NaOH

solution, by water until colorless portions of filtrate appear. This sorbent actively absorbs low molecular organic acids (LMOA), uronic acids, amino acids and polyphenols, as well as FA [17, 30, 32]. The level of pollution of the boreal ecosystems was calculated using the author's method, based on experimental data [33]. The number of heavy metal ions (HM) was determined by atomic absorptive spectrophotometer AAS-3 (Germany), using standard solutions for adjusting. The coefficient of migration (K_{mig}) was determined by Perelman [32, 33, 34]; the organic carbon content was determined by Turin's method with a photometric end; the actual soil acidity (pH of aqueous extracts) and exchangeable acidity (in salt extract 1M KCl) - were determined potentiometrically on a pH meter; hydrolytic acidity was determined by Kappen's method with 1M CH_3COONa ; Al^{3+} ions were determined by Sokolov's method [29]. The reliability of the experimental results was analyzed by variation statistics methods [10].

Results and discussion

The soil covering and landscape features of the permanent experimental plots have been studied thoroughly [8, 9, 13, 20, 25, 32, 33], but the genesis of podzols formed on binomial deposits (sod-podzoluvisol) and the biogenic acidity of ecosystems have been investigated to a lesser extent. In this regard, the dynamics of physical and chemical properties, the forms of acidity and water migration of WOS in the sod-podzoluvisols of the CBFR, FES and the podzols of Petrozavodsky platform have all been carefully studied (Tables 1-4). It has been established that the hydrolytic acidity of the sod-podzols of the CBFR, FES and the Petrozavodsky permanent experimental plot in different seasons is characterised by high pH values throughout the entire soil profile (with a maximum pH value noticed in forest floor coverings and the pseudohumus-accumulative horizon). A similar pattern was previously observed by other authors [9, 13,15,20,25,28]. However, they did not explain the mechanisms of acid forming reaction and the specifics of the taiga ecosystem functioning [32]. Let us briefly examine these questions. It is known that the exchangeable acidity of soil has a complex nature, and its assessment has not been fully evaluated so far. It is believed that this form of soil acidity is due to the presence of exchangeable hydrogen cations, aluminum of soil colloids and minerals in the soil [1, 7, 14, 39]. S.N. Aleshin, e.g., believed [1] that soil exchangeable acidity was caused by hydrogen ions, while the ions of aluminum played a secondary role; it was connected with a concomitant transformational reaction of aluminum compounds with an aqueous solution of a neutral salt:



Aluminum chloride, being a salt made of a strong acid and a weak base, undergoes an acidic hydrolysis reaction in the solution, as shown in the formula below:



This explains, according to scientists, a highly acidic reaction of salt extracts from podzolic soils in model experiments. It should be noted that this exchangeable acidity is suitable for the soils of taiga zone landscape. For native soils and taiga ecosystems the situation is different.

The materials accumulated show that the aluminum in the taiga soils can exist in the form of exchangeable ions, aqueous complexes, hydrosols of aluminum hydroxide and aluminum-organic complex compounds [6, 7, 14, 18, 22, 29, 39]. In reactions (1 and 2), the obtained products do not conform to the natural ecosystems. Empirically,

Table 1

**Seasonal dynamics of physical and chemical properties of sod-podzol contact-clay soil
formed on binomial deposits of CFBR, quarter 95**

Horizon* and depth of soil sampling, cm	pH _{KCl}	H _r	Absorbed main elements		Content of particles less than 0,01 mm, %	C _{org} by Turin, %	Available compounds mg/kg	
			Ca ²⁺	Mg ²⁺			H ₂ PO ₄ ⁻	K ⁺
		mg-equiv./100 g						
<i>Cutting 1-IT. Parcel of bilberry – mixed herb spruce forest of various types (sample taken 21.05. 2011)</i>								
A ₀ /A ₁ 1–9	3.0±0.5	21.4±4.7	1.0±0.2	0.1±0.0	18.3	2.7±0.8	200±50	1210±70
Eh _g 9–17	3.5±0.7	12.5±2.3	0.4±0.1	0.04±0.0	16.4	1.4±0.5	80±20	780±40
B _{ftr} 17–27	3.9±0.4	6.8±1.7	0.3±0.1	0.02±0.0	19.5	0.8±0.3	290±30	470±30
EL' _g 45–55	4.0±0.3	4.4±0.4	0.5±0.2	0.04±0.0	30.9	0.5±0.2	1000±80	250±20
B _{2g} 67–77	3.5±0.4	5.0±0.3	3.23±0.8	0.7±0.1	44.7	0.4±0.1	2340±110	470±30
<i>Cutting 1-IT. Parcel of bilberry – mixed herb spruce forest of various types (sample taking 30.09. 2011)</i>								
A ₀ /A ₁ 3–10	3.2±0.9	24.2±5.3	4.3±1.5	1.4±0.7	17.1	3.0±0.9	890±80	590±70
Eh 20–30	3.4±0.8	16.9±3.6	0.7±0.4	0.3±0.1	15.6	2.3±1.1	50±10	550±30
B _{ftr} 32–39	4.1±0.4	5.6±1.7	0.6±0.2	0.2±0.0	19.0	0.7±0.5	230±30	280±20
EL' _g 39–49	4.0±0.3	2.8±0.9	1.0±0.5	0.3±0.0	32.7	0.4±0.1	950±80	240±20
B _{2g} 52–62	3.5±0.3	4.5±0.2	2.8±0.8	0.8±0.4	43.4	0.3±0.0	1650±90	440±50

* for soil horizon indices [see 32].

Table 2

**Physical and chemical properties of the A₀/E_h horizon (2-12 cm) of sod-podzoluvisol of FES,
soil sample collection date - 25.07.2009**

Q NNe quarter	Main tree type	Content of p articles less than 0.01 mm, %	CC _{org} , %	pH _{KCl}	Al ³⁺ , mg/100 g	Available compounds, mg /kg	
						H ₂ PO ₄ ⁻	K ⁺
8	Oak	18.5	4.7±0.1	4.1±0.05	3.62±0.03	2.5±0.05	11.1±0.4
7	Pine	12.8	2.4±1.3	3.2±0.0	5.94±0.20	1.2±0.0	8.4±1.0
9	Pine and birch	14.2	2.5±1.0	3.0±0.1	8.35±0.43	1.9±0.1	10.4±2.0
Mean for 3 quarters : x			3.2±1.3	3.43	5.97	1.87	9.97
Mean quarter deviation : σ			1.3	0.59	2.37	0.65	1.4

Table 3

pH_{KCl} values for the horizons of contact-clay sod podzols on binomial deposits of FES, soil sample collection date – 05.08.2009

Quarter of FES	Sampling plot	Approximate age of trees, years	Horizons of studied soils		
			A ₁ /E _h (2–12 cm)	E _h (25–35 cm)	B _{tr} (50–60 cm)
7 (pine)	«R»	34	3.10±0.48	3.89±0.66	3.53±0.08
8 (larch)	«V»	40	2.96±0.39	3.23±0.24	3.55±0.24
7 (spruce)	«P»	122	3.08±0.31	3.72±0.94	3.89±0.05
Mean for 3 quarters: \bar{x}			3.05	3.61	3.66
Mean quarterly deviation: σ			0.08	0.34	0.20

Table 4

Hydrolytic acidity H_n, mg-equiv.aqv/100 g in the sod-podzols of FES

Quarters of FES	Sampled plot	Maturity, years	Horizons and depth of sample taking, cm		
			A ₁ /E _h (2–12 cm)	E _h (25–35 cm)	B _{tr} (50–60 cm)
7 (pine)	«R»	34	10.90±2.71	2.55±3.17	1.12±2.18
8 (larch)	«V»	40	6.07±1.66	3.50±2.59	1.20±3.64
7 (pine)	«P»	122	13.27±3.43	2.96±0.45	1.34±0.56
Mean for 3 quarters: \bar{x}			10.08	3.00	1.22
Mean of quarterly deviation: σ			3.67	0.48	0.11

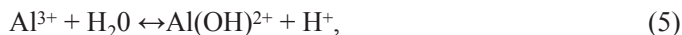
in the taiga ecosystems, the reagents appropriate to the functioning of the taiga soils were found. They are low molecular WOS of acidic nature, which determine the mobilization of Al³⁺ ions from the solid phase of soils into the solution [4, 5, 6, 15, 16-18, 26, 30-32, 33, 34] according to the following pattern:



In the reaction (3) with a solution of oxalic acid except complexes of Al-R and heteropolar Al₂(C₂O₄)₃ aluminum salts in aqueous solution, insoluble hydrosols of aluminum hydroxide (PR = 10⁻³⁴) are immediately formed. As they are kinetically and thermodynamically unstable, they precipitate into particles. They have a high sorption capacity. When they react with excessive hydrogen ions, they gradually form ions of aluminum - without any indication of water molecules:



which in aqueous solutions again become hydrated with water molecules as shown by the formula below:



Then the solution acidifies. Deduction from reactions (3 and 4) shows that to displace aluminum ions from exchangeable absorbed state of aluminum hydroxides colloids, a sizeable mass of hydrogen ions is lost (pH value decreases). Then there begins the replenishment of H^+ ions into solution by the conversion of aluminum compounds, including complex formations known as pH-effect [16]. Thus, vibrational reactions of mobilization and immobilization of Al^{3+} ions take place in podzols with the involvement of WOS.

The forms of aluminum in podzols are greatly diverse and interrelated, as it has been noted previously [16, 17, 30, 32]. In this context, it is obviously incorrect to consider Al^{3+} ions to be the source of acidity. Aluminum ions are toxic for crop plants in the taiga agroecosystems, but not for the taiga biota [1, 14, 29]: trees, mushrooms and berry plants grow safely on podzols in the taiga forest. The environmental role of aluminum in boreal ecosystems remains scarcely studied. Interrelation between high content of exchangeable Al^{3+} and low supply of available forms of phosphorus in podzols (see Table 2) has been established. At the same time, it has been observed that in the soils of CFBR, a low number of exchange-absorbed Al^{3+} ions correlate with high level of available forms of phosphorus, particularly in the lower layers of the sod-podzols on binomial deposits (sod-podzoluvisol) (see Table 1.). In the summer and winter seasons the drying up of podzols results in the colloid particles of $\text{Al}(\text{OH})_3$ becoming dehydrated and transforming into crystallized forms of $(\text{Al}_2\text{O}_3)_x \cdot \text{AlO}_2 \cdot \text{H}^+$, in which hydrogen ions are capable of exchanging with cations of K^+ , NH_4^+ , Na^+ , Ca^{2+} , Mn^{2+} , Pb^{2+} in acidic soil solutions [17, 30]. These cations are compensated for by potentially charged anions of aluminum colloids. Earlier it has been pointed out that aluminum oxide used in SL is known to absorb unchanged part of masses of WOS and Fe-organic complexes during their migration in the soil [16, 17, 30]. The research has also shown that this fact may be associated with the mobilization of aluminum ions from the same sorbent (Al_2O_3) with the formation of weakly dissociating complexes deposited on particles of aluminum oxide. Neither acid nor alkaline could dissolve these products in the laboratory. That is why the C_{org} of WOS has always been diagnosed directly by the weighing of Al_2O_3 as in the soil according to Turin's method. In the authors' view, a similar effect is observed in the sandy-loamy podzols under the formation of illuvial-ferruginous horizons. Therefore, it is more appropriate to name this horizon as Al-Fe horizon, because the accumulation of irons here is closely associated with aluminum (Al), the acidity of podzols and the transformation of colloids [30]. Let us review the factual data.

Podzols of old-aged pine and larch plantations of the Forest Experimental station usually have higher value of Hg and actual acidity. Obviously, this fact is genetically related to the mobilization in WOS and FA solutions with significantly strong acidic properties and the fulvic composition of humus [6] (see Table 2-4). In the forest-park taiga ecosystems, an active water migration of WOS helps to facilitate the mobilization into the solution from minerals of molecular ionic forms of aluminum and iron. According to several authors, this fact indicates a pronounced acidic decay of minerals and marked formation process of clay and podzol [26, 27, 38, 39]. The removal of Fe and Al compounds is observed after a significant depletion of minerals, by ions of Ca and Mg [15, 17, 27, 38]. Low molecular products of soil formations during migration are partly delayed in the sorption barriers (ho-

hizon B_p), ensuring their transformation [16, 33, 34]. Thus, hydrogels of Fe(OH)₃, having absorbed migrating WOS and complex Fe-organic compounds, eventually transform into illuvial-humus with iron compounds podzols [30]. Superficial gleyzation of sod-podzols is often connected with clay formation within the soil profile (on the borderline of rocks) and activates the lateral loss of ions of Ca²⁺, Mg²⁺ and also Fe³⁺, Al³⁺, involving WOS [30, 38]. In this case, the whitish (surface gleyzated) horizons during soil morphological evaluation of sod-podzoluvisol can be mistaken for podzols.

Clay formation drastically activates the mobilization of unoxidized components of WOS possessing acidic properties [17, 31, 38]. Therefore, when assessing biogenic acidity, it is important to know the scale of the seasonal mobilization and water migration of WOS (see Table 5, 6). It has been established that in the sod-podzols of FES and the podzols of Petrozavodsky experimental plot, the loss of WOS components is clearly pronounced: from the A₀ horizon of FES it reaches 24 g/m² of C_{org} during the autumn (this is one of the major migration peaks), and from the A₀^t horizon of Petrozavodsky platform - nearly 9 g/m². WOS leached from the moss layer can be absorbed by lower horizontal layers of peaty forest litter - A₀^{up} и A₀^p, that is why the sorption lysimeter (SL) was often placed under the whole layer of forest litter [16, 31, 33, 35]. It is appropriate to add that exactly in this layer, an intense accumulation of heavy metals takes place.

Table 5

The form and scale of downward migration of iron compounds and WOS components in the sod-podzoluvisol on FES placor, exposure 15.07 - 04.12.2010

Horizon and depth of lysimeter installation, cm	C _{org} WOS r/m ²				Mass of, firmly bound Fe ions, WOS, %	Scale of Fe ion migration, mg/m ²
	Total range of migration	In water-aceton solution out of coal (IOS)*	In ammonium solution out of coal (FA)	in Al ₂ O ₃		
A ₀ -3	23.5±7.9	7.6±4.2	13.4±8.3	2.5±1.8	59.1±23.4	254±32.6
E _n -12	7.6±2.3	2.1±0.7	4.5±1.8	1.0±0.7	65.2±29.1	116±19.7
B _{fg} -49	11.5±4.6	4.9±1.5	6.3±2.5	0.3±0.1	67.7±34.6	263±41.1

* hereinafter, individual organic substances are displaced: from activated carbon by aqueous acetone extract, from FA by ammonia.

In the sod-podzols of FES in the composition of WOS, the prevalence of specific components (FAs and their salts) is observed, which is connected with higher biological activity of FES soils in comparison with analogues of the mid-taiga subzone. It should be noted that FA have been studied by the authors [16, 17, 32], and a group of experts from the Institute of Geochemistry of Russian Academy of Science named after V.I. Vernadsky [27]. It was revealed that FA are highly chemically active, stable in solutions at migration, possess a marked ability to form stable complex compounds with metal ions and also possess well-pronounced acidity, thus causing mobilization into the solution, e.g., of Ca²⁺ ions and HM from CaCO₃ powder [30, 32]. Lysimeter observations showed that in the podzols of Petrozavodsky experimental plot there was a migration of both FA, and also, on a larger scale, of low-molecular WOS of individual nature, changing from activated carbon columns to

**Vertical scale of downward migration of WOS and iron compounds
in the sandy clay contact sod-podzoluvisol in the taiga forest park catena of Petrozavodsk**

Horizon and depth of lysimeter installation, cm	Removal of C_{org} WOS, g/m ² in 1 year.			Fe ³⁺ , mg/m ² in 1 year.	
	In water-aceton solution, from coal (IOS)	In ammonium solution, from coal (FA)	By sorption WOS Al ₂ O ₃	After WOS decomposition, 20% H ₂ O ₂	% ion mass of Fe ³⁺ , firmly bound with WOS
<i>Control. Profile pit 4p. Landscape autonomous (placor), non-transformed bilberry – green moss spruce forest: 07.07. – 11.11.2009</i>					
A ₀ ^t – 3	5.2±1.5	2.4±0.9	1.3±0.5	449.2±18.2	54.3
E _h – 14	4.6±1.3	2.1±0.8	0.9±0.1	316.6±27.4	59.6
B _f – 36	0.5±0.1	0.9±0.2	0.1±0.0	38.5±5.7	72.4
<i>Profile 5p. Landscape transformed: opening (trees cut down) (hollow depression – bilberry – sphagnum area; middle part of slope)</i>					
A ₀ ^{tp} – 5	17.9±3.5	8.3±1.6	4.7±1.5	429.4±44.9	67.2
E _{hg} – 12	14.1±3.2	10.9±1.9	2.5±0.7	697.5±72.1	70.4
B _{mg(tr.)} – 39	3.7±1.1	14.4±2.4	0.8±0.3	722.5±95.7	70.8
B _{m(not tr.)} – 38	1.9±0.7	4.9±1.6	0.5±0.1	189.2±17.4	76.3
<i>Profile pit 3p. Landscape transaccumulative: opening at forest edge – lower third of slope – (bilberry spruce forest)</i>					
A ₀ ^m – 5	14.7±3.1	6.8±1.4	5.8±1.9	543.9±112.2	59.6
E _{hg(tr.)} – 15	8.5±1.8	9.6±2.2	4.1±1.3	705.3±23.8	38.4
B _{fg(tr.)} – 40	2.3±0.8	3.7±1.1	2.0±0.6	198.2±63.7	29.7

aqueous acetone eluate (Table 5, 6). By the methods of paper and column chromatography low molecular organic acids, polyphenols, and uronic acid were diagnosed to be included in the composition of WOS [16, 31]. The migratory ability of complexes with metal ions is higher in FA, than in aliphatic acids and polyphenols [3, 6, 10, 11, 15, 18, 22, 26, 27, 37]. Based on the experimental data of several authors, some chemical elements' coefficients of water migration k_{mig} in the elementary geochemical landscapes (EGL) of Petrozavodsky catena were calculated. (Table 7).

The k_{mig} values for the studied samples of EGL were extremely high, which indicates the active sorption-desorption processes of heavy metals (HM). It was discovered that the peaty forest litter, on one hand, is a very capacious absorbent of metal ions, soot, dust particles and moisture, and, on the other hand, is the source of WOS and HM ions,

Table 7

Coefficient of migration k_{mig} of studied chemical elements in the horizons of sod-podzoluvisol in the facies of Petrozavodsk taiga forest park

Depth of lysimeter installation, cm	Dry residue, g/l	C _{org} WOS	Fe	Pb	Zn	Cu	Cd
		k_{mig} by Perelman					
<i>Profile pit 4p. Illuvial-iron podzol under dead litter spruce forest; placor - autonomous EGL</i>							
A ₀ ^t – 3	0.12	322	6.7	4166	287	637	2292
B _r – 36	0.08	215	5.0	1250	129	588	1875
<i>Profile pit 5p. podzol pseudogley under bilberry sphagnum area, hollow depression, opening (trees cut down) – transaccumulative EGL</i>							
A ₀ ^{tp} – 7	0.17	793	5.9	968	3125	519	4118
B _{tr} – 36	0.23	278	6.4	87	544	307	98
<i>Profile pit 3p. Podzol pseudogley under bilberry spruce forest, lower third of slope – migration relief zone – transeluvial (downslope) EGL</i>							
A ₀ ^{tp} – 5	0.29	370	3.7	448	216	219	3218
B _{tr} – 40	0.34	124	2.0	32	101	363	342

contaminating mushrooms and berries. Biopolymers of forest litter and tree fallings (lignin, cellulose and hemicellulose) are both WOS sources and also their sorbents. Forest litters act as thick organogenic sorption migration barriers [33, 35].

In hollow depressions (on profile pit sites) k_{mig} showed a high amount of Pb (968), Zn (3125) and Cd (4118). In autonomous EGL (on placor) k_{mig} was the highest in lead (4166) and a little less in cadmium (2292). The driving forces of water migration of HM ions in sod-podzoluvisol are high acidity, clay formation throughout the soil profile, sustained mobilization of WOS into the solution and stagnant-washing water regime of soils. In this regard, the dynamics of heavy metal content in the soils of the FES, Moscow and also CFBR, where the anthropogenic load is almost absent were studied (see Table 8). It was revealed that in 2012, in comparison with 2008 in the sod-podzols of FES metropolis there was a significant increase in the total amount of Zn, Ni, Cd, Cu, which by means of WOS were actively mobilized into the solution and were included in the streams of migration (biogenic and water). In the landscapes of the baseline platform of CFBR gradual chemical contamination of Cd, Ni, Pb through the podzol profile was noted (in the horizons of the forest covering and the lower layers of the soil). Most recently, some relevant published sources noted that CFBR soils were not contaminated with HM and were characterized by an exceptionally favorable ecological condition [13, 15, 26]. According to the authors, the cause of the pollution is as transatlantic transfer from European countries by air mass containing anions of both strong mineral acids and particles of soot and dust (which absorb HM ions and other toxicants).

Dynamics of the total HM contents in the sod-podzoluvisol during the monitoring of forest and forest park facies 2008 -2012, mg/kg

Level of soil sampling, cm	Cd	Pb	Zn	Cu	Ni
<i>FES. Placor of the hill, pine site; soil sampling 05.07.2008*</i>					
A _{1h} /E _h 2–12	0.27±0.07	5.1±0.7	34.4±12.1	17.4±3.4	0.26±0.09
E _{hg} 16–26	0.18±0.04	2.7±0.4	18.3±8.8	19.1±4.7	0.70±0.08
E _{gh} 39–42	0.11±0.03	0.15±0.02	9.4±2.5	8.3±3.2	1.17±0.13
B _{fg} 42–52	not identified	0.72±0.08	not identified	not identified	0.50±0.06
EL'g 53–59	not identified	0.44±0.06	not identified	not identified	0.86±0.15
B _{2g} 79–89	not identified	0.49±0.05	not identified	not identified	1.06±0.18
<i>FES. Placor of the hill, pine site; soil sampling after snow melting 16.04.2009.</i>					
A _{1h} /E _h 2–11	0.20±0.09	24.8±8.7	30.5±10.1	11.3±3.9	not identified
<i>FES. Placor of the hill, pine site; soil sampling 07.07.2011</i>					
A _{1h} /E _h 2–10	0.22±0.04	89.2±18.3	21.9±2.6	12.9 2.6	not identified
<i>FES. Placor of the hill, pine site; soil sampling 07.07.2012</i>					
A _{1h} /E _h 2–12	0.36±0.08	12.7±1.9	61.2±14.3	21.5±4.9	0.43±0.08
E _{hg} 16–26	0.27±0.03	5.9±1.4	31.1±7.1	22.2±5.6	0.26±0.06
E _{gh} 39–42	0.12±0.01	0.9±0.04	11.8±3.4	10.7±4.3	0.87±0.23
<i>CBFR. Placor, bilberry spruce forest site; soil sampling 30.09.2011</i>					
A _{0A} 1–9	0.19±0.04	14.0±4.8	8.0±2.7	1.6±0.8	0.6±0.09
A _{1h} /E _h 9–17	0.09±0.02	6.8±1.9	15.6±4.4	1.7±0.9	2.1±0.2
B _{1tr} 17–27	0.20±0.06	6.7±2.1	19.5±5.3	1.9±0.7	3.1±0.4
EL'g 45–55	0.24±0.08	3.5±0.9	15.0±4.1	2.2±0.9	4.0±0.6
B _{2g} 67–77	0.13±0.02	3.3±0.8	20.1±6.8	5.0±1.4	5.9±0.8

* analyses were performed by E. Naumova, The increased amount of HM in the sod-podzols of CFBR correlates with the abnormally high amounts of available forms of phosphorus, which requires additional testing (see Table 2).

This situation requires further substantiation, but one aspect is clear: the use of soils and CBFR ecosystems as a former standard for baseline monitoring should be done with caution, considering the historical facts of destruction and degradation of soils in many landscapes during the Great Patriotic War of 1941-1945 and the postwar industrial forest cuttings at the reserve in the 50's and 60's of the 20th century [13].

Analysis of accumulated information [3, 10-12, 15, 16-18, 23, 27, 30-39] enables us to review various components of WOS with acidic properties as target mobile products, reflecting the specifics of boreal (taiga) ecosystems functioning and interactions between the leading biospheric processes — photosynthesis and humification.

Conclusions

1. The morphology, chemical properties of soils developed on sod-podzoluvisol deposits in pine-larch facies of FES and in the spruce platform of Petrozavodsky stationary have been studied (in the catena plactor-slope-base of a sloppy hill). They are found to have two different types of the podzolic horizon genesis: one has a upper, whitish-gray, veiled by WOS migrating (related to the biogeochemical cycle of nutrients - biogenic and water migration), and the second - thicker - one - at the edge of another layer: sandy mini-podzol soil and loamy moraine (formed by physical and chemical processes during seasonal saturation with the participation of WOS and anaerobic microorganisms). Podzols and sod-podzoluvisol have a very high actual acidity (e.g., pH_{KCl} reaches about 3,0-3,9) and a considerable amount of exchangeable aluminum.

2. The transformational reactions of aluminum compounds and the mobilization of Al^{3+} ions into the solution have been reviewed. In the latter case, the displacement of hydrogen ions and the reduction of soil acidity in the fluctuating reactions was observed; a stable mobilization of WOS into the solution (particularly, LMOA) and complex formations significantly increase the acidity of podzols. Fluctuating processes of activation and reduction in acidic load can also be observed, while the biogenic vector of acidity is connected with the physical and chemical reactions in the soil.

3. The concept of the ecological features of clay and podzol formation processes in podzols and sod-podzols of the forest parks of Moscow (FES) and Petrozavodsk has been clarified and enriched. It was noted that clay formation is a horizontal process that involves anaerobic microorganisms and WOS. It actively increases in land clearings and micro depressions, promoting waterlogging. Podzol formation is atypical soil-geochemical process, which occurs on the higher ecosystemic level; in the biogenic field of taiga parcels, profiles of podzol soils with eluvial vectoral migration are formed. Clay formation is connected with the formation of podzols, contributing to more intense and widespread mobilization into the WOS solution from forest floor coverings and plant fallen material, Al^{3+} ions from minerals, as well as colloidal hydrogels $\text{Al}(\text{O}_\text{H})_3$, significantly increase the acidity of the soils on noncarbonated rocks.

4. The seasonal and annual scale of water migration of WOS with acidic properties in the sod-podzols and sod-podzoluvisols in the forest park catenae of FES and Petrozavodsk have been studied using the sorption lysimeter method. From the forest floor covering in the sod-podzoluvisols of the mid-taiga forest park, the loss of C_{org} to WOS averaged 10,9 g/m^2 , penetrating deeper into the profile it averaged 7.2 g/m^2 C_{org} (observations from 16.07. to 12.11.2011) - it is the autumn migration peak; in the sod-podzols of FES (an annual observation cycle) in the placor, WOS loss is found to be about 3.8-10.1 and in the middle parts of sloppy hills - about 3.5-12.3 g/m^2 . The downward water migration of soil formation products on sod-podzoluvisols occurs in clay-formed profile. In the dry seasons, the EL_{hg} and B_{hg} horizons become heavily compacted, segregation of Fe and Mn compounds into small nodules can be observed, where also HM ions are attracted. When migrating through the illuvial-ferruginous barrier in WOS composition FK content significantly increases, which is connected with complex formations and transformation of hydrogels of aluminum and iron hydroxides.

5. The biogenic acidity status of a boreal ecosystem has been formulated. It reflects one of living organisms' adaptation mechanisms to the adverse environmental conditions in the taiga zone. The components of WOS not only mobilize HM ions into the solution, but also inactivate their toxic properties when complex formation takes place. During water migration, regular soil self-cleaning in the lateral networks of the elementary geochemical landscapes occurs.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ ПОЧВЕННОЙ БИОГЕННОЙ КИСЛОТНОСТИ НА ПОДЗОЛООБРАЗОВАНИЕ

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Аннотация: Рассмотрены и обобщены сведения о формах почвенной биогенной кислотности на примере изучения подзолов на двучленах и таежных экосистем Центрально-лесного биосферного заповедника (ЦЛГПБЗ) в Тверской области, Лесной опытной дачи (ЛОД) РГАУ-МСХА имени К.А. Тимирязева (г. Москва) и стационара в таежном лесопарке Петрозаводска*. Мониторинг форм кислотности проводится авторами с 2002 по 2012 гг. Отмечено, что при изучении кислотности существуют два научных направления: химическое и почвенно-экологическое. Первое охватывает почвы аграрных экосистем и предопределяет регулирование кислотности путем известкования. Почвенно-экологическая оценка связана с диагностикой биогенной кислотности таежной экосистемы и учитывает биогеохимический круговорот органического углерода, формирование при фотосинтезе и гумификации низкомолекулярных органических кислот (НМОК), полифенолов и фульвокислот (ФК). Оценку биогенной кислотности осуществляли путем изучения водной миграции ВОВ с кислотными свойствами. Для этого использовали метод сорбционных лизиметров (МСЛ). Установлено, что дерново-подзолы старо возрастных посадок лиственницы и сосны Лесной опытной дачи и ЦЛГПБЗ, а также подзолы стационара «Петрозаводский» отличаются наиболее высокими значениями H_e и актуальной кислотности. Этот факт генетически связан с мобилизацией в раствор ВОВ и ФК с кислотными свойствами. Вынос соединений Fe, Al из верхних горизонтов подзолов наблюдается после заметного обеднения минералов ионами кальция и магния. Поверхностное оглеение дерново-подзолов сопряжено с внутриверхневым глееобразованием (на контакте смены пород) и активизирует латеральный вынос ионов Ca^{2+} , Mg^{2+} , а также Fe^{3+} , Al^{3+} при участии ВОВ. В дерново-подзолах ЛОД вынос ВОВ из гор. A_0 достигает $24 \text{ г/м}^2 \text{ C}_{орг}$ за осенний период (это один главных пиков миграции), а из гор. A_0^m стационара «Петрозаводский» — $16-21 \text{ г/м}^2$.

Ключевые слова: кислотность, подзолы и дерново-подзолы на двучленах, сорбционные лизиметры, трансформация соединений алюминия, водорастворимые органические вещества с кислотными и комплексообразующими свойствами.

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