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Biogeochemical Processes in Urban Soils: A Study of Ecosystems Developing in Large (Isolated) Lysimeters at the Moscow State University Soil Station

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Abstract—The operation of stationary soil lysimeters is largely determined by the areal and vertical limitations of the soil mass. The areal spatial limitations of large lysimeters operating at the Moscow State University Soil Station and the proximity of phytocoenoses developing in them to each other contribute to the additional transport of plant litterfall by wind, while the vertical limitations eliminate the role of groundwaters and their soil-forming effects. The absence of lateral subsurface flow that is typical for natural landscapes and the increased inflow of alkaline-earth elements with atmospheric precipitation and dust reduce the manifestation of the eluvial–illuvial process. Comparative analysis of lysimetric waters in 1967–1968 and in 2014–2015 shows a significant increase in concentrations of such cations as calcium, sodium, magnesium, and potassium and such anions as chloride and sulfate over this period. The local spatial geochemical contrast of lysimetric waters caused by the impact of deicing agents does not affect the relative migration capacity of elements. Based on their biogeochemical accumulation levels in the soil, macroelements form the following series $\text{Ca} > \text{K} > \text{Al} > \text{Mg} > \text{N}$; microelements: $\text{Zn} > \text{Sr} > \text{Cu} > \text{Ba}$. The above patterns persist in all types of lysimeters. The calcium concentration in soils increases in the series: broadleaf forest > mixed forest > spruce forest > black fallow. The increased accumulation of elements in soils of spruce forests correlates with the humus type (moder-like) formed under them; this humus type is determined by the combination of coniferous and deciduous litterfall.

Keywords: biogeochemistry, primary soil formation, macroelements, microelements, deicing agents, atmospheric precipitation

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INTRODUCTION

The history of lysimetric observations goes back more than 300 years, but precision lysimetry started developing only in the last 50 years [30]. In the early 1970s [22] and late 1990s [2], Russian specialists produced reviews of literature on lysimetric studies. Currently, lysimeters are used in several fields. The first field relates to the lysimeter usage methodology in soil science and environmental studies [23]. The second field involves the development of mass transport models, studies of the kinetics of soil processes [13], and temperature regime modeling [2]. The third field includes lysimetric studies of soil properties in various natural conditions [3, 15]. All these fields of research are presented in studies carried out at the Moscow State University Soil Station since 1961 and involving large piled lysimeters ([7, 8, 10, 14, 21], etc.).

Distinctive features of piled lysimeters at the Moscow State University Soil Station are their vertical and

areal limitations. The areal limitations with closely spaced (within 1 m) types of phytocoenoses result in an active interbiogeocoenotic exchange of plant litterfall that is also observed in natural phytocoenoses. An essential feature of the vertical limitations and lysimeter design is the elimination of active groundwater effects on the soil formation processes due to the disturbance of interactions between capillary supported and capillary perched waters (these phenomena are typical for the humid soil formation zone). The horizontal position of the lysimeters excludes the full-scale lateral subsurface runoff whose role in the eluvial–illuvial soil formation was emphasized by N.P. Remezov [17]. N.P. Remezov writes: “what calls attention to itself is the significant value of the subsurface horizontal runoff under the forest.” The horizontal runoff can exceed the vertical one by 7.5 times on slopes in sod–podzolic loamy soils. This migration type is addressed in landscape geochemistry at the regional and local

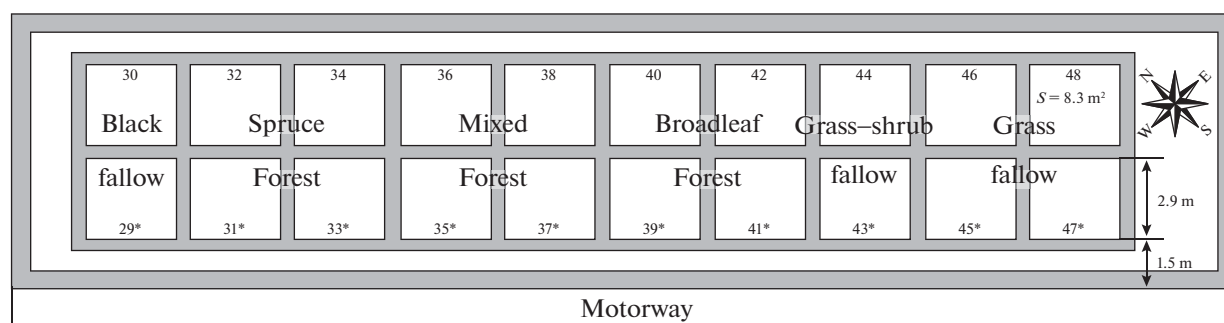


Fig. 1. Physical layout of lysimeters, their numbers, and types of phytocoenoses (lysimeters marked by the * character are located in the zone affected by deicing agents).

levels. It is established that magnetic particles [9] and colloids labeled with deuterium and DNA can be successfully used in migration-related studies, both in inclined lysimeters and in natural landscapes, with the purpose to get an understanding of transport processes [25] in catchment landscapes.

In urban conditions, the operation of lysimeters is affected by the increased impacts of dust [27] and heavy metals [14, 26, 28] that are often combined with polycyclic hydrocarbons [29].

The purpose of this study was to highlight some new aspects of modern biogeochemical processes observed in lysimeters in urban conditions, including litterfall inflow patterns, turnover degree determination, and migration of macro- and microelements under modern pollution conditions, including the impacts of deicing agents and atmospheric dust.

This article is dedicated to the memory of Aleksandr Petrovich Lobutev, one of the first researchers of large lysimeters at the Moscow State University Soil Station.

MATERIALS AND METHODS

The subjects of this study were the large lysimeters at the Moscow State University Soil Station. The lysimeters are filled with mantle clay loam from the Podolsk quarry, Moscow oblast. The total depth of lysimeters reaches 1.75 m [7]. Each lysimeter, except the for black fallow, represents a distinct phytocoenosis type: spruce forest, mixed forest, broadleaf forest, grass-shrub fallow, and grass fallow; the area of each phytocoenosis is 8 m² (Fig. 1). Receivers for lysimetric solutions are located in the lower part of the lysimeters. The lysimetric water inflow was continuously monitored throughout the year, including monthly water samplings. To compare the composition of the studied lysimetric waters with those in natural objects within landscapes typical for the coniferous-broadleaf zone, the snow cover and natural waters were studied at Chashnikovo Training and Experimental Soil Ecological Center of the Moscow State University (Moscow oblast). The snow cover was studied in

2013–2019 within a geochemical landscape sequentially encompassing the eluvial, transit, transit-accumulative, and supraqual landscapes of the Klyazma River (56.052541° N, 37.178749° E); the snow cover depth in each landscape was measured with a 50-fold replication. The seasonal studies of natural waters in the same periods were carried out in the system “springs—streams—ponds—Klyazma River” in the same geographical conditions. The collected data on the snow cover and natural waters have been published earlier (6). This study uses long-time average annual data on the composition of natural waters. The snow cover depth on sites accommodating the large lysimeters of the Moscow State University was measured with at least a 10–15-fold replication for each lysimeter with subsequent snow cover density measurements.

The litterfall dynamics were studied using round litterfall collectors 36 cm in diameter and some 30–40 cm in height consisting of wire frames and removable bags secured on the frames with clothespins. Terylen bags with a mesh size of 1.3 mm were used for deciduous phytocoenoses. Bags made of nonwoven polymer fabric (spunbond) were used as litterfall collectors in phytocoenoses where litterfall includes substantial amounts of small needles. Litterfall collectors 36 cm in diameter have been used since June 29, 2015, through today: one litterfall collector per each of the 20 lysimeters. The litterfall accumulation periods roughly correspond to the growing seasons: litterfall collection is usually performed prior to the beginning of the leaf fall period (late September–early October), then at the end of the leaf fall period (late November–early December), immediately after the snow melt (March–April), and after the frondescence (beginning of June). A large litterfall collector occupies 1.23% of the lysimeter area. The continuous litterfall collection has been commenced in October 2013. Accordingly, this paper presents litterfall monitoring data for a 6-year period (2013–2019).

Litters were sampled layer by layer from plots 25 × 20 cm in size; to minimize the impact on the soil cover of the lysimeters, the number of sampling plots was limited to two plots per lysimeter. In autumn 2020, the

litter sampling was performed after the leaf fall completion with the purpose of computing the litterfall litter reserves for this year. It is impractical to measure litter reserves in the summer period since they are represented at that time by the last year's partially decomposed litterfall, and their values are minimum. The litter was separated into the following subhorizons: O1 (litter), O2 (enzymatic subhorizon representing litterfall of past years, partially decomposed but retaining its structure), and O3 (humified horizon, usually of dark tones, representing well-decomposed plant residues). Then the litters were sorted out according to their fractional composition and, if necessary, sifted through a sieve. Parts of the litter horizon containing organomineral fractions representing, in fact, mineral admixtures in the detritus (in the lowest litter horizons) were not used in computations of the litter–litterfall coefficient. The litters were classified in accordance with the author's methodology [5]. Dust precipitation on the soil surface of lysimeters was studied in July–September 2015: 25 special plastic containers with a fixed mass and an area of $7.8 \times 10^{-3} \text{ m}^2$ were exposed for 40 days on a flat surface located at a height of 80–100 cm above the ground. Large fragments of plant litterfall were removed from the containers prior to the weighing. The dust impact was computed using the formula: $P_n = P_0/(St)$ where P_0 is the weight (g), S is the container area (m^2), and t is the number of days.

The dust samples obtained were studied morphologically using a binocular magnifying glass at a magnification of $\times 32$ – $\times 56$. Submicromorphological analysis and elemental analysis of the samples were performed at the Institute of Geography, Russian Academy of Sciences, using a JEOL 6610 LV scanning electron microscope (SEM) with an INCA XACT energy-dispersive microanalyzer (microscopist V.A. Shishkov, Ph.D.). Such systems are used for the collection of atmospheric dust aerosol with subsequent examination of the particle morphology and composition both in treeless areas and in the taiga zone [20, 24].

Atmospheric precipitation was collected in polyethylene containers 15 cm in diameter and 25 cm in height; the containers were installed on the snow cover surface; sampling and subsequent melting were performed on a regular basis. The same containers were used in studies carried out at Chashnikovo Training and Experimental Soil Ecological Center.

The large lysimeters of the Moscow State University are located 1.5 meters from a motorway (Fig. 1). As a result, 50% of their areas directly contacting with the road were affected in winter by deicing agents dispersed by trucks. The other parts of the lysimeters were not affected by deicing agents. Subsequent snow melting and liquid atmospheric precipitation resulted in the dissolution of deicing chemicals and their inflow into lysimetric waters. Currently, the lysimetric sites are fenced with monolithic polycarbonate sheets

80 cm high that prevent the inflow of deicing agents on the surface of the lysimeters.

Concentrations of macro- and microelements in lysimetric and natural waters and in aqueous extracts of deicing agents at (sample to water ratio = 1 : 5 [1]) were measured using an AAS-3 atomic absorption spectrophotometer. In the case of low concentrations, inductively coupled plasma mass spectrometry (an Agilent 7500a ICP-MS spectrometer) was used. Concentrations of anions were measured with a Dionex 2000 ion chromatography system. The total content of macro- and microelements in the soil was determined using the method described by A.I. Obukhov and I.O. Plekhanova (16).

To assess the mantle clay loam transformation degree in the course of soil formation, biogeochemical accumulation coefficients were computed as ratios between the content of macro- and microelements in the upper mineral soil horizons (0–10 cm) under various phytocoenoses and their content at a depth of 1 m in the black fallow soil conditionally taken as the control variant.

RESULTS

Litterfall Decomposition and Accumulation

The studies have shown that for the black fallow, the average annual litterfall inflow (mainly fallen leaves transported from adjacent phytocoenoses) amounts to 31 g/m^2 . The long-time average annual litterfall inflow values gradually increase in the series: grass fallow—grass—shrub fallow—spruce forest—mixed forest—broadleaf forest; in the last phytocoenosis, the annual litterfall inflow reaches the maximum value: 633 g/m^2 (Table 1). The lowest variation in the average annual litterfall inflow was registered in broadleaf phytocoenoses followed by mixed phytocoenoses, fallow lands, and black fallow. The greatest range of average annual litterfall inflow values was registered in the spruce forest: from 31 to 76%.

It is necessary to note a high share of active fractions in the litterfall: from 70 to 90%. The seasonal litterfall inflow contrast is determined by the litterfall share entering the soil surface in the leaf fall period (Table 1). Expectedly, the lowest degree of contrast was registered in broadleaf phytocoenoses and soils of lysimeters under fallow lands.

The minimum contrast degree values are typical for spruce phytocoenoses since needles fall off throughout the year and their fall is not strictly confined to the autumn period. It is necessary to note that the litterfall inflow to the black fallow is also unrelated to the autumn leaf fall period due to the close contact between the black fallow and the spruce phytocoenosis. By the relative degree of contrast in terms of the annual litterfall (taking its inflow in the broadleaf forest as a unit), the phytocoenoses form the following sequential series: broadleaf forest—grass—shrub fal-

Table 1. Main litterfall inflow parameters computed for lysimeters at the Moscow State University Soil Station (2013–2019). $N = 596$

Phytocoenosis	Lysimeter no.	Average annual litterfall inflow ($\text{g}/\text{m}^2\cdot\text{year} \pm \text{variation coefficient } V (n = 6) (\%)$)		Active fractions** (% of the average annual value)		Inflow in leaf fall periods (October –November)			
						Mean value ($\text{g}/\text{m}^2 \pm \text{variation coefficient } V (n = 6) (\%)$)		Share in the average annual value	
Black fallow	29	$26.3 \pm 54\%$	*31.1	99.7	73.9	$16.8 \pm 67\%$	13.6	0.64	0.46
	30	$35.8 \pm 59\%$		48.0		$10.4 \pm 24\%$		0.29	
Spruce forest	31	$169.4 \pm 76\%$	332.2	81.8	90.1	$88.9 \pm 113\%$	166.0	0.53	0.51
	32	$410.0 \pm 50\%$		94.9		$185.1 \pm 85\%$		0.45	
	33	$304.5 \pm 31\%$		89.3		$189.6 \pm 44\%$		0.62	
	34	$445.0 \pm 49\%$		94.3		$200.5 \pm 86\%$		0.45	
Mixed forest	35	$391.1 \pm 36\%$	436.4	96.6	89.1	$221.9 \pm 38\%$	278.1	0.57	0.64
	36	$500.4 \pm 43\%$		83.9		$291.2 \pm 71\%$		0.58	
	37	$430.4 \pm 26\%$		87.0		$299.7 \pm 38\%$		0.70	
	38	$423.7 \pm 20\%$		89.0		$299.6 \pm 27\%$		0.71	
Broadleaf forest	39	$498.1 \pm 33\%$	633.4	92.8	89.1	$385.5 \pm 44\%$	504.2	0.77	0.79
	40	$576.7 \pm 13\%$		91.7		$459.4 \pm 15\%$		0.80	
	41	$714.8 \pm 18\%$		85.9		$561.6 \pm 22\%$		0.79	
	42	$744.0 \pm 30\%$		85.8		$610.2 \pm 38\%$		0.82	
Grass–shrub fallow	43	$501.5 \pm 48\%$	533.1	94.6	92.5	$396.5 \pm 47\%$	435.1	0.79	0.82
	44	$564.7 \pm 39\%$		90.4		$473.7 \pm 30\%$		0.84	
Grass fallow	45	$234.4 \pm 48\%$	206.8	99.3	99.3	$197.3 \pm 24\%$	175.3	0.84	0.85
	46	$268.1 \pm 33\%$		98.6		$217.0 \pm 35\%$		0.81	
	47	$168.1 \pm 69\%$		99.1		$152.8 \pm 75\%$		0.91	
	48	$156.5 \pm 45\%$		100.0		$134.1 \pm 51\%$		0.86	

*Merged cells provide mean litterfall inflow values computed for each group of lysimeters. **Leaves, needles, seeds, etc.

low—mixed forest—spruce forest—grass fallow—black fallow (1 : 0.8 : 0.7 : 0.7 : 0.3).

The obtained data on the interbiogeocoenotic litterfall exchange indicate that in pure spruce forests, the leaf fall share amounts to 20% on an average; by contrast, the needle fall share in broadleaf stands is pretty low and does not exceed 3% of the total annual inflow. In the grass fallow, the share of transported foliage reaches 40%. The collected data on the litter morphology indicate that degradative, enzymatic, and humified litter types are typical for spruce forests; while enzymatic and humified types, for broadleaf and mixed phytocoenoses. The total litter reserves reach $2831 \text{ g}/\text{m}^2$ in the spruce forest, $3913 \text{ g}/\text{m}^2$ in the mixed forest, and $2926 \text{ g}/\text{m}^2$ in broadleaf phytocoenoses. Concurrently, the variation in litter reserves ranges from 700 to $800 \text{ g}/\text{m}^2$ in each phytocoenosis. The litter–litterfall coefficients computed as the ratio between average organic matter reserves contained in litter and

litterfall vary within the range of 6–8, thus, making it possible to characterize the turnover degree as inhibited and overinhibited in accordance with the classification proposed by L.E. Rodina and N.I. Bazilevich [18]. Comparison of average annual litterfall inflow values for the period of 2013–2019 with the litterfall inflow data collected in 1999 [8] indicates that they are quite consistent.

Chemical Composition of Lysimetric Waters

The chemical composition of lysimeters is determined by a number of factors. First, changes occur over time due to the increasing volume of elements involved in the cycle, which is caused by the general growth of phytomass. Comparative analysis of lysimetric waters in 1967–1968 and in 2014–2015 shows a significant increase in their mineralization (Table 2).

It is necessary to specially note a significant increase in the potassium, calcium, and magnesium

Table 2. Averaged composition of lysimetric waters in 2014–2015/1967–1968 (mg/L), $n = 138$

Lysimeter type	Ca	Mg	Na	K	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	N	PO ₄ ³⁻	Al	Fe
Black fallow ($n = 20$)	7.21	2.11	4.66	0.57	3.94	37.98	35.99	0.16	0.02	1.46	0.27
	28.09	7.33	9.86	2.56	10.44	119.18	31.52	Traces	Traces	Traces	Traces
Spruce forest ($n = 16$)	62.54	14.22	19.58	8.53	111.38	69.27	65.58	0.34	Traces	Traces	Traces
	20.99	5.67	8.57	1.09	9.99	105.19	29.89	Traces	Traces	Traces	Traces
Mixed forest ($n = 7$)	88.78	20.79	34.46	23.72	165.89	169.79	59.48	0.91	0.20	Traces	Traces
	21.43	4.60	8.30	0.80	8.55	105.12	25.10	Traces	Traces	Traces	Traces
Broadleaf forest ($n = 31$)	95.21	24.57	22.72	4.26	80.66	38.48	51.51	0.32	0.14	0.57	0.13
	18.39	5.14	8.07	0.59	8.08	112.74	23.58	Traces	Traces	Traces	Traces
Fallow land ($n = 64$)	23.86	6.12	10.31	6.30	56.90	22.99	57.78	0.37	0.47	3.24	1.26
	14.69	4.00	8.79	0.69	8.86	108.24	21.51	Traces	Traces	Traces	Traces
Mean	55.52	13.56	18.35	8.68	83.76	67.70	54.07	0.42	0.17	1.76	0.33
	20.72	5.35	8.72	1.15	9.18	110.10	26.32	Traces	Traces	Traces	Traces

concentrations, an increase in the chloride ion concentration, and an upward trend in the migration of phosphate ions in all lysimetric waters over the studied period. The general series reflecting the increase in the average concentration of water-soluble components in lysimetric waters of all phytocoenoses at present time in comparison with the period of 1967–1968 is as follows: $\text{Cl}_{18}\text{K}_6\text{Ca}_2 = \text{Mg}_2\text{Na}_{1.7}$. The greatest increase in the content of the main components is observed in modern lysimetric waters of mixed and broadleaf phytocoenoses followed by the spruce forest.

Statistical analysis shows that, in general, the content of macro- and microelements in lysimetric waters in unpolluted phytocoenoses demonstrates in the long-term perspective a pretty high variability. This is explained not only by the differences between phytocoenoses, but also by conditions of various years.

Concurrently, it turned out that lysimetric waters under the black fallow are distinguished by the lowest variability of their composition at the minimum concentrations of elements: the average variation coefficient for such leading elements as sodium, magnesium, potassium, and calcium amounts to 43%. In lysimetric waters under mixed and broadleaf forests, the value of this parameter increases to 70%; in fallow conditions, to 90%; and the same variability level is typical for lysimetric waters under spruce phytocoenoses.

Abiotic Conditions Affecting the Operation of Large Lysimeters at the Moscow State University

A distinctive feature of the modern operation of large lysimeters at the Moscow State University Soil Station in urban conditions is the additional inflow of biophile element with atmospheric precipitation. Comparison of snow waters at Chashnikovo Training and Experimental Soil Ecological Center and snow

waters of large soil lysimeters confirms this. In Chashnikovo, the average calcium content in snow waters is 2.7 mg/L; in the Botanical Garden of the Moscow State University, 4.5 mg/L; while in large soil lysimeters, it increases to 8.5 mg/L.

This pattern is consistent with the precipitation composition. It is established that solid winter precipitation in urban conditions is significantly enriched in calcium, magnesium, sodium, and potassium in comparison with precipitation in relatively unpolluted landscapes of Moscow oblast. This aspect has been discussed in more detail in one of our earlier publications [6].

Additional studies have shown that the annual inflow of dust to large lysimeters at the soil station is up to 37 g/m², which indicates a low pollution level. The modern values are of the same magnitude with the data collected back in 1989 [10], which indicates a long-term and constant dust inflow level. Micromorphological studies indicate that, in addition to silicate grains, atmospheric precipitation contains mineral grains forming black microaggregates with a characteristic oily shine: asphalt particles (Fig. 2). White isomorphic aggregates consisting of salts or a mixture of salts and silicate particles (solid contraction mortars), as well as metal magnetic particles and fragments of red asphalt are present in large numbers.

Overall, clastic and rounded (apparently, transported over long distances) particles are noted regardless of the composition. Particles constituting the air plankton are present as well: fragments of fungal mycelium, red–brown algae, pollen, fragments of invertebrate bodies, and plant microfragments.

It is established that C, O, and Si are the predominant elements in almost all dust samples (hydrogen is excluded from the studied spectra). Aside from the high calcium content, dust contains such biophile elements as Mg, Fe, Na, K, S, and Cl. It is necessary to

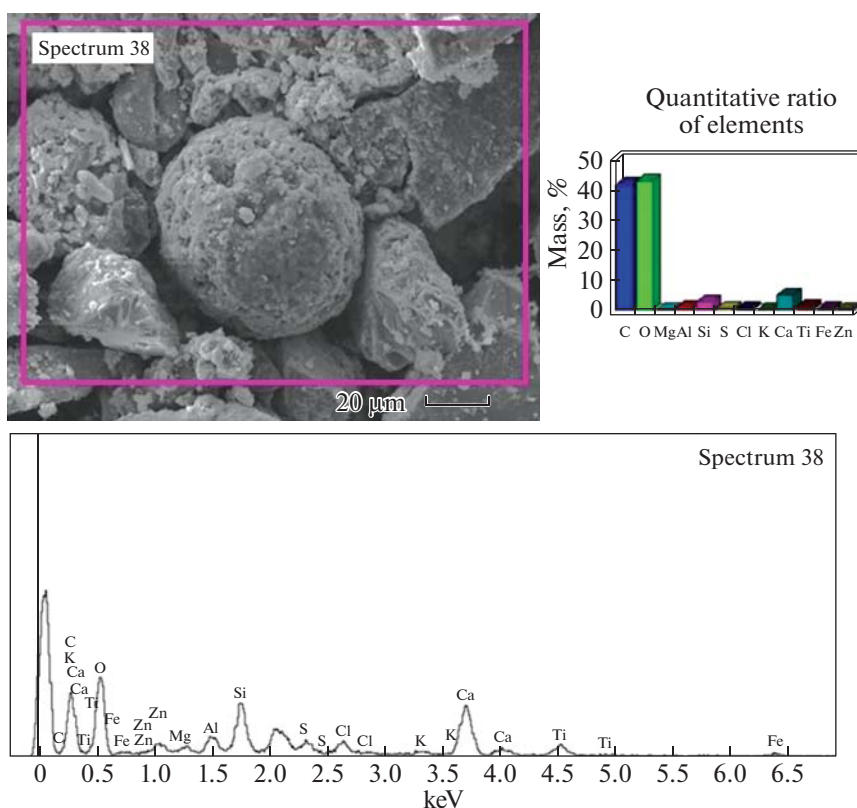


Fig. 2. SEM image of summer dust aerosol, its composition, and quantitative ratio of elements.

note that the microanalyzer detects only those elements whose concentration is close to 1% or more. Zn can be present in the spectra due to the motor transport impact, while Ti can enter the dust aerosol from soils, rocks, construction materials, and with technogenic magnetic particles.

The content of Si, Fe, Mg, and Al is high because soil and rock mineral particles constitute the bulk of the dust aerosol; this applies both to particles raised from the soil and ground surface and to those used in artificial materials (road surfaces, construction materials, etc.).

Another abiotic factor of anthropogenic origin is the impact of deicing agents [4]. Deicing reagents contain large amounts of calcium and potassium, as well as such anions as chloride, sulfate, and bromide. Microelements are represented by strontium, zinc, and iron (Table 3). The subsequent dissolution of deicing agents by snow waters and liquid atmospheric precipitation caused the differentiation of lysimeters by the composition of migrating waters. Comparative analysis of lysimetric waters contaminated by deicing agents and waters in lysimeters located far from the road shows that the average contamination degrees form the following series for all studied lysimeters: $\text{NO}_3 16 > \text{Cl} 8 > \text{Ca} 5 > \text{Mg} 4 > \text{Na} 2 = \text{N} 2 = \text{K} 2 > \text{Cl} 1.7 > \text{F} 1.4 > \text{SO}_4 0.7$. The highest contamination levels were

registered for nitrate, phosphate, and chloride ions. Currently, the lysimeters are shielded from the road by a monolithic polycarbonate fence that prevents the inflow of deicing agents on the surface of the lysimeters.

Expectedly, the highest contamination levels were registered for the most mobile nitrate and chloride ions present in deicing agents. Water migration coefficients computed for lysimetric waters indicate that calcium, magnesium, and sodium demonstrate the highest relative migration capacity in conditions relatively remote from the pollution source; among anions, sulfates feature the highest relative migration capacity. In phytocoenoses contaminated with deicing agents, the average migration capacity of calcium and magnesium remains at the same level as in phytocoenoses located outside the active contamination zone.

Biogeochemistry of Macro- and Microelements in Soils of Large Lysimeters of the Moscow State University

The computed biogeochemical accumulation coefficients (BACs) make it possible to assess the current trend in the nature of changes observed in the uppermost mineral horizons of soils formed under various phytocoenoses (Fig. 3).

It is established that the same type of geochemical spectra remains in all soils formed under various phy-

toconoses (Fig. 3), including the studied macroelements, elements of the iron family, zinc, and strontium. However, the coefficient values vary in a broad range. For instance, weak leaching of the majority of the studied macro- and microelements ($BAC = 0.8-1$), including iron, is typical for the upper soil horizons of the black fallow, except for zinc ($BAC = 2.5$) and mercury ($BAC = 3.4$). By contrast, a clearly manifested macroelement accumulation trend is observed in soils under tree stands; among them, calcium ($BAC = 2.6-6.2$), attracts special attention. With regards to microelements, the accumulation of zinc in soils under tree stands ($BAC = 9.5-15$) is especially characteristic, as is, to a lesser degree, the accumulation of strontium, barium, and lead.

DISCUSSION

The time of biogeochemical processes can be counted from the moment of differentiation of lysimeters by the types of phytocoenoses developing in them. This differentiation determined the formation of certain types of litterfall, and, eventually, different types of litter. According to M.A. Glazovskaya [11], detritogenesis, as a biogeochemical process, is the accumulation of underoxidized organic materials in landscapes, including litterfall and litter.

The discovered interbiogeocoenotic transport of leaf fall to spruce ecosystems results in partial neutralization of inflowing acidic needle fall products that play the role of so-called 'hot spots' intensifying the litterfall decomposition. This phenomenon results in the convergence of the forming forest humus types in the "spruce forest—broadleaf stands" series; in [19], this humus type is defined as moder-like. This is consistent with the litter typology described above. What

Table 3. Concentrations of macro- and microelements in deicing agents (mg/kg) based on the analysis of their aqueous extracts in 2013–2014 ($n = 3$)

Component	Concentration (mg/kg)
P	Traces
K	1088.6
Ca	66076.9
Ti	Traces
Mn	Traces
Fe	35.8
Ni	7.0
Cu	10.5
Zn	31.3
As	Traces
Sr	153.3
Pb	Traces
F (–)	Traces
Cl (–)	472484.0
Br (–)	674.7
NO ₃ (–)	25.3
SO ₄ (2–)	9964.8

calls attention to itself is the complex structure of litters under broadleaf stands: in the zone of coniferous—deciduous forests such phytocoenoses normally feature degradative litters; most of those are undifferentiated into subhorizons and represent litterfall of past years. The significantly reduced turnover degrees presented above do not raise doubts in the case of spruce and mixed forests; however, with regards to broadleaf

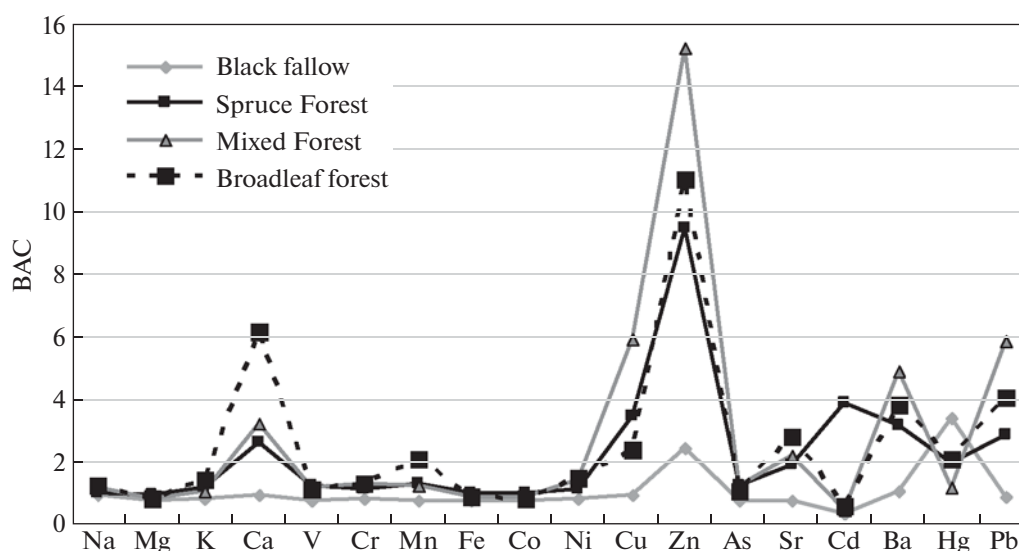


Fig. 3. Biogeochemical accumulation coefficients (BACs) of macro- and microelements in the upper soil horizons computed for various types of lysimeters.

stands, they seem somewhat unexpected. So, what is the turnover inhibition mechanism in broadleaf stands developing in a lysimeter? The point is that the litter-fall inflow in the broadleaf phytocoenoses is limited by concrete walls of lysimeters towering above the soil surface; as a result, the formed litters are up to 10–15 cm thick and feature a distinctive and clearly manifested layered structure. Stagnant moisture and poor ventilation increase the litter depth and decrease the turnover degree. By contrast, thin and usually degradative litters are typical for the Botanical Garden of the Moscow State University. Therefore, the design of large lysimeters that inherently determines the litter decomposition features in spaces limited by concrete walls must be recognized a specific condition. This condition is characteristic exclusively for the described objects and cannot be fully applied to natural phytocoenoses (although it can characterize anthropogenically created ones, including urban greening). The formation of phytocoenoses accompanied by litter divergence has consistently led to the differentiation of modern lysimetric waters in terms of their chemical composition. Two key factors determine the current specifics of lysimetric waters. The first one is the inflow of a number of elements with dust and atmospheric precipitation; these elements have an eutrophication effect on soils. The second factor relates to deicing agents that cause an inflow of chloride ions and other anions and cations into lysimetric waters.

Long-term leaching of mantle clay loam in conditions of the black fallow or even a fallow land functioning for a long time without active biological cycle (that is present under the forest canopy) results in a noticeable increase in concentrations of the main components of lysimetric waters amid minimal changes in the black fallow and fallow land conditions. In addition, the minimum variation in the composition of lysimetric waters observed in the black fallow expectedly increases under woody vegetation due to both the uneven annual litterfall inflow and its interbiogeocoenotic transport. Distinctive features of phytocoenoses are expectedly reflected in patterns determining the accumulation of elements in the soil. Weak accumulation of elements is typical for the upper horizons of the black fallow; by contrast, in soils formed under vegetation, the accumulation of elements is intense. For instance, the relatively high level of calcium accumulation in soils under broadleaf stands is quite natural and can be trivially explained by the nature of the biogeochemical cycle. The accumulation of zinc, in our opinion, is explained not only by its inflow with dust and atmospheric precipitation, but also by the fact that the lysimetric site remained for a long time under a zinc-plated grid; this grid could serve as a source of additional accumulation of this element on the surface of the forming soils. Therefore, the aerial contamination of lysimeters that eutrophicates soils in urban conditions serves as an additional factor determining the specifics of biogeochemical

processes. Integrally, the general balance of elements and organic matter in the studied lysimeters is determined primarily by the vertical outflow with a minimum lateral component. A similar situation can develop in natural conditions in vast leveled areas with a deep groundwater level. Such landscapes probably can be defined as a subtype of eluvial landscapes with chorilateral-subsoil functioning (“choris” means “without” in Greek).

CONCLUSIONS

The observed differences in the rates of biogeochemical processes in large lysimeters at the Moscow State University Soil Station are determined by the types of phytocoenoses; due to the proximity of the lysimeters, these differences are partially reduced by the interbiogeocoenotic litterfall exchange. The inflow of deicing agents on the soil surface in a number of lysimeters results in uniformly elevated concentrations of alkaline and alkaline-earth elements in lysimetric waters; this also applies to chloride ions. The main modern trend in the composition of lysimetric waters in comparison with the 1960s is the biogeochemical intensification of migration processes of such elements as calcium, magnesium, phosphorus, and potassium. Unlike black fallow soils, the upper soil horizons under tree stands actively accumulate calcium and zinc. The accumulation of macro- and microelements in soils under spruce phytocoenoses confirms the hypothesis about the dualistic nature of spruce stands proposed by L.O. Karpachevsky, one of the brilliant researchers of forest soils: in favorable soil conditions, spruce stands enhance soils; but in soils formed on rocks with poor mineralogical composition, they intensify the podzolization processes.

The weak leaching of iron from the upper soil horizons ($BAC = 0.8–1$) confirms the findings of the previous study [19]: in large lysimeters at the Moscow State University Soil Station, soils develop according to the burozemic type with slight illimerization signs. The absence of lateral runoff and groundwaters is one of the reasons why the eluvial–illuvial differentiation of soils in lysimeters is manifested poorly amid the continuous aerial inflow of calcium and accompanying elements.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of Interest

The authors declare that they have no conflicts of interest.

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