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SOIL CHEMISTRY

Effect of Individual Trees on the pH and the Content of Heavy Metals in Forest Litters upon Industrial Contamination

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Abstract—The influence of individual spruce and birch trees on the distribution of heavy metals (Cu, Pb, Cd, and Zn) and hydrogen ions in the forest litter is considered in a territory subjected to long-term industrial pollution by emissions of the Ural copper smelter (town of Revda, Sverdlovsk oblast, southern taiga). In the background territory, the content of the elements regularly decreases from the tree trunks to the canopy gaps, whereas, in the contaminated territory, this relationship is either not traced at all (for the metal concentrations) or more weakly pronounced (for the metal reserves and pH values). The influence of trees on the spatial distribution of metals in the litter is specific for various elements and differs in coniferous and deciduous biotopes.

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INTRODUCTION

The analysis of individual trees' influence on the morphological, physicochemical, and biological properties appears to be a classic problem in forest soil science [6, 7, 10, 11, 18, 51, 62]. The regularities of the atmospheric precipitation pattern, as well as of the macro- and microelement ions in it redistributed by the tree crowns, have been intensely studied in forest hydrology and the biogeochemistry of forest landscapes [5, 22, 29, 44–46]. There are numerous investigations of trees' influence on the light, heat, and wind habitat regimes [43]; the living soil cover [13]; and the tree stand regeneration [60]. These investigations are actual, because the results obtained permit us to elucidate the mechanisms of the formation of both the soil cover and forest ecosystems as a whole, to understand the regularities in biogeochemical cycles of substances in forest landscapes, to revise the parameters of the hydrological and biochemical models for areas covered by forests, and to work out adequate methodological approbation schemes for assessing the content of elements in the environment.

In most cases, this problem has been studied in places not suffering from heavy local technogenic loads. A number of investigations considered the role of trees in modifying the chemical composition of the atmospheric precipitation in places with a high regional level of pollution ingress [26, 34, 41, 53, 54]. Although the heavy metal (HM) flux patterns have been comprehensively studied in ecosystems [29], publications are scarce that scrutinize the role of trees in the biochemical cycle modification in a markedly pronounced pollution gradient caused by point sources of industrial emissions. The few studies performed near smelters in Finland [50], Chile [36], and England [58] and on the Kola Peninsula [1, 16, 17, 19, 20] are exceptions. Similarly, only a few works have investigated the influence of trees on the microclimate and subordinate vegetation stories in technogenically affected territories [8, 32, 63]. The insufficiency of the data on sites around industrial enterprises prevents us from drawing conclusions about to what extent the modifying role of trees changes under technogenic loads.

The present investigation is aimed at the analysis of the tree influence on the distribution of the pH and heavy metals in the forest litter upon strong industrial pollution. Two working hypotheses that proceed from the following facts were checked in the course of our work. On the one hand, the suppression of trees by industrial pollution, which is manifested in the thinning of a forest stand, as well as the tree crowns, appears to be a well documented fact [38]. On the other hand, a positive correlation exists between the degree of the forest crown development and the strength of its environmental effect [44, 45]. Therefore, the first hypothesis implies that the effect of trees on the distribution of pollutants is weaker in technogenically affected territories as compared to the undisturbed areas, while the second hypothesis suggests that the difference of the modifying effect between coniferous and deciduous trees becomes less in technogenic territories.

The content of four heavy metals, i.e., Cu, Pb, Cd, and Zn, in the litters was assessed in this work. These particular elements were chosen because, first, they are highly toxic for terrestrial biota; second, they prevail in the solid phase of emissions from the enterprises of the regarded type; and, third, they are more easily determined analytically as compared to other toxicants (e.g.,

As and Hg). The forest litter was selected because it is this very horizon that acts as the main depot of pollutants in the forest ecosystem. Two contrasting biotopes differing in the degree of the tree–edificator influence were investigated, i.e., the stronger effect produced in the cenoses with predominating spruce and silver fir and the weaker effect exerted by birch cenoses.

Different systems of ideas and terms describing the horizontal structure of forest ecosystems have been formed by different scientific schools. In Russian biocenology, the approach representing the horizontal forest structure as a mosaic of vegetation parcellas [7] and soil tesseras [10] is the most widespread. Many authors use the terms of gap- [60] and patch-dynamics [27] of forest ecosystems. In this study, we use the idea of a phytogenic field (or an ecological field, as referred to by other authors [57]), which appears to be a convenient theoretical construction introduced by Uranov for describing the integral effect of an individual plant on the abiotic and biotic surroundings [13]. The phytogenic field is created by the environment-forming action of both surface and subsurface plant parts, while its intensity is controlled by the allelopathic activity of a plant; the transformation degree of the light, water, temperature, and wind regimes; and the redistribution of incoming elements due to the varying chemical specifics of the crown and stem flows and the leaf fall off. The gradually decreasing intensity of this field with the increasing distance from an individual plant (a tree, in our case) appears to be the most important property of this field.

OBJECTS AND METHODS

The data were collected in 2003 in the area affected by the Mid-Urals copper smelter (SUMZ) located near the town of Revda in Sverdlovsk oblast (the southern taiga subzone). The enterprise has been operating since 1940, and it emitted above 135 thousand tons of pollutants per year in the late 1980s. Gaseous sulfur compounds and dust particles with adsorbed toxic elements (Cu, Pb, Cd, Zn, As, Hg, Fe, etc.) are the main emission constituents. The long-term impact formed zones around the smelter with different degrees of damage to the ecosystems; the shape of these zones partially fits the predominating eastward direction of the winds in the region. The studies were carried out to the west of the SUMZ, because the contamination gradient is more protracted in the eastward direction and is overlapped by the pollution zones produced by other sources (the Yekaterinburg urban agglomeration, above all).

Two biotopes that are widespread in the southern taiga of the Middle Urals, i.e., spruce–fir forests (SF) and secondary birch forests (SB), were selected. The soil cover at the studied sites is represented by combinations of mountain-forest brown, soddy–podzolic, and gray forest soils transformed by technogenic factors to different degrees.

Three modified zones were distinguished according to the higher vegetation status, i.e., the impact zone (1 km from the enterprise for the SB and 2 km for the SF), the buffer zone (5 km for the SB and 4 km for the SF), and the background zone (20 km for the SB and 30 km for the SF). The changes in the ecosystems around the SUMZ were characterized in detail earlier [3, 4, 9]. Of the many aspects of technogenic degradation of forest biocenoses, the tree storey suppression (thinning of the tree stand, decreasing of the tree stock and crown density, and increasing of the share of dead wood), the decrease of the species diversity and of the abundance of the grass–shrub storey, the slowing down of the decomposition of organic residues due to the suppressed activity of saprotrophic soil biota, and the resulting increasing thickness of the forest litter are worth noting. The manifestation of these processes differs in different zones. The background zone represents a relatively undisturbed biocenosis affected only by the regional precipitation of pollutants. In the buffer zone, the structural rearrangement of the ecosystems caused by the local pollution takes place; the development of more sustainable plant species and groups of species compensates for the destruction of the vulnerable ones; and, as a result, the intensity of the production and destruction processes is not significantly weakened. The ecosystems are most degraded in the impact zone in which the technogenic degradation of the plant communities is the severest, the structure and functioning of which radically differ from the background ones.

Ten model trees were selected in each zone and in each biotope: spruce (*Picea obovata* Ledeb.) in the SF, and birch (*Betula pubescens* Ehrh. or *B. pendula* Roth.) in the SB. The neighborhood of the forest canopy gap (but not to large meadows or the forest edges) at least to one tree side was the main selection criterion for the model trees. The model trees that were chosen had to be maximally similar in their habitus (with a trunk height of no less than 15 m, a diameter of no less than 15 cm for the birch and 30 cm for the spruce, a well developed crown, and the absence of visible mechanical damage). The distance between the model trees within one biotope in the background and buffer zones ranged within 15–80 m, and it ranged within 10–150 m in the impact zone. The diameter, height, and the area of the crown horizontal projection (the projection was approximated by eight radii) were measured for each model tree. The projection coverage of the grass–shrub and moss canopies was visually estimated (three samples 50 × 50 cm in size were collected for each tree-base site, the circumference of the crown cover, and the canopy gap).

The sampling points were allocated as follows. Three lines were chosen at an angle of no less than 45° (usually 90°–120°). Four litter samples were collected along each line: the first (I) sample was taken at the tree-base site (20–30 cm from the trunk); the second, (II) in the middle of the crown projection; the third (III), in the periphery of the crown projection; and the fourth

(IV), in the stand gap. A total of 720 samples near 60 model trees were collected. The sampling was performed with a sharp knife with the help of a 10×10 cm frame for the depth of the horizon.

In the laboratory, the samples were dried to the air-dry state and ground into 1–2 mm particles. The actual acidity was measured in the water extract (the litter : water ratio was equal to 1 : 25) in each sample, as well as the concentration of the mobile forms of Cu, Cd, Pb, and Zn, which were extracted using 5% HNO_3 (with the litter : acid ratio equal to 1 : 10, and the extraction period constituting one day and night after a single shaking.) This reagent, which is similar to other strong acids, permits us to analyze not only the HM forms available to plants but also those that are potentially mobile [14]. This shows the general amount of the HM ingress to the environment more adequately in comparison with the other extracting agents (e.g., an acetate–ammonium buffer or complexones).

The HM concentration was measured using an AAS Vario 6 atomic-absorption spectrometer produced by Analytic Jena Co. in Germany; the pH was controlled ionometrically. The analytical laboratory was technically certified (certificate no. POCC.RU0001.515630). To assess the litter stock and to measure the pH, the samples were weighed with an accuracy of 0.01 g, and the accuracy of the HM extraction was equal to 0.0001 g. The HM reserve in the litter (g/m^2) was calculated as the product of the HM concentration (μg/g or mg/kg) in the sample per the litter stock in the given sample (kg/m^2). Because of the low absolute values, the Cd amount is expressed in mg/m^2.

The average relative difference (*RD*) between the under-tree and between-tree sites was used as an index that vividly characterizes the trend and the strength of the tree influence on the distribution of a certain parameter. This index was calculated according to the equation

$$RD = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i - W_i}{C_i + W_i}100,$$

where C_i is the average parameter value under the crown of the *i*-th tree (for the tree-base site and the middle of the crown projection), W_i is the average value of the parameter outside the *i*-th tree crown projection (i.e., for the crown projection periphery and the canopy gap), and *n* is the number of trees. The *RD* lies in the interval ranging from –100% (the parameter under the crown is zero) to +100% (the parameter outside the crown is zero). By a number of properties (the symmetry of the contribution between the positive and negative differences), this index is recognized to be the best for solving a similar problem, i.e., the characterization of the interaction the between species in the cenosis [25] and the preferable interaction as compared to the commonly used competition index (which reduces the difference to the greater of two values [47]). When performing the ANOVA, logarithms were found for the concentrations and HM reserves. Nonparametric criteria were used, such as the paired test by Wilcoxon for the absolute values, and the Mann–Whitney test for comparing the relative differences.

RESULTS

The diameter and height of the model trees are approximately equal in the background and buffer zones, whereas they are lower in the impact zone (Table 1). The area of the crown projection in the SB decreases by a factor of 1.8 from the background zone to the impact zone, and the sampling points in the forest stand gap were moved by 1.2–1.5 m closer to the trunks. In the SF, the trees growing in the buffer and background zones are specified by the maximal and the minimal crown projections, respectively, while the impact zone occupies an intermediate position. At the same time, the difference between the zones at the position of the two extreme sampling points is not so substantial as compared to the SB (0.5–0.6 m). The difference of the model tree habitus between the three zones (which is inevitable in the case of strong contamination) restricts the possibility of the complete unification of the sampling scheme, which must be taken into account upon the further interpretation of the results.

The projective coverage of the grass–shrub and moss layers changes both by the phytogenic field and by the contamination gradient. In all the zones, the grass–shrub storey is the most developed in the gaps between the trees, while its projective coverage decreases with approaching a tree trunk. As affected by the contamination, the density of the grass–shrub storey becomes less, while the moss layer becomes more advanced. The difference between the under-tree sites and the canopy gaps is most pronounced in the impact zone.

The litter stock is considerably higher in the impact zone as compared to the background territory: the difference is equal to 3.7–5.1 times in the SF, and it appears to be somewhat lower in the SB. In all the zones, the litter stock decreases with the increasing distance from a tree trunk, and the ratio between the reserves in the tree-base and canopy-gap sites varies within 2.9–3.6 and 1.4–2.9 for the SF and SB, respectively.

The significance of the difference between the zones under study ($F_{2;678} = 738$—-13764, $P \ll 0.00001$), the biotopes ($F_{1;678} = 20.6$—1628.6, $P < 0.00001$), and the choices of the locations with respect to the tree trunks ($F_{3;678} = 29.1$—170.7, $P < 0.00001$) exceeds the 5% level for the HM concentrations and the stocks for the bulk of the cases. The cadmium reserve, which does not differ between the biotopes ($F = 0.8$, $P = 0.366$), as well as the lead concentration, which does not depend on the position with respect to the tree trunks ($F = 1.4$, $P = 0.228$), is the exception. The significant interaction between the type of the zone and the biotope option ($F_{2;678} = 9.0 – 270.5$,

Table 1. Characteristics of model trees in different biotopes and pollution zones

Parameter	Spruce–fir forest			Birch forest		
	background	buffer	impact	background	buffer	impact
Stem diameter, cm	42.69 ± 3.16	43.58 ± 1.93	36.74 ± 1.75	26.97 ± 2.10	26.66 ± 1.33	17.57 ± 1.41
Crown projection area, m^2	17.93 ± 2.34	29.63 ± 2.51	23.00 ± 1.76	26.32 ± 3.03	20.81 ± 2.64	14.24 ± 2.74
Tree height, m	24.90 ± 0.73	25.75 ± 0.75	19.45 ± 0.78	22.45 ± 0.58	21.85 ± 0.65	15.05 ± 1.32
D, m:						
I	0.38 ± 0.02	0.61 ± 0.04	0.56 ± 0.13	0.32 ± 0.02	0.32 ± 0.01	0.26 ± 0.02
II	1.26 ± 0.10	1.76 ± 0.09	1.36 ± 0.08	1.69 ± 0.12	1.53 ± 0.12	1.16 ± 0.06
III	2.52 ± 0.23	3.18 ± 0.14	2.60 ± 0.12	3.48 ± 0.22	3.14 ± 0.26	2.31 ± 0.11
IV	4.27 ± 0.25	4.66 ± 0.21	4.17 ± 0.15	5.32 ± 0.40	5.01 ± 0.28	3.81 ± 0.08
Litter stock, kg/m^2:						
I	3.94 ± 0.42	9.03 ± 0.88	14.45 ± 0.73	2.19 ± 0.25	3.83 ± 0.31	5.81 ± 0.53
II	2.47 ± 0.24	6.39 ± 0.58	10.89 ± 0.63	0.91 ± 0.07	3.21 ± 0.23	3.97 ± 0.52
III	1.43 ± 0.14	3.57 ± 0.28	7.22 ± 0.47	0.80 ± 0.05	2.66 ± 0.19	3.20 ± 0.39
IV	1.09 ± 0.11	3.15 ± 0.26	4.92 ± 0.83	0.75 ± 0.05	2.70 ± 0.13	2.65 ± 0.44
PC of the grass–shrub canopy, %:						
I	52.62 ± 4.71	1.25 ± 0.41	0.50 ± 0.18	39.17 ± 5.71	20.98 ± 5.43	7.00 ± 4.83
III	70.90 ± 4.78	13.48 ± 2.92	2.93 ± 0.75	75.14 ± 4.01	24.50 ± 4.57	15.17 ± 10.30
IV	78.84 ± 8.23	33.78 ± 4.74	5.60 ± 2.66	78.45 ± 9.39	30.60 ± 4.25	27.64 ± 13.79
PC of the moss layer, %:						
I	11.60 ± 2.77	19.87 ± 7.38	4.33 ± 3.13	2.83 ± 0.92	1.97 ± 0.49	2.28 ± 0.48
III	11.03 ± 2.84	42.43 ± 6.59	39.52 ± 5.83	2.87 ± 0.59	1.08 ± 0.42	31.92 ± 8.33
IV	19.38 ± 4.32	15.80 ± 4.89	45.87 ± 7.70	2.92 ± 0.80	1.52 ± 0.47	32.68 ± 10.90

Note: *D* is the distance from a trunk to a sampling point, and PC is the projection coverage. Hereinafter, the point position with respect to the trunk is designated as (I) the tree-base site, (II) the middle of the crown coverage, (III) the periphery of the crown coverage, and (IV) the forest canopy gap.

$P < 0.0001$) testifies to the unequal difference between the SF and SB upon different contamination, while the type of the zone × position with respect to the trunk relationship ($F_{6;678} = 2.3$—17.2, $P < 0.032$) proves that the pollution modifies the mode of the HM distribution with respect to the tree trunks.

The acidity of the forest litter is higher near the tree trunks for both biotopes in the background territory, as the difference between the tree-base and canopy-gap sites constitutes 0.2 and 0.4 pH units in the SF and SB, respectively (Table 2). The contamination increases the acidity by 0.7–1.2 units on average with the mode of its distribution with respect to the tree trunks being preserved in this case (the interaction between the pollution zone and the position with respect to the trunks is insignificant: $F_{6;678} = 0.2$, $P = 0.983$). In the impact zone, the absolute difference between the tree-base and gap sites increases in the SF and decreases in the SB.

The HM concentrations in the litter exceed the background values by a factor of 2.8 (Zn) to 52.3 (Cu) in the impact zone and by a factor of 1.8 (Zn) to 17.8 (Cu) in the buffer zone (Table 2) for the SF. The difference between the contaminated and background sites is more pronounced in the SB. Note that the content of the two elements in the SB litter in the buffer zone exceeds that in the impact zone by a factor of 1.9 (for Zn) and 1.4 (for Cd).

In the background area, the Cu concentration in the SF litter is higher than that in the SB litter, the content of Cd and Pb is nearly the same, and the content of Zn is lower. In the buffer and impact zones, higher concentrations are registered for all the HMs in the SB as compared to the SF.

The HM concentrations decrease from the tree trunks to the canopy gaps in the SF litter of the background zone. Of all the elements considered, this trend is most pronounced for Cu, as the concentration at the tree-base site is 2.2 times higher than that at the canopy-base site. For Cd and Zn, this value is equal to 1.5, and it constitutes 1.2 for Pb. The same (though less pronounced) dependence was revealed for the SB in the background zone.

The tree influence on the HM distribution is also traced in the SF litter in the buffer zone, although to a lesser degree than in the background territory. The

Table 2. Concentrations of metals (μg/g) and the pH_{water} in the litter at different distances from tree trunks in different biotopes and pollution zones

Parameter	Position	Spruce–fir forest			Birch forest		
		background	buffer	impact	background	buffer	impact
Cu	I	119.36 ± 4.93	1829.15 ± 77.77	4258.33 ± 185.44	84.42 ± 6.68	1953.17 ± 96.16	5797.35 ± 261.58
	II	102.80 ± 6.82	1509.63 ± 75.36	4163.23 ± 211.60	53.21 ± 2.24	2395.85 ± 115.34	5875.44 ± 310.34
	III	56.09 ± 2.81	1323.19 ± 64.7	4609.73 ± 272.39	45.75 ± 1.64	2121.53 ± 93.95	5512.57 ± 315.74
	IV	53.49 ± 2.25	1227.41 ± 72.87	4306.65 ± 285.04	48.90 ± 2.30	2154.16 ± 95.81	4833.03 ± 390.26
Pb	I	108.22 ± 3.87	688.91 ± 25.92	1321.80 ± 50.31	123.90 ± 5.90	884.03 ± 26.48	1939.02 ± 95.47
	II	106.24 ± 4.85	710.8 ± 32.61	1445.42 ± 78.10	109.20 ± 4.83	1065.99 ± 34.91	2137.01 ± 121.32
	III	85.39 ± 4.46	773.26 ± 35.64	1440.61 ± 72.30	99.96 ± 3.80	1043.17 ± 32.08	1972.40 ± 118.70
	IV	92.32 ± 3.74	843.42 ± 40.77	1500.57 ± 96.82	109.74 ± 3.37	1111.98 ± 35.86	1759.26 ± 162.66
Cd	I	3.96 ± 0.17	9.34 ± 0.48	13.79 ± 0.97	4.23 ± 0.22	29.34 ± 0.82	26.27 ± 1.99
	II	3.76 ± 0.18	8.41 ± 0.61	15.54 ± 1.16	3.27 ± 0.12	32.38 ± 1.13	24.37 ± 2.72
	III	2.70 ± 0.12	7.66 ± 0.58	14.94 ± 1.18	2.81 ± 0.09	30.29 ± 0.85	18.06 ± 1.90
	IV	2.61 ± 0.08	6.89 ± 0.61	13.30 ± 1.35	2.92 ± 0.10	29.41 ± 0.71	15.07 ± 1.65
Zn	I	262.45 ± 8.33	448.08 ± 21.85	574.08 ± 32.69	550.54 ± 17.50	1697.89 ± 34.7	1147.11 ± 74.41
	II	234.18 ± 8.9	404.18 ± 24.88	630.57 ± 34.29	465.12 ± 17.25	1797.25 ± 52.07	1078.18 ± 122.26
	III	186.45 ± 6.78	364.09 ± 26.22	652.96 ± 43.51	407.74 ± 15.71	1767.90 ± 46.67	779.80 ± 68.42
	IV	176.37 ± 5.33	333.70 ± 28.43	579.65 ± 51.76	409.90 ± 14.57	1673.85 ± 37.27	657.95 ± 51.33
pH_{water}	I	4.98 ± 0.07	4.37 ± 0.04	4.20 ± 0.07	5.52 ± 0.07	5.43 ± 0.04	4.39 ± 0.05
	II	4.99 ± 0.08	4.54 ± 0.04	4.23 ± 0.06	5.83 ± 0.04	5.54 ± 0.03	4.59 ± 0.06
	III	5.21 ± 0.05	4.77 ± 0.04	4.47 ± 0.07	5.92 ± 0.04	5.57 ± 0.03	4.59 ± 0.05
	IV	5.21 ± 0.06	4.84 ± 0.03	4.50 ± 0.06	5.93 ± 0.05	5.57 ± 0.04	4.64 ± 0.05

Note: Here and in Table 3, the average values ± of the error are provided, and a sample is an accounting unit, where $n = 30$.

maximal concentrations of Cu, Cd, and Zn are registered at the tree-base sites, and the minimal values are revealed in the canopy gap. Unlike the other elements, the maximal concentrations of Pb are noted in the gap, and the minimal concentrations are registered at the tree-base site (the difference reaches 1.2 times).

The pattern is quite different in the SB of the buffer zone and the SF of the impact zone: the concentrations of the elements are almost independent of the sampling point position as regards the trunks. The Cd and Zn distributions in the SB of the impact zone are close to their behavior in the background territory, whereas the ratio between their concentrations at the tree-base and gap sites even exceeds the background value. At the same time, these differences are minimal for Cu and Pb.

The HM stock in the litter differs between the three zones (as expected) to a greater extent than the concentrations do (Table 3). The excess over the background levels reaches 187 and 37 times in the SF of the background and buffer zones, respectively. Similar to as for the concentrations, the difference in the HM stock between the polluted and background sites is still more pronounced for the SB. When comparing the same zones, the HM stock is found to be higher in the SF than in the SB nearly in all the cases. The Cd and Zn in the buffer zone are exceptions.

The difference between the microbiotopes is more markedly pronounced for the HM stock than for the concentrations: with the growing distance from the tree trunks towards the canopy gap, the decrease in the elements ranges from 3.5 (Pb) to 8.2 times (Cu) in the background zone. The difference is less in the buffer and impact zones; however, the dependence between the HM stock and the position as regards the trunks is tracked in all the cases.

The average relative difference (RD) of the HM content between the under-tree and the between-tree sites appears to be maximal in the background territory for Cu, reaching 35% for the concentrations and 70% for the stock (Fig. 1). A marked regularity is manifested in the SF; i.e., the *RD* in the concentrations and HM reserves decreases with the growing pollution. In the impact zone, no significant difference in the concentration is found between the under-tree and the between-tree sites for all the HM, whereas, for the HM stock, the difference is significant. The *RD* is positive in all the cases, though being significantly lower as compared to the background territories. In the SB, this regularity is registered only for Cu and Pb, while the inversion

Table 3. The metal reserves in the litter at different distances from tree trunks in different biotopes and pollution zones

Parameter	Position	Spruce–fir forest			Birch forest		
		background	buffer	impact	background	buffer	impact
Cu, g/m^2	I	0.49 ± 0.05	16.18 ± 1.16	62.75 ± 4.28	0.20 ± 0.03	7.70 ± 0.63	35.33 ± 3.30
	II	0.27 ± 0.03	9.37 ± 0.65	46.22 ± 3.53	0.05 ± 0.01	7.95 ± 0.64	25.90 ± 2.84
	III	0.08 ± 0.01	4.85 ± 0.49	33.49 ± 3.63	0.04 ± 0.01	5.81 ± 0.46	21.01 ± 2.25
	IV	0.06 ± 0.01	3.87 ± 0.35	26.91 ± 3.13	0.04 ± 0.01	5.96 ± 0.43	17.07 ± 2.05
Pb, g/m^2	I	0.43 ± 0.04	6.06 ± 0.39	19.01 ± 1.00	0.28 ± 0.03	3.39 ± 0.22	11.05 ± 0.76
	II	0.27 ± 0.02	4.44 ± 0.34	15.74 ± 1.09	0.10 ± 0.01	3.43 ± 0.22	8.77 ± 0.66
	III	0.12 ± 0.01	2.78 ± 0.25	10.08 ± 0.87	0.08 ± 0.01	2.78 ± 0.18	7.52 ± 0.79
	IV	0.10 ± 0.01	2.63 ± 0.21	9.53 ± 1.26	0.08 ± 0.01	3.05 ± 0.18	5.99 ± 0.67
Cd, mg/m^2	I	15.51 ± 1.27	84.92 ± 7.71	204.48 ± 18.45	9.60 ± 1.14	111.12 ± 6.54	155.73 ± 15.7
	II	9.30 ± 0.80	52.93 ± 5.54	174.84 ± 16.25	3.06 ± 0.23	104.21 ± 6.93	99.63 ± 12.3
	III	3.85 ± 0.32	28.44 ± 3.16	113.99 ± 17.26	2.28 ± 0.15	79.67 ± 4.13	72.33 ± 11.76
	IV	2.80 ± 0.28	22.84 ± 2.89	88.20 ± 14.22	2.16 ± 0.15	79.64 ± 3.79	51.05 ± 6.57
Zn, g/m^2	I	1.01 ± 0.07	4.06 ± 0.35	8.47 ± 0.67	1.21 ± 0.11	6.46 ± 0.36	6.87 ± 0.67
	II	0.57 ± 0.04	2.54 ± 0.23	7.04 ± 0.57	0.44 ± 0.03	5.80 ± 0.38	4.47 ± 0.56
	III	0.26 ± 0.02	1.35 ± 0.15	4.99 ± 0.72	0.33 ± 0.03	4.65 ± 0.24	3.05 ± 0.42
	IV	0.18 ± 0.02	1.10 ± 0.14	3.79 ± 0.57	0.30 ± 0.02	4.52 ± 0.20	2.31 ± 0.28

between the buffer and impact zones is observed for Cd and Zn: the *RD* decrease in the buffer zone is replaced by its increase in the impact zone, and the absolute values are either equal to the background values (for the HM stock) or even exceed them (for the concentrations).

The *RD* is always positive for the litter stock and its acidity (Fig. 2). A marked decrease in the *RD* is manifested for the H^+ concentration in the SB, whereas no such decrease is observed for the litter stock, and the *RD* increases for the H^+ concentration in the SF.

The difference between the SF and SB in the *RD* is significant in all the zones for the Cu concentrations, as well as for the Cu and Pb stock; however, it is insignificant for the Pb concentrations. The *RD* in the litter stock differs significantly between the SF and SB only in the buffer zone. For the Cd and Zn stock *RD*, the difference between the SF and SB attenuates upon the transition from the background zone toward the impact zone, while this difference, on the contrary, becomes greater for the RD in the concentrations of these elements and H^+.

DISCUSSION

The soil cover heterogeneity in forests is known to result from the operation of many differently oriented processes [10]. If we put aside the pedoturbations of various genesis, the recharging of the budget of chemical elements at any particular point consists of several constituents, i.e., the direct precipitation of aerosols; the direct ingress of liquid and solid sediments with dissolved elements and adsorbed dust particles; the stem flow and through fall of precipitation enriched by the washed-off dust particles and the elements washed out from plant tissues; and the ingress with the falling leaves, in which elements are adsorbed on dust particles and are incorporated into plant tissues. The discharge part includes vertical migration to the mineral soil horizons (due to water transfer, the biogenic destruction of organic substances by animals, and the suction by fine plant roots) as well as horizontal migration (by water, wind, and zoogenic transfer).

The proportion between the components of the chemical element flow varies in different parts of the phytogenic field of a tree and depends on numerous factors, i.e., the size and structure of the crown; the thickness and pattern of the forest stand; the size and shape of the gaps; the meso- and microrelief; the heat, water, and wind regime of the habitat; and on the weather conditions. The vertical flow components increase the soil cover heterogeneity, while the horizontal components mitigate it in the absence of marked topographic gradients. The elevated ingress of HMs to technogenic areas considerably complicates the pattern complex *per se*, since the contamination may either directly or indirectly influence both all the element budget components and all the factors modifying the biogeochemical fluxes.

The trees in a forest are a classic example of *ecosystem engineers* [39]. Therefore, it is no wonder that a marked regularity is traced for both biotopes in the background territory: both the content of hydrogen ion

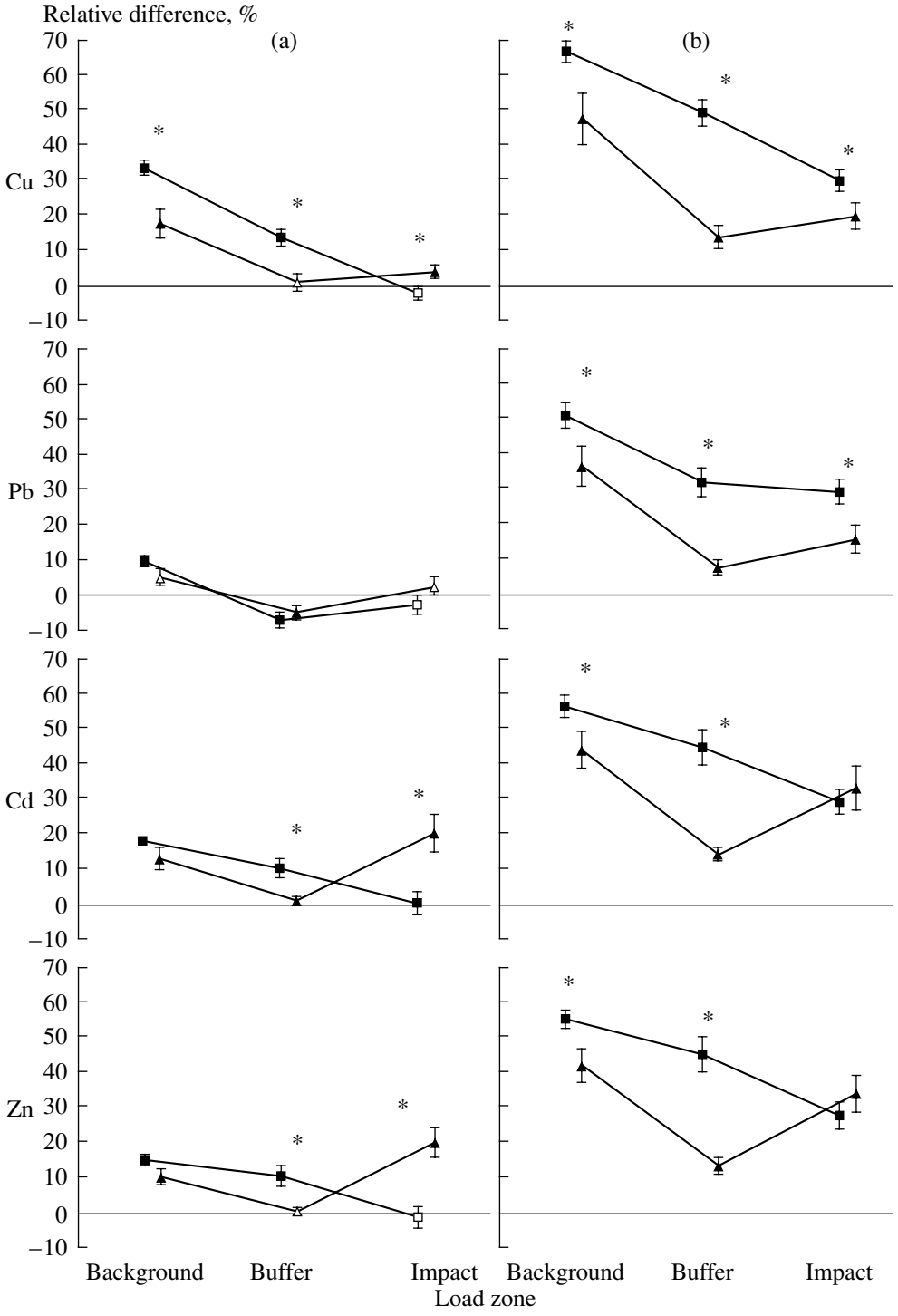

Fig. 1. The relative difference in the (a) concentrations and (b) reserves of metals in different pollution zones within the spruce–fir (squares) and birch (triangles) forests. Hereinafter, a filled symbol designates a significant difference between the under-tree and the between-tree sites in absolute values according to the Wilcoxon criterion (P <0.05), and an empty symbol stands for an insignificant difference. A significant difference between the spruce–fir and birch forests in the RD ($P < 0.05$) according to the Mann–Whitney criterion is indicated by asterisks, and the vertical lines stand for the standard error ($n = 10$).

and all the HMs is maximal near the tree trunks, and it decreases gradually towards the tree stand gaps. As a result, a regular horizontal pattern is developed under the forest canopy consisting of concentric microzones regularly substituting for each other with high, medium, and low contents of elements. Beginning with the work by Zinke [62], this pattern was described by many authors at least for large trees and the pH distri-

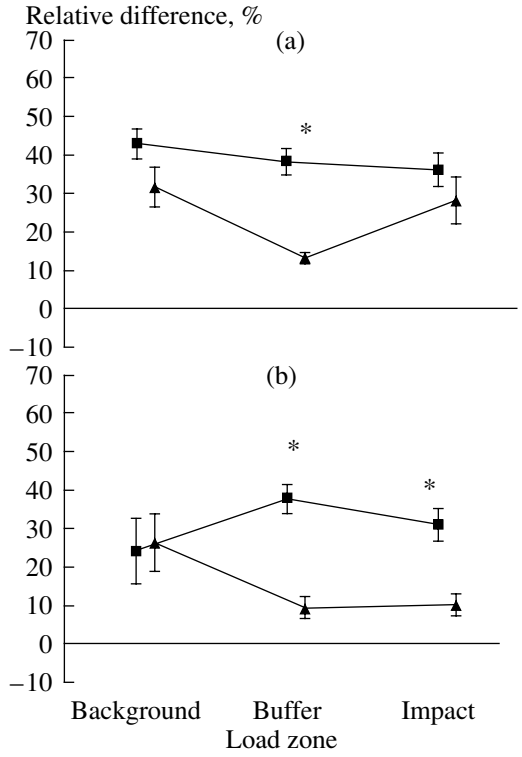

Fig. 2. The relative difference between the (a) litter pools and (b) H^+ concentrations in different pollution zones within the spruce–fir (squares) and birch (triangles) forests.

bution [6, 10, 11, 18, 21, 28, 31, 33, 35, 40, 42, 48, 54, 59, 62]; the cation exchange capacity and the content of exchangeable calcium, magnesium, manganese, aluminum, and potassium [11, 15, 21, 23, 31, 33, 35, 42, 59, 62]; the total nitrogen [23, 31, 48, 62]; the phosphorus [31, 51]; the organic carbon [6, 11, 31, 33, 35, 51]; the sulfate and ammonium ions [48, 51]; the total sulfur [31]; and a number of other soil parameters. Among the HMs, elevated concentrations are registered in the soil near the tree trunks for Cu and Pb (but not for Zn) in the background region of the Czech Republic [53], and in the litter (but not in the soil) for Cu and Ni (but not for Pb) in the background region of the Kola Peninsula [1]. In a number of cases, information is provided either about the absence of a dependence between the soil parameters and the distance from the tree trunks, for example, for the pH [52], total nitrogen, and carbon [42], or about differently directed trends in the organogenic and mineral horizons [1, 15, 15, 23].

Most of the authors explain the decrease in the element content from the tree trunks to the gaps by an elevated ingress of elements under the tree canopy. There are several reasons for this. First, trees catch atmospheric precipitation and aerosols, which raise the stem flow and through fall [29, 44, 45]. Second, the stem flow and through fall are enriched in elements that are washed out from the leaves and bark [18, 44, 45]. Third, the leaf fall containing adsorbed and incorporated elements is localized mainly under the tree crowns despite the lateral transfer [37]. Fourth, specific microclimatic conditions may be formed inside the crowns and beneath them [43] favoring HM adsorption on aerosol particles; aggregation of particles; and, hence, their more intense sedimentation [5, 22]. In addition, the vertical migration of elements from the soil litter to the underlying mineral horizons may be higher in tree stand gaps due to the high speed of the organic matter decomposition [7, 40]. We may also suppose, at least for the microelements, i.e., Cu and Zn, their more intense consumption by plants: although the amount of fine tree roots decreases exponentially with the increasing distance from a trunk [49], the intense development of the grass–shrub stage in the canopy gaps excessively compensates for this decrease, and the total consumption in these microbiotopes may be higher.

In the contaminated areas, the dependence between the HM content in the litter and the distance from the trunks is less markedly pronounced. This may be interpreted in support of the first working hypothesis about the decreasing influence of trees on the distribution of elements. The suppression of trees and the corresponding thinning of the crowns (including the shorter lifetime of the needles) may be considered to be the original cause of lowering the environment-forming role of trees under the conditions of strong industrial pollution. The reduction in absolute size of the crowns is also of certain importance. As a result, the trees catch precipitation and aerosols less efficiently, and, therefore, the chemical composition of the stem flow and through fall appears to be less modified as compared to the precipitation falling immediately on the soil surface.

In technogenic territories, in the immediate vicinity of the emission source, specifically, the direct sedimentation of coarse dust particles on the litter surface may be of much more importance as compared to the background sites. The phytogenic field gradient affects this sedimentation very insignificantly with the reduced screening role of the grass–shrub layer, in particular. This explanation may be also supported by the fact that the tree influence on the hydrogen ion content (the distribution of which depends far less on the coarse dust particles) is preserved intact in all the pollution zones. The secondary redistribution of coarse dust particles already settled on the surface by wind transfer should not be excluded either, which also mitigates the heterogeneity caused by the phytogenic gradient. Along with the above-mentioned reasons, the mitigating impact of the trees may be related to the decreasing difference of the influence of the vertical migration of elements in various parts of the phytogenic field due to the suppressed functioning of the soil biota, which is well registered for the given territory [3, 4, 9].

At the same time, the mitigating influence of the trees on the distribution of the elements turned out to be far more complicated than was initially supposed. The conclusion about the degree of the influence decrease

depends on three aspects, i.e., the mode of the element content expression (either concentration or stock), the particular element, and the biotope type.

At the contaminated sites, the HM concentrations in the litter are virtually independent of the sampling point position as regards the trunks. At the same time, we may state only an insignificant decrease in the tree effect on the HM stock. The reason is evident: the litter reserve is much higher at the tree-base sites as compared to the canopy-gap sites in all the pollution zones due to the leaf fall-off accumulation immediately under the tree crowns both because of its higher ingress and slower decomposition. Accordingly, the difference in the HM stock between the different positions as regards the trunks is controlled, above all, by the difference in the litter stock rather than by the HM concentrations. In other words, the HM reserves are the highest near the tree trunks because the litter amount is higher there, rather than because it is more strongly polluted in this place.

The results obtained are in good agreement with the data of other authors. Blagodatskaya and coauthors [1] noted a decrease of the difference between the under-tree and between-tree sites in the concentrations of Cu, Ni, and Pb in the litter near the copper–nickel enterprise on the Kola Peninsula. Nikonov and Lukina [16, 17, 19, 20] investigated in detail the modification of the chemical composition of the atmospheric precipitation falling though tree crowns, as well as the lysimetric water from the different soil horizons, near several nonferrous metallurgical enterprises on the Kola Peninsula. According to their data, the ingress of Cu and Ni with the precipitation and their removal from the litter was higher under the crowns as compared to the canopy-gap sites both in the background territories and in the zone of high industrial contamination. An increased role of the trees in capturing Cu, Ni, and Fe coming with the rainfall (with a decrease in the general amount of captured precipitation) was registered near a copper–nickel enterprise in Finland [50]. Higher concentrations of Cu, Cd, Zn, Pb, and Ni in the upper mineral soil horizon (as compared to the canopy-gap sites) were noted near a copper smelter in England [58]. Similar results were obtained in the vicinity of a copper smelter in Chile, where the Cu concentration in the soil was higher under arboreous shrubs as compared to open places [36]. In the regions with an elevated regional background of atmospheric precipitation in Switzerland [54] and Austria [41], the concentrations of Cu, Pb, and Zn in the soil were also higher near tree trunks as compared to canopy gaps.

Indirectly, these data prove that the HM ingress to and the content in the litter is higher beneath the crowns at all pollution levels. At first glance, this contradicts the results obtained in our study. However, if we make the grounded assumption that the concentrations of the elements in the lysimetric water in the litter or in the soil mineral horizons are more closely related to their stock in the litter than to their concentrations, then there are no contradictions between the results obtained by us and by other authors, as they testify to the same phenomenon; i.e., the distribution of the element stocks (unlike the element concentrations) in the litter below the tree crowns is weakly modified in the polluted territories.

Our results on the litter acidity do not coincide with the data obtained for the Kola Peninsula [1, 16], where a complex and contradictory pattern of the interparcellar difference upon the technogenic contamination is revealed. This is most probably caused by the specific features of the Al–Fe-humus podzols in the northern taiga [15].

The influence of trees on the HM distribution in the litter is specific for different elements. Three groups of HMs differing in their behavior may be distinguished: the first group includes Cu, the second group corresponds to Pb, while the third group encompasses Cd and Zn. The subdivision into these groups is logically explained by the difference in the chemical properties of the elements as well as by the fact that they are associated with dust particles of different sizes and are bound to different compounds emitted by the enterprise [61]. These differences may control both the ways of the elements ingress and their further translocation in the forest litter. Coarse disperse aerosol particles precipitate predominantly near the emission sources, whereas the finer particles are transported a great distance [24]. Although the mineralogy of dust particles of industrial origin has been poorly studied as yet, HMs are known to isomorphically replace iron in the crystalline lattice of ferromagnetics (hematite, magnetite, maghemite, etc.) that are included in the relatively large technogenic spherules [2]. Cu is shown to be associated with coarse-dispersed aerosols, whereas Pb and Cd, with more fine-dispersed aerosols [24, 61]. The Cd and Zn mobility in a soil depends more strongly on the acidity, whereas that of Cu and Pb is controlled by the organic substance concentration [29].

As regards the difference between coniferous and deciduous biotopes, it is worth noting that the total leaf-area index converted to the horizontal crown projection unit is higher for coniferous trees as compared to deciduous trees [56]; therefore, deciduous trees catch rainfall and aerosols more intensely [29, 45]. Direct measurements show that the potential dust-retaining capacity is 18 times higher for spruce than for birch [12]. In addition, coniferous trees modify the chemical composition of the precipitation falling through their crowns more efficiently as compared to deciduous trees [45, 46]. Higher concentrations of HMs might also have been expected beneath the crowns of the coniferous rather than the deciduous trees. However, we observed this regularity only in the background territory, while the pattern is the opposite on the contaminated sites. This may be caused by the following. First, the SF litter shows higher acidity and, hence, higher mobility of ele-

ments, which results in the more intense migrations from the litter to the underlying soil horizons [29]. Second, leaves are more subject to mechanical deformation and biochemical transformation than spruce needles are. This determines the higher sorption capacity of the leaf litter and the more complete sedimentation of the dust particles (and, HM fixation, respectively) upon the rainfall filtration through the litter. Third, the rate of the organic matter decomposition is usually higher in the SB [55], which leads to the HM "concentration" in the litter.

When the stock of the elements is considered, the ratio between the coniferous and deciduous biotopes is changed to the opposite in the bulk of the cases, which is connected with the much higher litter reserves in the SF as compared to the SB. In turn, this is caused by similar reasons, i.e., the difference in the physicochemical properties control the lower decomposition rate of the conifer needles, and the less favorable hydrothermal conditions in the SF determine the lower activity of the saprotrophic block of soil biota. In addition, the leaf fall off recharge is, as a rule, higher in the SF than in the SB [30].

The second working hypothesis implying that the difference between the coniferous and deciduous biotopes in the degree of the tree influence on the distribution of the elements is mitigated in the technogenic territories is also supported only partially (as the first hypothesis). The difference between the SF and the SB decreases for a number of parameters (e.g., the stock of Cd and Zn), while, for the other parameters, it may either rise (the concentration of Cd, Zn, and H^+) or remain the same (the concentration of Cu and Pb).

The revealed *inversion* of the impact and buffer zones in the SB appears to be the most unexpected result, and it is this fact that mainly makes the support of the initial working hypotheses incomplete. This inversion is pronounced in the fact that the influence of the trees on the distribution of Cd and Zn decreases in the buffer zone and it grows again in the impact zone. Another important thing is that the concentration of these elements (unlike the others) is higher in the buffer zone as compared to the impact zone. Therefore, if we correlate the degree of the tree effect with the absolute concentration values rather than with the pollution zones, the so-called inversion disappears and everything becomes normal; i.e., the force of the tree influence on the Cd and Zn distribution (as well as for the other elements) falls regularly with the increasing technogenic load. The above-mentioned specific behavior of the Cd and Zn, as well as the modified structure of the pollutant flux under the contamination conditions, may possibly explain this phenomenon. Taking into account that these elements are most probably associated with the finer particles (as compared to Cu [24, 61]) and, therefore, they are transferred a greater distance from the emission source, the mode of their distribution in the buffer zone is similar to that of Cu in the impact zone.

CONCLUSIONS

In the background territory, trees play an important part in the spatial distribution of the hydrogen ions and HMs in the forest ecosystem. The content of the elements in the forest litter regularly falls with the growing distance from the tree trunks both in the coniferous and deciduous biotopes. Under the effect of the industrial pollution, the influence of the trees on the distribution of the elements becomes weaker, though it does not disappear completely. In the contaminated areas, the HM concentrations in the litter do not depend on the point position with respect to the trunks, which attests to the decreasing role of the trees in the transformation of the HM fluxes. On the other hand, the HM stock decreases from the tree trunks towards the canopy gaps due to the predominant accumulation of the leaf fall-off under the tree crowns for all the contamination levels. The type of dependence between the hydrogen ion content in the litter and the distance from the trunk also remains intact upon the contamination. Hence, one of the principal conclusions of the study performed is that we cannot unambiguously answer the following question: Does the contamination modify the role of the trees in the HMs distribution? The answer depends on the parameter (the concentration or the reserves in the forest litter) that is accepted as the index of their content.

Note that both aspects are important. From the standpoint of investigating the biogeochemical cycles of the elements, modeling the HM migration in the forest ecosystem, and predicting the transformation processes in the underlying mineral soil horizons, it is necessary to estimate the reserves of elements in the litter. The concentrations appear to be important for understanding the operating regularities of the biota as related to the litter (the plants whose root systems are concentrated in the given horizon, as well as the soil fauna and microflora). Note that the microscale spatial variation of the soil toxicity, which depends both on the stock and concentrations, is considered to be an important factor that determines the biota survivability upon strong contamination [36, 58].

Upon interpreting the obtained results, it should be taken into account that the trees with crowns bordering the forest canopy gaps are just models convenient for the study of the forest stand effect on the soil properties. As any other model, it simplifies the actual situation. However, single trees growing in open spaces covered by grass (which are traditional objects of study within the problem considered) are still more crude models [51]. The overlapping of the tree crowns observed in actual forest ecosystems may conceal in a certain way the influence of individual trees [6].

Unfortunately, there are few works analyzing the HM distribution in dependence on the distance to tree trunks in technogenic areas. By comparing the results of our study with the data obtained by other researchers on the HM concentrations in the undercrown and lysimetric water [16, 17, 19, 20], as well as in the organo-

genic [1] and mineral soil horizons [36, 58], we may draw a conclusion about the coincidence of the found regularities. However, the fragmentary data on other emission sources prevent us from judging about their general character as yet.

It is worth noting that the presented data do not allow us to strictly differentiate between the input of different components of the discharging and recharging parts of the chemical elements budget in the territories with different levels of pollutant supply. Therefore, all the conclusions regarding the possible mechanisms are of speculative character. At the same time, the revealed deviation from a simple pattern implying a similar (for all the parameters and biotopes) decrease in the role of the trees with the increasing contamination may prove that it is the change in the element flux structure that forms the basis of the mechanisms. This should be separately investigated.

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