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BIOGEOCHEMICAL CHANGES IN FOREST ECOSYSTEMS POLLUTED BY INDUSTRIAL EMISSIONS, EAST SIBERIA, RUSSIA

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Abstract

The biogeochemical data of pine (*Pinus sylvestris* L.) forests have been studied in the impact and buffer zones of the influence of technogenic emissions from the large industrial center Usolie-Sibirskoe (East Siberia, Russia). Changes in the acid-base balance, accumulation and migration of elements-pollutants, the content of nutrient elements in the components of forest ecosystem – tree-stands, forest litter, soil horizons – on contaminated areas compared to the background sample plot have been revealed. A significant shift in the acid-base balance to the alkaline range and an active migration of elements-pollutants in soil horizons and forest litter have been shown to be key processes causing a disturbance of exchange reactions of Ca^{2+}, Mg^{2+}, K^+, Na^+ cations in the soil absorbing complex (SAC) and a decrease in nutrient elements migration into root systems of trees. Pronounced changes in the acid-base balance, high accumulation of elements-pollutants, binding of nutrient elements by pollutants in the soil horizons and in plant tissues lead to the disruption of nutrition and to the inhibition of pine trees growth processes. The biogeochemical parameters observed are characterized by interconnected changes in the main components of the forest ecosystem (soil and tree-stand) and can serve as adequate criteria for assessing its state under technogenic pollution.

Key words: acid-base balance, elements migration, pine forests, soil profile, technogenic pollution.

Introduction

Nowadays, increasing technogenic pollution is one of the significant factors in the destabilization of forest ecosystems. The negative impact of industrial pollution appears in the disfunction of biogeochemical processes due to unregulated flux of elements-pollutants (Mikhailova and Shergina 2010). Technogenic fluxes of many hazardous pollutants, such as, for example, sulphur compounds and heavy metals, become commensurate with the quantities of substances naturally involved in the biogenic circulation (Alekseenko 2000). The resulting ecosystem disbalance of elements can cause a significant deterioration in the nutritional status of forests, which can later lead to their structural and functional transformation continuing until the break-up of biogeocoenosis (Paoletti et al. 2010, Dmuchowski et al. 2011, Mikhailova et al. 2016). The results of many studies show that in forest ecosystems, natural soils and tree-stands are the most sensitive to atmospheric pollution (Kaigorodova 1996, Motuzova 2013, Mikhailova et al. 2017b). To assess the negative anthropogenic impact on forest ecosystems, a complex of various data is used. Biogeochemical data which characterize the functioning of the soil and woody plants are quite informative. At the same time, monitoring methods in most cases are based on the state analysis of a single component of the forest ecosystem (Lindenmayer et al. 2000, Moffat 2003, De Vries and Groenenberg 2009, Burrascano et al. 2011). For example, soil pollution is often assessed by disturbing the acid-base balance of the soil solution, and there is no unequivocal judgment about its effect on the migration of nutrient elements in the soil profile. Some authors believe that the acidic conditions in the soil medium impede the redistribution of nutrients in the soil (Kaigorodova and Vorobeichik 1996, Schroth et al. 2007). Others point out that the mobility of nutrient elements directly depends on an increase in soil alkalinity (Makarov et al. 1995, Maslova 2008). In such studies, experimental soils are usually used (Fokin et al. 1982, Alewell and Matzner 1993, Alewell 2002, Selim et al. 2004), which is not quite acceptable, since these soils differ significantly from natural ones according to many characteristics. In a number of works on the deterioration of forest ecosystem, the authors judge by the content of pollutants in the polluted air and their quantity adsorbed by the soil, as well as by the change in some parameters of this component (Zhang and Sparks 1990, Piirainen et al. 2002, Malinova 2009, Vašát et al. 2015, Medvedev and Derevyagin 2017). However, in our opinion, for a more adequate judgment of the state of technogenic polluted forest ecosystem, data that characterize the disturbance degree of the biogeochemical correlation of its main components – soil and tree-stand – are needed. On the basis of such data, it is possible to estimate how disturbed this correlation is due to technogenic fluxes of pollutants and what the future vector of the ecosystem transformation is. Such studies are especially significant for areas that have been subjected to the prolonged exposure to technogenic emissions, since in such areas it is possible to clearly establish the direction of pathological biogeochemical disturbances and adequately assess the state of the ecosystems. In the Russian Federation, such studies are relevant for the Siberian region, where a large number of industrial centers are concentrated; therefore, their emissions have a large negative impact on the natural migration of biogenic elements in forest ecosystems. The purpose of this work is to identify changes in the complex of biogeochemical data: acid-base balance, accumulation and migration of elements-pollutants, content of biogenic elements in the forest ecosystem' components – soil, forest litter, and tree-stands – under technogenic pollution.

Material and Methods

Studies were conducted in 2015–2017 in forest ecosystems polluted by technogenic emissions from a large industrial center located near town Usolie-Sibirskoe, Eastern Siberia, Russia (52°45'N, 103°38'E) (Fig. 1). Most of the industrial enterprises of the center are concentrated in the northwestern direction from the town. The main transfer of technogenic emissions, in which are dominated by sulphur oxides and aerosols of heavy metals occurs in the

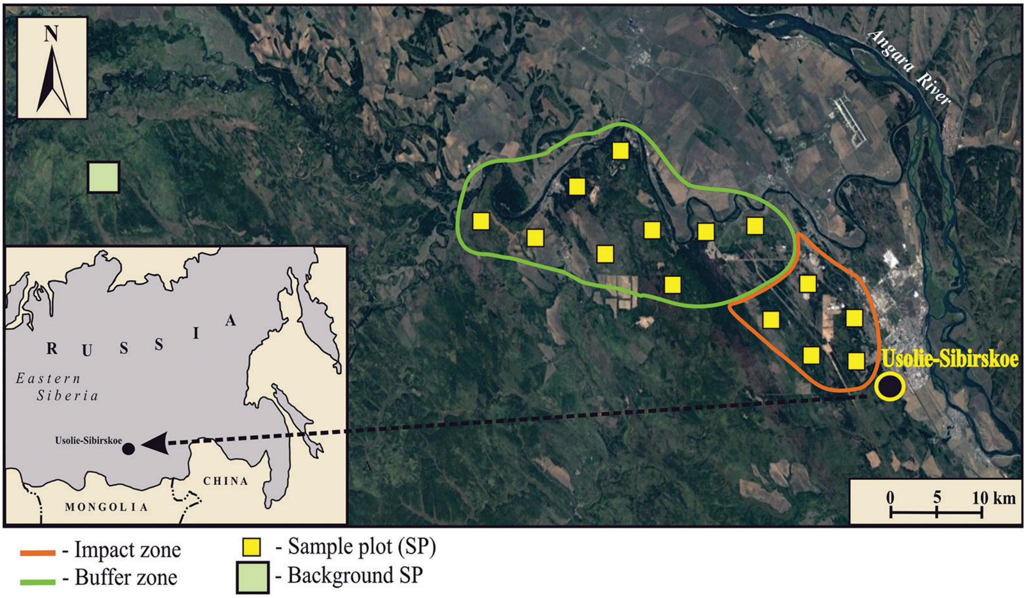

Fig. 1. Location of sample plots in impact and buffer zones.

same direction (Review ... 2016–2017). The technogenic load on the polluted territory is characterized as heavy (State ... 2017).

Field studies in forests were carried out on 14 sample plots (SP) with a size of 0.1 ha each. They were created using the ICP Forest international method (Manual ... 2010). In the studied area, the impact and buffer zones of technogenic influence were established according to the method of the Roshydromet of the Russian Federation (Guidelines ... 1991, Ecological ... 1999, Atlas … 2004). The impact zone was located at a distance of up to 10 km from the industrial center, and its area was about 45 km^2. The buffer zone is up to 35 km far from the industrial center, and its area is about 180 km^2 (Fig. 1). Five SP were created within the impact zone, and nine – in the buffer zone. Background SP was laid at a distance of 80 km from the industrial center (52°55'N, 102°07'E, 604 m a.s.l.) in a healthy forest, not subjected to the influence of technogenic emissions.

Scots pine (*Pinus sylvestris* L.) forests dominate in the study area. They are located within the boundaries of one soil okrug with the predominance of gray forest soils (WRB, 2006. Greyic Phaeozems Albic) occurring on Jurassic sandstones and mudstones (Regional ... 1998). In the study area, herbaceous pine forests of III class of bonitet are common; fullness of tree-stands (Stand density index) varies from 0.4 to 0.5. The description of the soil type was carried out in accordance with the generally accepted in the Russian Federation classification (Classification ... 1977); the designation of horizon indices was given in accordance with the soil classification of Vorobieva (1999). We have shown that soil profiles in all the SPs are represented by the following set of horizons: O – Ad – A – AB – B – BE – Bt,f – BC – C (Unified State Register of Soil Resources (EGRPR), 2006. A0 – A1 – A1A2 – Bt – BC – C), in which zones of humus accumulation and eluvio-illuvial redistribution of elements and their compounds are distinguished. Forest litter was studied by use the square pocket method for taking averaged samples in a fivefold replication. A survey of pine stands was carried out according to the methods adopted in forestry, as well as using the recommendations of the international manual of ICP Forests (Methodical ... 1981, Manual ... 2010). To determine the content of nutrient elements and elements-pollutants, samples of needles were taken from shoots of the second year of life from 5–6 pine trees of 40–45 years of age. The samples of pine needles, forest litter and soil horizons from all the SPs collected during the field studies were delivered to the laboratory for analytical studies. Determination of Ca, Mg, K, and Na in pine needles was carried out after the preliminary ashing of the samples at temperature of 450°C in a muffle furnace, followed by the dissolution the ash in concentrated hydrochloric acid. Their mobile forms, which are part of the soil adsorption complex (SAC), were extracted with ammonium acetate buffer (1 M CH_3COONH_4) with pH 4.8 (Hue and Evans 1983, Burt 2004). Mobile forms of sulphur and heavy metals were replaced with a normal solution of hydrochloric acid. The content of chemical elements in soil and plant samples was determined by atomic absorption spectrophotometry, flame photometry, photocolourimetry (Ermakov 1987, Carter and Gregorich 2008). Certified techniques and analytical equipment of the Center 'Bioanalitica' (SIFIBR SB RAS) were used. The measurements were performed with flame photometer Flavo (Carl Zeiss, Germany), AAS vario 6 FL (Germany), FT-IR Spectrum One spectrophotometer (Perkin Elmer, AAA, Czech Republic).

For statistical processing of the data obtained, computer programs 'R statistical computing medium', version 3.1.1., were used (Shipunov et al. 2014). The following factors were calculated: the Pearson linear correlation coefficient (r_{xy}), the coefficient of determination (R^2) of the functional dependence between the data (Schabenberger and Pierce 2002). Data processing and their graphical representation were performed in Microsoft Excel, Mathcad 12. The schematic map was made using Corel DRAW (version 13) and Google Earth Pro (version 7.1.8.3036).

Results and Discussion

Changes in the pH of forest ecosystem components

Acid-base balance largely determines the chemical activity of the elements both in the soil and in the plant (Pierzynski et al. 2005, Shamrikova et al. 2006, Molla and Velizarova 2015). Therefore, in our studies, it was prior to determine the level of acid-base balance in the horizons of soil profile, forest litter, and pine assimilative organs on the technogenic polluted territory. A pronounced change in this indicator towards alkaline values has been revealed, especially in the impact zone (Fig. 2). The actual acidity (pH_{H2O}) in the forest litter is recorded from 6.40 (buffer zone) to 7.80 (impact zone); in the upper soil horizons (Ad, A), where organic matter and humus accumulate – to 7.60; in the mineral part of the soil it is from 5.80 to 6.90. This indicates a technogenic influx of alkaline components of industrial emissions to the soil surface on the territory adjacent to the industrial complex. In the soil on the background SP, pH shift

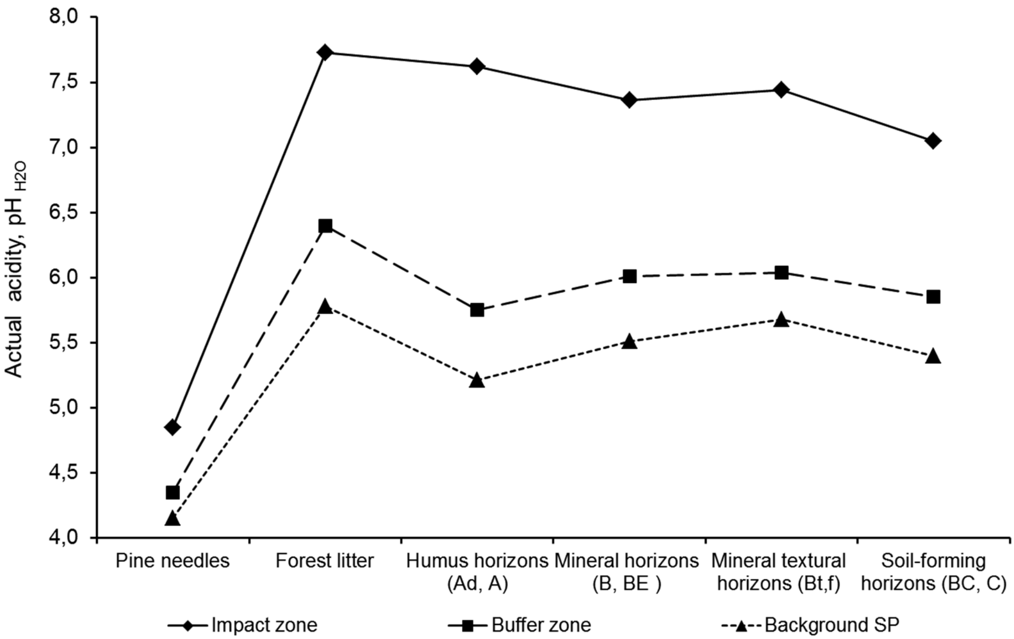

Fig. 2. Changes in the actual acidity in comparison with the background SP.

in the forest litter and the upper horizons is not recorded. This soil is characterized by a gradual decrease in pH_{H2O} down the profile from 5.70 to 5.40.

In pine needles in the polluted areas, pH_{H2O} varies less than in the soil horizons – from 4.35 (buffer zone) to 4.85 (impact zone). At the same time, the correlations between actual acidity indicators of soil horizons and the forest litter on the one hand, and acidity values of needles on the other hand, are high (r = 0.85–0.98, P = 0.05, n = 78). This suggests that changes in pH_{H2O} in the needles are closely related to changes in pH_{H2O} in the forest litter and soil. In general, the revealed substantial alkalinization of forest ecosystem components during technogenic pollution can significantly change the migration ability of elements-pollutants (sulphur, lead, cadmium) and their chemical affinity to biogenic elements.

Migration of pollutants (lead, cadmium and sulphur) in polluted soils

The change in the acid-base balance is a very significant factor contributing to the increased migration of heavy metals in the soil horizons (Latypova 2000, Motuzova 2000). Moreover, in most cases this happens when the balance shifts to the acid direction (Bezuglova and Orlov 2000). However, we have previously found an increase in the migration of mobile forms of heavy metals along the soil profile with increasing alkalinity (Shergina and Mikhailova 2011). In these studies, when determining the content of mobile forms of lead and cadmium in gray forest soils in the polluted zones, we have found an active illuvial redistribution with depth, as well as a high accumulation of these ions in the humus horizon (Fig. 3). As it can be seen from this Figure, the content of lead and

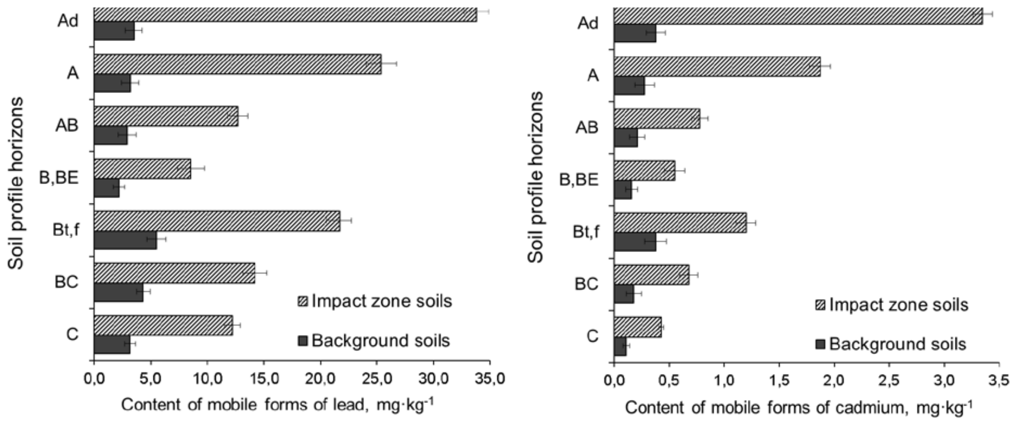

Fig. 3. Content of lead (left) and cadmium (right).

cadmium exceeds the background level by 7–10 times in the impact zone in the upper humus-accumulative horizons.

In the underlying illuvial horizon BE of the soil profile, the concentration of these elements decreases by 4–6 times relative to the accumulation in the humus horizons, and in the textural horizon Bt,f it increases again up to 3–4 times compared to the background. In the soil-forming horizons BC and C of the polluted soils, the accumulation of lead, cadmium is also significant – up to 14.25 and 0.68 mg·kg^{-1}, respectively. The data obtained indicate the active migration of heavy metals along the profile of polluted soils. Whereas other researchers report the accumulation of pollutant elements mainly in the upper soil horizons (Stroganova et al. 2003, Fedorets and Bahmet 2003).

Our studies on the accumulation and migration of sulphates in the polluted soils showed their high concentrations in all soil horizons. However, it should be noted that the limits of fluctuations between their minimum and maximum values are significant (Table 1). In the upper part of the soil profile, sulphur share in the form of sulphates is concentrated in the humus-accumulative horizons (Ad, A), that is, it is part of the organic matter. In the underlying soil horizons B and BE, a decrease in the level of sulphur is noted. However, in Bt,f, and BC horizons, its content slightly increases again. Such a vertical change in the concentration of mobile sulphates along the soil profile

Table 1. Minimum and maximum values of mobile sulphates content (mg·kg^{-1}).

Soil horizon index	Impact zone (*P*=0.05, *n*=15)	Buffer zone (*P*=0.05, *n*=27)	Background SP (*P*=0.05, *n*=9)
Ad	22.2–32.6	10.5–24.5	5.8±0.4
A	19.3–21.8	6.3–17.7	1.9±0.2
AB	10.2–15.3	4.8–10.2	1.2±0.1
B	9.3–13.6	3.9–9.6	0.7±0.1
BE	7.7–10.9	3.1–7.5	0.5±0.1
Bt,f	14.3–19.5	7.2–14.1	1.7±0.3
BC	7.6–11.2	5.1–8.8	0.8±0.2
C	5.7–8.4	2.1–6.7	0.3±0.1

can lead to the transformation of sulphur compounds and enhance the process of deep gleying under the anaerobic conditions in the soil profile.

An additional source of technogenic sulphur in the soil can be an increase in its content in fallen leaves and needles, correspondingly, in the forest litter (Hovland 1981). When determining the content of mobile sulphates in the forest litter in the impact zone, we have found an increase in their concentration from 2.5 to 5.4 times and from 2 to 2.6 times in the buffer zone, compared with the background level. The maximum values of mobile sulphur in the forest litter in the SPs of the impact zone reach 36–50 mg·kg^{-1}. Those values for the SPs in buffer zone reach 25–35 mg·kg^{-1}. A correlation relationship of a high confidence level (r=0.91, P=0.05, n=32) has been found between the sulphur content in the forest litter and its content in the upper humus horizons Ad and A. That confirms the presence of technogenic deposition of sulphur to the soil surface and the further fixation of sulphur containing compounds by organic matter, most often by humic acids.

Binding of exchange cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) by pollutants in polluted soils

Revealed soil alkalinization in SPs of the impact and buffer zones is a consequence of influence emissions from the Usolie-Sibirskoe industrial center, specifically, from the thermal power plants that use coal with a high content of alkaline-earth compounds (State ... 2017). Calcium compounds dominate among the alkaline components of the emissions. On this basis, the relationship between the content of polluting ions SO_4^{2-} and Pb^{2+} and a mobile form of Ca^{2+} in the soil horizons of the impact and buffer zones have been observed (Fig. 4). As it can be seen from the graphs, the relationship between these parameters is directly proportional. The areas of maximum conjugate accumulation of polluting ions and Ca^{2+} have been found in the humus horizons Ad and A, as well as in the textural horizon Bt,f (Fig. 4).

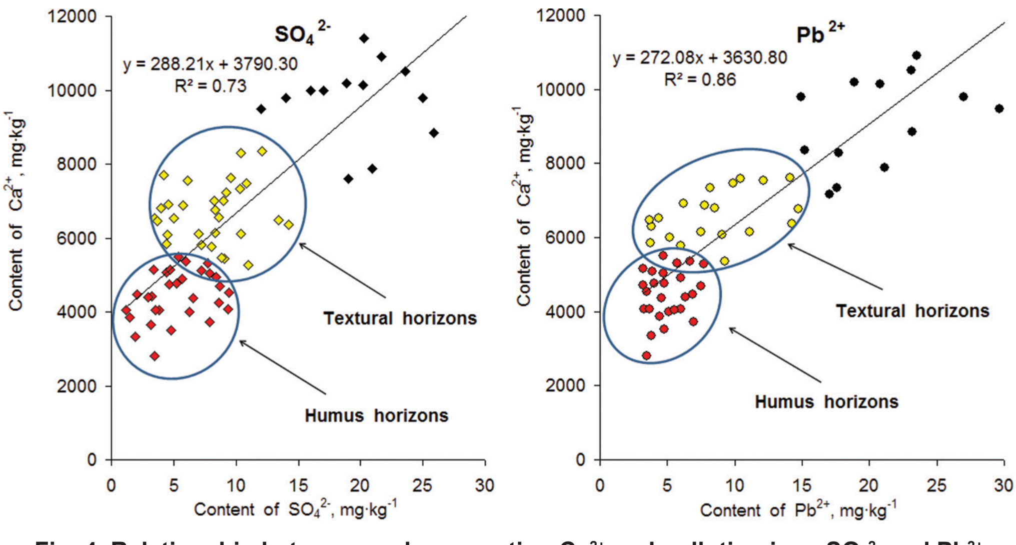

Fig. 4. Relationship between exchange cation Ca^{2+} and polluting ions SO_4^{2-} and Pb^{2+} in the polluted soils in the impact and buffer zones.

That is due to the presence of humic compounds and a thin silt fraction with high adsorption capacity. In the background soils, there is no accumulation of pollutants, and there is no correlation between the content of mobile forms of sulphur and calcium, as well as of lead and calcium.

In addition to calcium, a direct relationship has been found between the content of other SAC cations (Mg^{2+}, K^+, Na^+) and sulphur ions (and lead ions) in the polluted soils. Moreover, for all the soil horizons in the impact and buffer zones, these relationships are reliable (r=0.58–0.78, P=0.05, n=52). Based on the data obtained for polluted soils, the following sequence of the SAC cations correlation (in order of weakening) with sulphate ion (SO_4^{2-}) and lead ion (Pb^{2+}) within the soil profile can be represented: Ca^{2+}(r=0.85) > Na^+(r=0.78) > Mg^{2+}(r=0.67) > K^+(r=0.58). This means that the closest correlation of the polluting ions is observed with the divalent calcium cation (Ca^{2+}), and the smallest – with the monovalent K^+ cation. Thus, the binding of SAC ions with polluting ions is one of the main reasons for the disturbance of biogeochemical migration of nutrient elements in the soil profile and for the decrease in their flux into plant root systems.

Accumulation of elements-pollutants in the needles of pine trees

The results of the analysis of pine needles samples showed a significant accumulation of pollutants (sulphur, lead, cadmium) in the assimilative organs of trees. The highest level is recorded in the impact zone. For instance, the sulphur concentration rises by 2–6 times (400–1200 mg·kg^{-1}), lead – by 5–17 times (0.45–1.53 mg·kg^{-1}), cadmium – by 4–10 times (0.15–0.38 mg·kg^{-1}) compared to background values. The calculation of correlations between the content of elements-pollutants in the needles and in soil horizons showed that these are correlations of a high level of significance (Table 2). They indicate the presence of an active influx of pollutants (sulphur, lead, cadmium) from the soil horizons through the root system with xylem transport into the assimilative organs of plants.

In turn, the high accumulation of elements-pollutants causes a disturbance of the ratio of nutrients in the needles of trees. It is shown that an increase in the proportion of sulphur, cadmium, and especially lead in the needles causes a significant decrease in the degree of biogenic elements in it (Table 3). It has been found

Table 2. Correlation coefficients between pollutant content in the soils and pine needles in the impact zone of pollution (*P*=0.05, *n*=45).

Soil horizon index	Sulphur	Lead	Cadmium
	Needles	Needles	Needles
O	0.85	0.79	0.65
Ad	0.76	0.74	0.63
A	0.66	0.60	0.59
AB	0.61	0.52	0.54
B	0.58	0.51	0.49
BE	0.54	0.49	0.48
Bt,f	0.78	0.71	0.67
BC	0.69	0.65	0.61
C	0.62	0.59	0.52

Table 3. Changes in concentration ratios (in %) of elements in pine needles.

Elements ratios	Impact zone	Buffer zone	Background SP
Ca:S	85:15	90:10	96:4
Mg:S	80:20	87:13	93:7
K:S	76:24	81:19	92:8
Na:S	72:28	77:23	91:9
Ca:Pb	90:10	95:5	97:3
Mg:Pb	80:20	88:12	94:6
K:Pb	70:30	79:21	92:8
Na:Pb	68:32	75:25	91:9
Ca:Cd	95:5	98:2	99:1
Mg:Cd	87:13	92:8	97:3
K:Cd	79:21	86:14	94:6
Na:Cd	76:24	82:18	92:8

that in the assimilative organs of trees in the impact zone of the Usolie-Sibirskoe industrial center, the strongest decrease in the level of nutrient elements is observed against the increasing concentrations of elements-pollutants. In the buffer zone, the imbalance of elements in the needles is smaller, but nevertheless, it is clearly expressed in comparison with the background SP.

Consequently, in the polluted soils (impact and buffer zones), there is a pronounced disturbance of the nutrition pine trees due to a lack of basic nutrient elements. It should also be noted that needles aerially absorb elements-pollutants from the polluted air. This fact plays an important role in the imbalance of the ratio of nutrient elements and the disturbance of pine mineral nutrition. The activity of this way of entry of pollutants can be judged by comparing the concentration coefficients of elements-pollutants in needles with the exceeding frequency of their maximum permissible concentrations (MPC) in the atmospheric air polluted with emissions from the Usolie-Sibirskoe industrial center (Fig. 5). This figure shows the correspondence between the excess of MPC of sulphur, lead, cadmium and the excess of their concentration coefficients in needles. In addition, during the aerial absorption of pollutants in the process of gas exchange, both the mineral nutrition and the process of photosynthesis are disturbed at the same time (Mikhailova et al. 2017a). Consequently, the negative change in the nu-

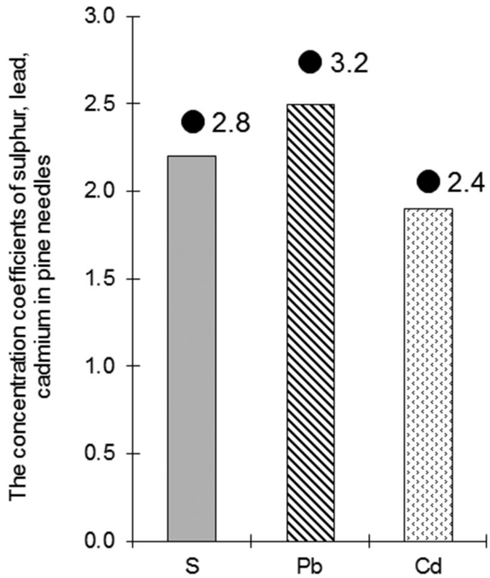

Fig. 5. Concentration coefficients of elements-pollutants in pine needles and MPC (black circles) in the atmospheric air of Usolie-Sibirskoe industrial center.

tritional status of pine trees in the polluted area is due to the influence of pollutants both through the soil on the root food, and through the direct aerial absorption by the assimilative organs. The disturbance of pine mineral nutrition appears primarily in the inhibition of the growth processes of assimilative organs. Thus, in the impact zone, the weight of one needle is reduced twice compared with the background value, the needles weight on the shoot – by 4.5–5 times, the number of needles on the shoot – by 2–3 times, the lifetime of the needles is reduced to 2–3 years, the level of crown defoliation increases to 50–60 %. In the buffer zone, growth data are reduced to a lesser degree – the weight of one needle is reduced by 1.3 times, the needle weight on the shoot – by 2.5–3.5 times, the number of needles on the shoot – by 1.5–2 times, the lifetime of the needles is reduced to 3 years, the level of crown defoliation is 30–45 %. Thus, the morphostructural data of trees indicate a pronounced damaging effect of industrial emissions on the vital state of pine trees, especially in the impact zone of pollution by emissions from Usolie-Sibirskoe industrial center.

Conclusion

The complex of biogeochemical parameters of pine (*P. sylvestris*) forests in the impact and buffer zones of the influence of technogenic emissions of the large industrial center Usolie-Sibirskoe (Eastern Siberia, Russia) has been studied. It has been revealed that the technogenic impact has led to a significant shift in the acid-base balance towards alkaline values in the forest litter and upper soil horizons. The impaired acid-base balance caused a change in the migration fluxes of elements-pollutants in the soil. The active movement and accumulation of sulphate ion and mobile forms of lead and cadmium in all the horizons of gray forest soils, up to the soil-forming one, has been detected. The content of these pollutants in the soil horizons exceeded the background values from 14 to 28 times. Mobile forms of heavy metals and sulphur have been shown to alter the migration ability and the quantity of the exchange cations Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} in the SAC of humus and mineral horizons. The binding of SAC ions with pollutant ions can be considered as one of the main causes of the disturbance of biogeochemical migration of nutrient elements in the soil profile, and changes in their nutritional regime, that bring about a decrease in the migration flux of nutrients to the root systems of plants. It is shown that the active coming of elements-pollutants from the soil and polluted air into the assimilative organs leads to the imbalance of nutrient elements in the needles and, as a result, to the suppression of their growth processes. This is evidenced by a significant reduction in many morphostructural parameters of trees. The studied biogeochemical parameters are characterized by interconnected changes in the main components of the forest ecosystem (soil and tree-stands), so they can serve as adequate criteria for assessing its condition under technogenic pollution.

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