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Biogeochemical Redistribution of Lead in an Urban Ecosystem be the Example of Irkutsk Territory

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Abstract

Lead content in woody vegetation at the genetic profile level was investigated at the territory of Irkutsk, a large industrial centre of Eastern Siberia. It was demonstrated that lead income caused by technogenic emissions contributes significantly to the pollution of the urban ecosystem. Lead accumulation in needles and leaves of the woody plants at the urban area can exceed the background levels more than 10 times, maximally up to 25 times. The high level of lead is also revealed in the top humus and humus accumulative horizons. Its active vertical migration into textural illuvial and pedogenic horizons of the soil genetic profile was discovered. It is shown that the redistribution of the labile lead in the soil solution of the organic and mineral horizons is accompanied by its interaction with phosphate and sulphate ions, exchange cations (sodium, potassium, magnesium), and heavy metal ions (zinc, copper, cadmium, manganese). Reliable direct correlations between the content of mobile lead in urban soil and lead concentration in the assimilative organs of woody plants are revealed.

Key words: urban ecosystem, technogenic lead income, genetic soil profile, woody plants

INTRODUCTION

Technogenic pollution of the cities becomes more and more significant problem of mankind, its scale and hazard is proved by the data on considerable contamination of the urbanized territories by toxicants [1, 2]. In a range of polluting substances of urban environment heavy metals, especially lead and lead compounds occupy a prominent place. This element belongs to extremely hazardous toxicants, possesses high solubility, biochemical activity and carcinogenicity; has a high tendency to bioconcentration and complexation; can occur both in mineral and organic forms in environment [3]. Lead in atmosphere is capable to form various oxides, to enter reactions with acids and alkalis. Exhaust gases, aerosols of motor transport and technogenic dust with a large amount of lead in the form of poorly water soluble compounds, for example, oxides and sulphides [4], belong to the main sources of lead as polluting element. Total intake of lead in the atmosphere from motor transport in the territory of the Russian Federation is estimated at 30 000 t annually [5]. Leaded petrol used by automobilists contains tetraethyl lead, and it is especially dangerous. Though in Russia leaded petrol was forbidden by the Federal law (No. 34-FZ from 2003), State Standard GOST 2084–77 which allows the issue of both clear petrol (lead concentration is 0.015 g/L) and new generation leaded petrol (lead content is lowered from 0.45–0.35 to 0.15 g/L) still acts at the territory of the Russian Federation. In this regard the problem of lead environmental pollution is of current interest, and its decision is connected with complete rejection of use of leaded gasoline.

At combustion of automobile fuel about 70 % of lead which was added to gasoline with ethyl fluid, get to environment with exhaust gases, from these 30 % accumulate at the surface at once, and 40 % remain in the atmosphere [6]. Peculiarity of the atmosphere pollution by motor transport is that harmful substances don't concentrate in a certain zone with limited radius, but extend on all the territory of the city.

Technogenic intake of lead compounds in urban ecosystem results in significantly raising content of this toxicant in all the components of this system. Thus, it is established that soil pollution by lead is mainly irreversible (its half life in soils is 740–5900 years), therefore lead accumulation in soils doesn't stop even in the case of its small intake [3]. Lead content is especially high in soils and plants located along highways. Lead compounds have a negative effect on microbiological activity of soils and plant growth. Lead input to the plant body breaks photosynthesis and breath processes, cell division, water absorption by root systems, the whole metabolism, and inhibits a number of enzymes. Besides, lead can essentially reduce availability of many biogenic elements to the plants [7, 8].

Studying of biogeochemical lead redistribution in the major components of the urban ecosystem, such as plants and soil, allows to gain an impression of intensity of technogenic processes and the main flows of migration of this toxicant in the urbanized territory.

The purpose of this work is research of accumulation and redistribution of technogenic lead in genetic profile of city soils, detection of association of these processes with its accumulation in assimilative phytomass of woody plants.

OBJECTS AND METHODS OF RESEARCHES

Researches were carried out in the territory of Irkutsk – the large industrial centre of Eastern Siberia. According to Ministry for Protection of the Environment and Natural Resources of Russia [9], Irkutsk is one of ten the most polluted cities of the country: its air pollution index is 21.1 [10], and about 60 % of total city emissions are those from motor transport. The ecological situation is also aggravated with existence of the numerous heating enterprises, which use coal of poor quality providing emission of a large amount of heavy metals including toxic lead in the atmosphere of the city during its combustion. One more factor causing high degree of city pollution is the difficult orographic and climatic conditions resulting in air stagnation and accumulation of polluting substances in the city territory [11]. By results of ecological researches, the area of the increased lead concentration is placed in the central part of the city, where its content in air is up to 7.6 μg/m^3 (while a maximum concentration limit is 0.3 μg/m^3), in soil – 60–100 mg/kg, in snow precipitation – 220 mg/kg [12].

Irkutsk is located in a zone of subtaiga pine forests. The topsoil of the territories adjacent to the city is presented by mainly gray forest soils with sandy and loamy structure. The soils were formed on the Quaternary loamy deposits which have been genetically connected with the Jurassic sandstones and slates, that defines in many respects their structure and properties [13].

Researches were carried out in 2002–2007 in the parks and green belts of the different districts of Irkutsk. The regions for researches have been chosen according to the map of air pollution [14]. On the city territory 16 stationary test plots (TP) were arranged, of theses, 13 – with gray forest soils [11] are widespread. In the central part of the city the Central recreation park, park in Lisikha urban district, Commune of Parizhskoy Kommuny park, forest park near the "Angara" resort were examined; in a northwest part of the city – Railway (Zheleznodorozhny) park in Novo-Lenino, forest park in the 6th urban district of Novo-Lenino, park in Irkutsk-2; in east part – park in the Baikalskiy urban district, forest park near the airport; on city suburbs – the green space of Irkutsk Akademgorodok, the green space in the Yubileiny urban district, the green space near Regional Young Naturalists' Station, the green space in the suburban settlement Iskra. Background GP were arranged in the territories with identical soil formation type, located at considerable distances from the city (50–120 km).

Gray forest soils and tree species: pine (*Pinus sylvestris* L.), Siberian larch (*Larix sibirica* Ledeb.), silver birch (*Betula pendula* Roth.), poplar (*Populus* sp.) were the test subjects for research. In parallel with inspection of wood vegetation at the TP a complex soil cover investigation was carried out. The city soils investigated are natural, with different degree the top horizons mixing. The field survey of soils was carried out using a soil profile to a depth of 1.5 m and averaged square grid sampling. Definition of mobile and gross lead in vegetative and soil samples by atomic absorption method with electrothermal atomization on an AAS Vario-6 (Analytic Jena) device was carried out in laboratory conditions. Estimation error at the detection limit level is 10–30 %. Estimation of the lead content in vegetative samples and forest litter was carried out after preliminary combustion of a material with hydrochloric acid. Measurement of mobile lead in soil samples was carried out in 1 M HC1 solution extract. Besides, in soil samples the phosphorus test was made by photocolorimetric method with a phosphorus-molybdenum complex formation in sulphuric extract (the Truog method); the sulphur test – by turbidimetric method of sulphate precipitation by barium chloride in a salt extract; the potassium and sodium test – by flame emission photometry method in the extract with acetic ammonium; the calcium, magnesium, manganese, zinc, copper tests – by method of atomic absorption spectroscopy with flame atomization in acetic and muriatic extracts; the cadmium test – by method of atomic absorption with electrothermal atomization in a muriatic extract [15–17]. All field and laboratory tests of soils and woody plants were carried out according to the international technique of ICP Forests [18].

RESULTS AND DISCUSSION

During determination of the lead content in needles and leaves of woody plants its significant increase at the whole city territory in comparison with background level was revealed (Fig. 1). The highest lead content is registered in the central part of the city where it is 13.5 times larger than background values in pine needles, 9 times – in larch needles, 8 times – in birch leaves, 6 times – in poplar. Rather high lead content in assimilative organs of plants is registered also in the northwest part of the city exposed to the air pollution coming from the enterprises of the neighbouring large industrial centre – Angarsk city. It is necessary to note that on the local sites in the central and northwest parts of the city abnormally high concentration of lead in needles and leaves of the trees – more than 20–25 times larger than background – is found.

In the suburbs of the city lead content in assimilative parts of plants is much lower: its

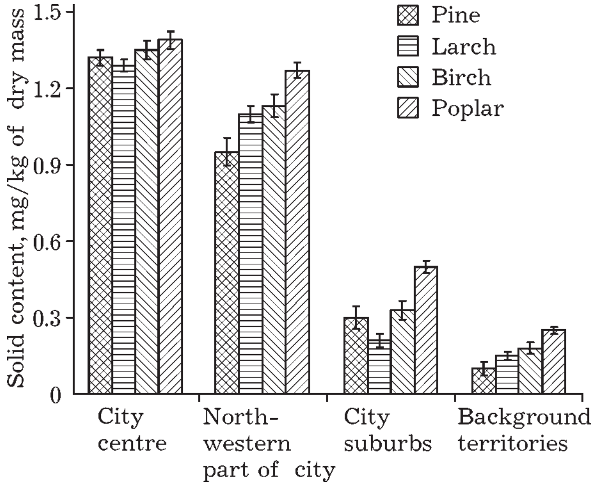

Fig. 1. Lead content in needles and leaves of wood plants in the different regions of Irkutsk.

content is 1.5–3 times larger than background values (see Fig. 1). According to the data in [7, 19], even the twofold increase of the lead content in needles and leaves of plants in industrial regions is an evidence of technogenic environmental pollution. Therefore, it is possible to speak about considerable pollution of Irkutsk by lead compounds.

It is necessary to note that results of phytometry give an overall picture of pollution of some ecosystem, *i. e.* it is a result of both air and soil pollution of the environment. To determine the degree of soil pollution by lead, the geochemical behaviour of this toxicant is investigated and possibility of its absorption by root systems of plants is estimated.

The whole genetic profile of the soils of Irkutsk was analyzed including a set of the following horizons: O–Ad–A–AB–B(BE)–Bt,f–BC–C. It is revealed that an organic litter O (forest litter) of the city soil, as a rule, is thin (usually less than 2 cm) and poorly decomposed. When studying the mobile and gross lead content in a litter a reliably high level of correlation between these indicators (r = 0.86) is found out, and it testifies that there are two combined processes – active release of mobile forms of lead into the soil solution and its accumulations in organic substance. Thus mobile forms of lead in an organic litter of the city soils constitute 65–75 % from the gross content. The level of concentration of mobile lead in the forest litter in the territory of the city is 1.5–17 times larger than background values, the

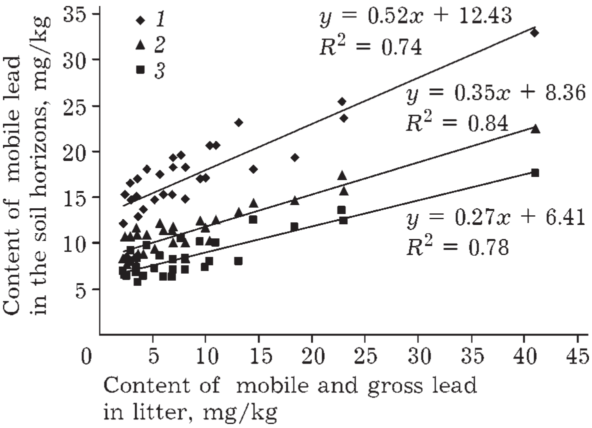

Fig. 2. Relation between the lead content in litter and in the soil horizons of city soils: *1* – Ad horizons, *2* – Bt,f horizons, *3* – C horizons.

maximum value is noted in the central part of the city and is 42 mg/kg, solid content (the background is 2.5 mg/kg).

The major defining factor of behaviour of lead compounds in a litter and their further redistribution in a soil profile is acidity of soil solution. The level of potential acidity of the litter of parks and forest parks of Irkutsk is in a range of neutral and alkalescent values (pH_{KCl} 5.6–6.5). Hydroxide $Pb(OH)_2$ and mobile fulvic acids–lead complexes are known to be able to form at such acidity level of litter solution [20]. Thus, linear dependence between the content of mobile lead in the litter and in the genetic soil horizons are revealed: Ad (humus accumulative), Bt,f (illuvial textural), C (pedogenic) (Fig. 2). These results are the evidence of considerable arrival of lead compounds from technogenic emissions on the soil surface and their subsequent fixation in the organic substance (Ad horizon) and clay fraction (Bt,f horizon). The presence of lead compounds in the depth of pedogenic C horizon is evidence of their high flow ability in the whole soil stratum.

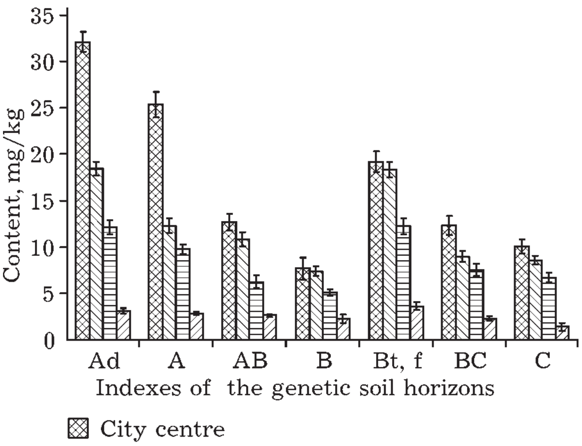

Fig. 3. Content of mobile lead in the genetic horizons of city and background soils.

Thus, in gray forest soils of Irkutsk redistribution of mobile forms of lead occurs in the whole genetic profile. The content of mobile lead in city soils is much above that of background soils (Fig. 3). At the same time the genetic horizons show different ability in accumulation of technogenic lead. The main part of mobile forms of lead in city soils is concentrated in the top humus-accumulative Ad and A horizons where its concentration is 9–10 times larger than background values, the maximum concentration (57.5 mg/kg) is registered in the top soil of the Central park of the city. In the underlying AB and B city soil horizons the significant decrease in mobile lead content is noted, while in mineral Bt,f horizons its concentration increases again: it could be explained by strong fixation of lead ions by illuvial colloids.

Investigation of migrating ability of mobile lead in soil solution of the genetic horizons revealed correlation between the content of mobile forms of this toxicant and exchange forms of calcium, magnesium, sodium, mobile forms of sulphur, phosphorus, cadmium, copper, zinc, manganese are found. Thus, the revealed dependence between the content of mobile lead and exchange calcium (Fig. 4) indicates joint migration of the compounds of these elements in the soil profile system. Such

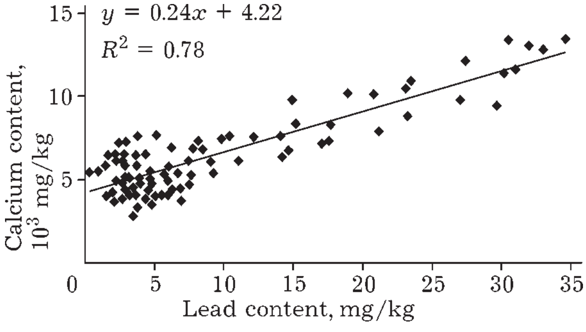

Fig. 4. Relation between the maintenance of mobile forms of lead and exchange forms of calcium in a genetic profile of soils.

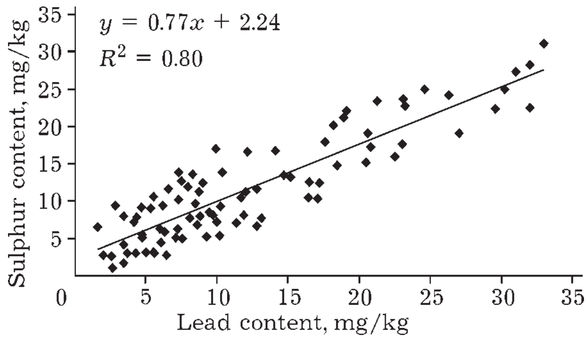

Fig. 5. Relationship between the content of mobile lead and sulphur in genetic profile of soil.

TABLE 1

Correlation between the lead content (x) and other heavy metals (y) in gray forest soils of Irkutsk (P = 0.05, n = 80)

Elements	Linear equation	R^{2*}
Zinc	$y = 0.46x + 6.36$	0.71
Copper	$y = 0.17x + 1.92$	0.65
Cadmium	$y = 0.10x + 0.42$	0.60
Manganese	$y = 0.05x + 1.87$	0.48

*Reliability of approximation value.

pattern of interaction between lead and calcium compounds is investigated in a number of works [21, 22]. Researchers consider that during this chemical process the formation of charged complexes $[Pb(OH)]^+$ and lead carbonate, low-soluble salt takes place. The regression analysis of data on the content of mobile lead and exchange sodium in the horizons of genetic profile of city soils the direct dependence between these values (r = 0.68) is also revealed that testifies joint migration of mobile lead and sodium compounds. For top humus-accumulative horizons of soil mantle of the city the direct correlation between the content of mobile lead and exchange magnesium (r = 0.73), as well as mobile phosphorus (r = 0.45) is found out, and it indicates the joint presence of these elements in the organic soil compounds. Besides, for all soil horizons high positive correlation between the maintenance of mobile forms of lead and sulphur (r = 0.90), which is one of the most widespread technogenic pollutants in the urban environment (Fig. 5) is found. The researchers [20, 23] suppose that mobile forms of lead in soil solution interact with mobile sulphur compounds, and the behaviour and migration of lead compounds essentially depend on an acid mode of soils.

As to the maintenance of mobile forms of heavy metals, as a matter of record for city soils the following number of their correlations (in decreasing order) with mobile lead within a soil profile is revealed: Zn > Cu > Cd > Mn. Thus, we may say about common mechanisms of migration of lead compounds and zinc, copper, cadmium, manganese compounds in a soil profile system. Dependences between the content of mobile lead and other heavy metals in genetic profile of city soils are described by the linear equations (Table 1).

By comparison of data on the lead content in the soil horizons with that in needles and leaves of trees in the territory of Irkutsk a reliable direct correlation between these parameters is revealed (Table 2).

Essentially for all soil horizons the relations of a high significance value are established. Therefore, the data obtained on profile genetic redistribution of technogenic lead indicate possibility

TABLE 2

Significant coefficients of correlation between the lead content in soil and needles (leaves) of woody plants in the territory of Irkutsk (P = 0.05, n = 16)

Plant	Indexes of the soil profile horizons							
part	O	Ad	A	AB	B	Bt,f	BC	C
Pine needles	0.73	0.61	0.71	0.70	0.60	0.68	0.63	0.71
Larch needles	0.54	0.62	0.58	0.68	0.55	0.54	0.54	0.67
Poplar leaves	0.61	0.69	0.75	0.60	0.52	0.58	0.52	0.63
Birch leaves	0.59	0.74	0.62	0.54	0.67	0.65	0.62	0.61

of its active absorption from the polluted soils of the urbanized territories by roots of woody plants.

CONCLUSION

Intake of lead from technogenic emissions is an essential factor of pollution of urban ecosystem, and this is confirmed by the data on its accumulation and redistribution in soil profile horizons and in plants. The lead content in needles and leaves of woody plants in urban territory may be by an order or greater compared to background level. In some cases abnormally high concentration of lead in the assimilative organs, which are 25 times larger than background values are revealed. In all genetic horizons of city soil profile the considerable content of mobile lead is also revealed, and its concentration is 2–20 times larger than background values. The high content of mobile lead in an organic litter (O), the humus-accumulative horizons (Ad and A) and its active vertical migration to textural illuvial (Bt,f) and the pedogenic horizons (C) of genetic soil profile testifies to the expressed technogenic pollution of city soils. Reliable correlation dependences between the content of lead and biogenic elements (calcium, magnesium, sodium, sulphur, phosphorus), as well as heavy metals (zinc, copper, cadmium, manganese) in city soils are found; this indicates a common mechanism of migration of compounds of these elements in genetic profile system of city soils. On the basis of the direct connections revealed between the content of mobile lead in soils and its concentration in needles (leaves) of trees we may conclude that to a large extent the top soil of the city defines the extent of accumulation of technogenic lead in assimilative organs of plants.

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