

Research Articles

Features of Technogenic Metal Pollution of Roadside Soil According to X-Ray Fluorescence Monitoring Data

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Abstract. X-ray fluorescence monitoring of technogenic metal pollution of Moscow soil near two highways with heavy traffic was fulfilled. As a result of vehicles running, the macro and microelement composition of Moscow roadside soil was seen to substantially differ from the composition of both soddy podzolic soil (typical for Moscow region) and any other soil of the temperate climatic region of Russia. The average Fe, Mn and Ti contents in soil were found to exceed the usual background level by 2–5-fold, maximum Pb content – by 10–15-fold. The lateral and depth distribution of enumerated metal contents in soil near the highways was studied. It was shown that the behavior of lateral pollutant distribution in soil has no specific exponential shape. It has local extrema and depends on the metal nature and the roadside terrain topography. For Pb – one of the most dangerous pollutants – the mechanism of chemical transformations and the interrelation of the pollutant chemical form, its molecular weight, the dwelling time in atmosphere and the distance to the highway were discussed.

Keywords: Metal distribution; metal pollution; soil pollution, roadside; vehicle running; X-ray fluorescence monitoring

Introduction

The pollution of Moscow roadside soil by heavy metals in account of a constant increase of the number of automobiles became a considerable part of a common problem of the environmental aggravation. This leads to the death of roadside trees, erosion of roadside bends (as a result of a root frame lesion), the decrease of animal and insect populations, etc. [1].

Heavy metals enter the roadside soil mainly as a result of transport work. When engine barrels and other inner parts are abraded, iron enters the air; the combustion of ethylated fuel is the main source of lead. Aluminum, cobalt, copper, iron, manganese, lead, nickel, phosphorus, titanium, zinc and other elements enter the roadside soil as a result of tire abrasion. Bearings, boxes and brake oils are the sources of copper and zinc [2].

When some of the above mentioned pollutants enter the soil they may remain there for many decades. They can be accumulated by plants and may reach people soon through move-

ment via food chains, thereby causing serious diseases. Lead and cadmium are the most dangerous pollutants among heavy metals [1,3].

For conducting the effective monitoring of such a complicated object for analysis as soil, the analytical method should suit a number of requirements such as 1) simple sample preparation; 2) possibility of simultaneous qualitative and quantitative analysis; 3) large set of elements being determined; 4) wide range of element contents being determined; 5) good reproducibility of the results ($S_r < 0,05$); 6) express analysis; 7) relatively low cost of analysis, that is especially important for routine analysis of large amounts of samples and 8) possibility of conducting campestrial analyses [4,5]. In contradistinction to the classical methods of atomic optical spectroscopy traditionally used for inorganic soil analysis, the method of X-ray fluorescence spectroscopy suits all the above-mentioned demands.

The aim of our work is the study of features of heavy metal distribution in soil beside Moscow highways with heavy traffic thanks to the results of the X-ray fluorescence monitoring.

Iron, manganese, titanium and lead were chosen as being the determined metals. Aside from all of the enumerated elements are the natural temperate climatic region soil components which can all additionally enter soil as a result of running vehicles. Such an element choice lets us study the dynamics of both major (iron, manganese and titanium) and minor (lead) soil composition as a result of technogenic pollution.

1 Experimental

Sampling was conducted parallel to the leeward side of the road with heavy traffic moving alongside. Ten samples of soil from the ground surface on the equal distance to the highway and the distance 5 m from each other were collected. Samples were thoroughly mixed and, by the method of quartitation, the representative samples were prepared.

The first series of samples was collected aside the Moscow circle highway (MCH). The first representative sample was collected at a distance of 10 m from the MCH, the second at a distance of 20 m, other samples were collected at a distance of 20 m from the previous sample line. The last representative sample was collected at a distance of 200 m from the MCH.

The second series of samples was collected aside Minskaya Street. The first representative sample was collected at a distance of 5 m from the road, the second at a distance of 10 m, other samples were collected at a distance of 10 m from the previous sample line. The last representative sample was collected at a distance of 60 m from the road.

Investigating the character of heavy metal content distribution moving depth, an arbitrary point at a distance of 5 m from the Minskaya Street roadside was chosen. The series of soil samples beginning from the ground surface and to a depth of 0.5 m with an interval of 7 cm was collected.

The soil samples were dried in the desiccator and thoroughly milled. Analysis of soil samples was conducted by a portable wave-dispersive X-ray fluorescence spectrometer 'Spectroscan' (Spectron, Russia). X-ray tube of the spectrometer was completed by copper anode, working voltage 40 kV. Qualitative and quantitative analysis was conducted by the method of external standard using FeK_{α} , MnK_{α} , TiK_{α} and PbL_{α} spectral lines. Some samples were also analyzed by the wave-dispersive X-ray fluorescence spectrometer SRS-3400 (Siemens, Germany) by the method of fundamental physical parameters. These results comported finely with the previous 'Spectroscan' results.

2 Results and Discussion

The research shows that there is a background level (natural content of elements, which is distinctive for the given type of soil) excess for the four chosen elements (Table 1). The considerable iron, manganese and titanium content excess indicates the fundamental differences of the major-component content of Moscow soil from the content of both standard soddy podzolic soil (generic for Moscow region) and other types of soil. This accords finely with the results of a detailed multielemental X-ray fluorescence analysis of some samples of soil, which was carried out earlier [5,6].

It was discovered that the content of iron, manganese, titanium and lead in soil varied considerably and didn't obey evidently exponentially decreasing dependence when moving beside the road (Fig. 1–3). Analysis of experimental data shows the following features of element distribution.

The decrease of the content of iron moving aside the pollution source can be seen (series 1). In series 2, there is a content minimum at a distance ~30 m. This can be explained by the influence of natural barriers (at a distance of 5 m from

the road, lime-trees with a height of 10 m and at intervals of 10 m from each other were planted) on the element distribution. The common tendency to the specific element distribution – existence of maxima and minima and graduate decrease of the content – can be seen (series 2). Appearance of local maxima and minima may be connected with graduate precipitation of pollutants in different chemical forms or with the spatial diversity of the chemical content of soil. The maximum content of lead (38 $\mu\text{g/g}$) can be found at a distance of 100 m from the road for the first series of samples; and it is 42 $\mu\text{g/g}$ at a distance of 30 m from the road for the second series of samples.

It was earlier determined [1,6,7], that 75% of lead contained in fuel for internal-combustion engines had consisted of aerosols when entering the air and was then dispersed. Aerosol of lead-containing particles consists of several fractions with particles of different sizes. These particles precipitate on different distances from the roadside. The biggest (the most heavy) particles of the first fraction precipitate very closely to the road (at a distance 5–7 m). The lead compounds of smaller (second) fraction differ by better solubility, and they are more toxic consequently. This fraction of lead influences flora and fauna, and the area, it covers, runs to 30–100 m from the roadside. The smallest particles of the third fraction of lead can be wafted by the streams of air to the great distances (till 150 km) [8]. That's why their distribution is first of all connected with the meteorological conditions. The first and the second fractions compose 8 and 6% respectively; and the third fraction may compose till 86% (by some other data – till 56%) [9].

The investigation of the iron, manganese, titanium and lead content distribution by depth shows the following features. Apparent decrease of the content by the depth of about 30 cm can be seen for all elements except lead; in the case of lead there is an abrupt maximum in the beginning, then the lead content is slowly decreased. There is an abrupt maximum at a depth of 35 cm for all elements except lead; in the case of lead there is minimum content on this depth. There is an abrupt increase of content beginning from the depth of 40 cm for all the elements without exception.

In the literature, there is depth content distribution data only for lead [1]. Technogenic pollution of soil by lead was observed only at a depth of 10–15 cm, more seldom at a depth of 20 cm, as lead can be kept by the layer of humus and it also slightly migrates in soil. However plants contribute the migration of lead to deeper layers of soil.

Table 1: Heavy metal content of Moscow roadside soil in comparison with the background content of these elements in the soddy podzolic soil and other soil of the temperate climatic region of Russia [11,12]

Metal	Content, mass%				
	Soil of the temperate climatic region of Russia		Soddy podzolic soil	Moscow roadside soil	
	Min	Max		Near the road	Average content moving aside the road
Iron	0.69	3.4	0.69	2.1 ± 0.4	1.6 ± 0.3
Manganese	0.009	0.071	0.009	0.16 ± 0.03	0.038 ± 0.008
Titanium	0.17	0.50	0.17	0.31 ± 0.06	0.25 ± 0.05
Lead	0.0008	0.0018	0.0008	0.011 ± 0.003	0.003 ± 0.001

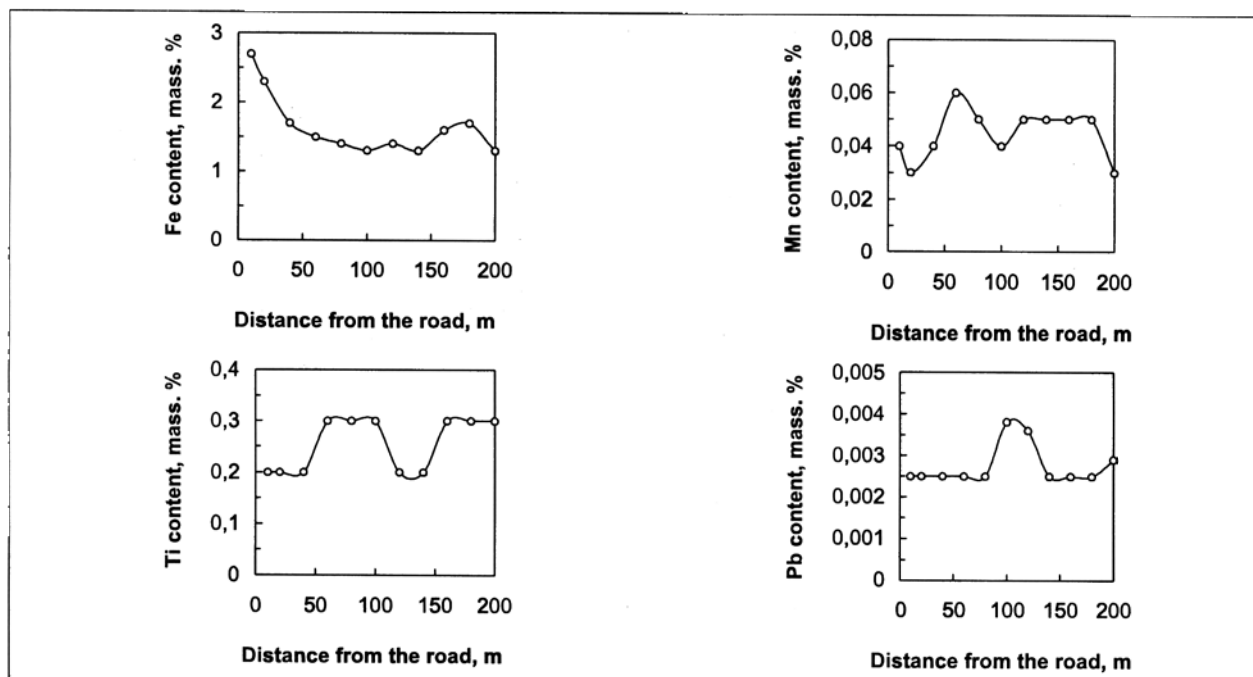


Fig. 1: The lateral distribution of metal content in soil near Moscow circle highway (MCH)

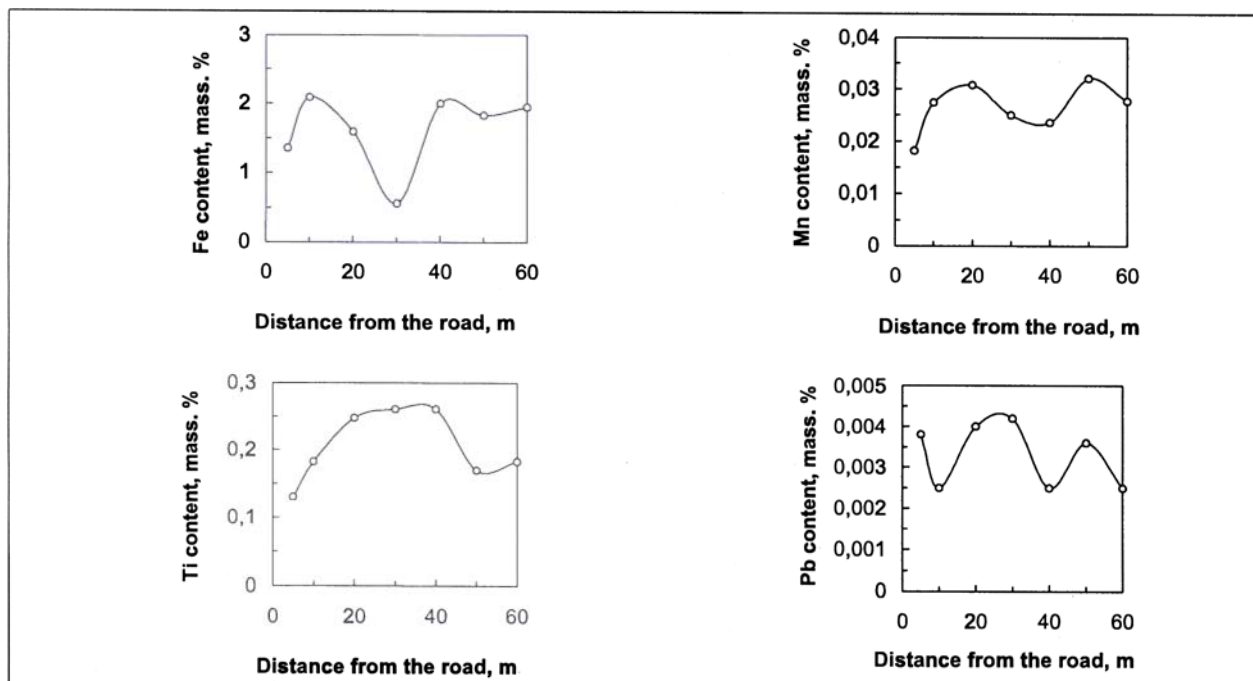
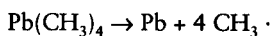
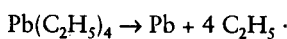


Fig. 2: The lateral distribution of metal content in soil near Minskaya Street

The contrast of X-ray fluorescence monitoring results with the data gained by other scientists [10] lets us demonstrate the following mechanism of roadside soil pollution by lead, which is one of the most dangerous soil toxicants.

In automobile engines, lead appears when alkyl-lead anti-knockers decompose. In combustion cameras, they decompose under high temperatures by the reactions:



Furthermore, lead is oxidized to lead dioxide, which degrades peroxides, thus preventing knocking; lead dioxide turns into lead monoxide:

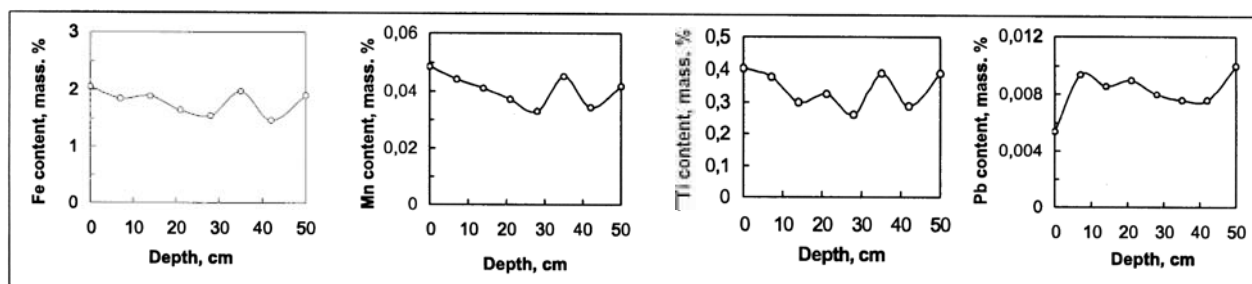
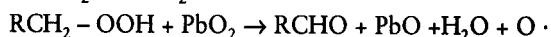
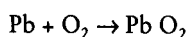
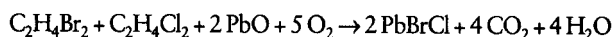


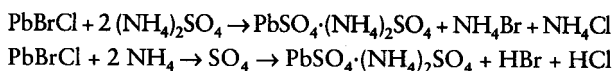
Fig. 3: The depth distribution of metal content in soil



Lead monoxide has a high melting temperature and it can precipitate on relatively cold engine parts as a 'solid thief'. To avoid this, and for the disposal of the solid lead oxides and antiknockers from the engine, special 'expellents' can be added to the fuel together with antiknockers. These 'expellents' are organic compounds of chlorine and bromine, for example bi-chlorine- and bi-bromine-ethanes. As a result, mixed halogenides of lead can appear:



In the air, polluted with neutral and acidic ammonium sulfates, the following reactions can occur:



Except for inorganic compounds of lead, traffic exhausts also contain non-burned (residual) quantities of a very toxic compound, tetra-alkyl-lead.

Thus, considerable quantities of lead (0.011 mass%) directly beside the road are apparently composed of PbBrCl par excellence (high molecular mass, small indwelling time in the atmosphere). The lead content may exceed the background level 10 – 15-fold in this case. More low specific quantities of lead in soil at a distance of 60 – 120 m from the road are probably composed of PbSO₄·(NH₄)₂SO₄ (smaller molecular mass, higher indwelling time in the atmosphere). This hypothesis will be tested in our further investigations.

3 Conclusions

The results of X-ray fluorescence analysis of the samples of soil, that were collected beside the Moscow highways with heavy traffic, show the excess of contents of four metals (iron, manganese, titanium and lead) in soil by 2–5-fold on average. It was found that the major and minor composition of examined samples of roadside soil did not accord the composition of standard soddy podzolic soil of the temperate climatic region of Russia. Distribution of the enumerated elements in soil moving alongside the road up to a distance of 100–200 m has no specific exponential features. For such comparatively brief distances, it substantially depends on the roadside terrain topography, the mechanism of chemical transformations

of metals in atmosphere, the ratio of the different chemical forms of the pollutant, their molecular weights, the dwelling time in atmosphere and so on. For the further detailed study of the distribution of different chemical forms of metal pollutants (lead, first of all) in roadside soil, we are planning to measure the distribution of sulfur, chlorine and bromine in soil with use of the adapted XRF techniques.

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