Case of soil surface chromium anomaly of a northern urban territory – preliminary results

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ABSTRACT

The aim of this paper is to present some results of a soil survey conducted at a northern city in Russia and analysis of origin of spots polluted by chromium. During the survey, 101 soil specimens were taken from different parts of the city using squared grid system with a spatial resolution of 250 m. Two soil specimens were also taken from distant background locations to exclude the influence the pollutant sources. Chemical analysis was performed on soluble and total forms of heavy metals, mineral oil products, as well as other concentrations of parameters were measured. According to spatial distribution of total chromium concentrations, two spots with high level of pollution have been recognized. Mean concentration of total chromium in the spots subgroup is ten times higher than in the subgroup of comparison. It was suggested that the origin of anomalous pollution is not associated with the industrial activity and could not be explained by atmospheric deposition only.

1. Introduction

Study of nature and levels of territorial pollution is one of the most relevant issues in environmental protection, since its results are the basis for assessment and forecasting the state of the components for environmental and health effects.

There are at least two main approaches for territorial pollution assessment: experimental surveys and modeling. Mathematical models are always the simplification of principal processes that take place in reality (Popovic, 2008). It demands more data, the considerable part of which could be obtained experimentally.

There are a number of pollution sources that are located irregularly in urban territories. Due to several reasons, their emissions could not be precisely evaluated. Climate, the character of building up, hydrogeological conditions, variable atmospheric conditions, instability of emissions, and many other factors introduce more ambiguity into the data (Berlyand, 1975). For these reasons, the results of modeling of pollution distributions are not fully reliable. However, they can be used for preliminary evaluations. The main advantages of modeling as compared to a sampling and analysis are their relatively low cost, ease of model modification, possibility of conducting multiple calculations (Gorelov, 1985). In comparison with modeling, the experimental survey is capable of evaluating the real situation of pollution (to some extent), but it has to be used within an optimized approach. Otherwise, its cost could also be high.

With time, different types of emissions appear to be accumulated into the environmental media (i.e., soil, biota, snow, water, and bottom sediment). Thus, different types of surfaces, accumulating emissions could be used to study the nature and characteristics of pollution. Mapping of spatial distribution of pollutants in an accumulated media allows to recognize the anomalies of different levels and provides important information for a GIS (geographic information system) environment (Salminen et al., 2004; Zhang et al., 2008; Omelkova et.al., 2009). Analyzing such anomalies depending on the type of accumulation media frame is useful to formulate some hypotheses on the nature of pollution.

Soil-ecological monitoring is the crucial constituent of studying the environment. Unlike water and air, which are migrating systems, soil is the most objective and steady indicator of man-caused ecosystem pollution. Finally, pollution of any environmental media leaves a print in the soil. Soil pollution clearly reflects the mechanism for emission of atmospheric pollutants and their actual distribution on landscape components (Saet et al., 1990; Kimbrough et al., 1999). Soil is one of the most steadily accumulating components of the environment, since its layers had been formed for decades. Unlike the accumulation of pollutants in different media, the spatial distribution in the soil is virtually the final reflection of territorial pollution. The issue is not only important in evaluation of the pollution level, but also in investigating the mechanism of pollutants transport, the source and scale of pollution (Chukanov et al., 2006; Chipres et al., 2008).

The available data on chemical agents' distributions in soil show that probability distributions of components concentration do not always follow the Gaussian distribution (Zhang et al., 2008). The type of the distribution function of the probability, especially considering multimodal distributions, could reveal pattern of chemical agents' spatial distribution. The analysis of these functions provides supplementary information on the nature and sources of pollution.

The aim of this paper is to present the results of the soil survey conducted at a northern city in Russia and analysis of possible origins of spots polluted by chromium.

2. Method of Soil Survey

Soil pollution data used in this study were drawn from a field survey in the frames of routine ecological monitoring program of Tarko-Sale town situated in Yamal-Nenets Autonomous District, Russia in 2007 (Figure 1). Tarko-Sale was founded in 1932, acquired the status of an industrial community in 1976, and town status in 2004. Oil and gas industries form the basis of the Purovsky district's economy. The agrarian companies and mining industry are absent.
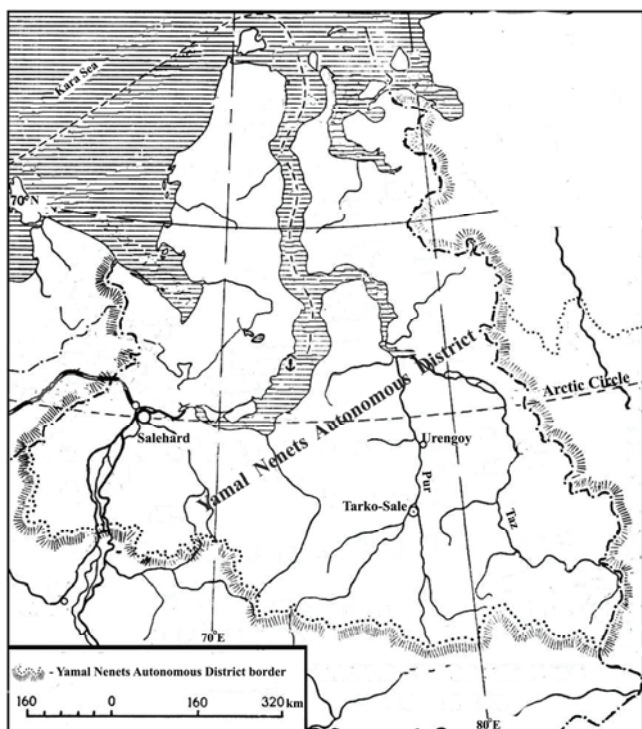

Figure 1. Yamal-Nenets Autonomous District schematic map.

Tarko-Sale is located on a flat plain. Altitude differences are less than 20 m. The local soils are alluvial-humus podzols with a little content of organic matter (Dobrovolsky et al., 2004). Podzolic soils were formed in Pyaku-Pur river drainage areas. The composition of the soil is 100% sand (size fraction less than 1 mm). There was no obvious reason to expect/detect chromium pollution in the area. Major pollutants could be phenols or mineral oils for example. This field survey was not planned to analyze the origin of chromium pollution, however obtained data allows testing this hypothesis.

Soil sampling at the urban territory was designed on a squared grid system with a spatial resolution of 250 m, and it was conducted in September 2007. Real locations of sample sites were determined after direct testing in situ based on necessity of taking

samples of undamaged natural sites of studied territory. Geographical positioning was carried out by means of the GPS-receiver.

The surface of sampling site was marked as 1.0 m^2. Nine cores of soil to the depth of 0.05 m were taken by the stainless steel grabber with the 0.051 m internal diameter in vertexes, middle of sides and center of marked square. Nine sampled cores were combined and packed in double polyethylene bags. The inside bag was marked with the specimen identifier. Thus, the total area of nine cores was 0.0184 m², and the total volume was 0.000919 m³. The mass of each dried specimen was approximately 1.5 kg.

During the survey, a total of 103 soil specimens were taken from different parts of the city, including inhabited and industrial zones. Regular samples included 101 specimens referred to a territory of 5 km², and two specimens were taken from distant background locations to exclude the influence the sources of pollution.

Preparation of soil specimens and chemical analysis were conducted in compliance with actual standard requirements. The chemical laboratory involved with soil sample preparation and analysis passed through the Russian federal certification system. The preparation steps included drying the specimens at a temperature less than 105 ^{o}C and sieving using a sieve with 1 mm diameter. The remained material over the sieve was not included in the analysis. After sieving and homogenizing of each specimen, 20 g of sub-samples were milled to 0.074 mm diameter grains for total metal analysis and remainders were used for further soluble fraction analysis.

Element concentrations in the soluble fraction were determined by extraction with a buffered 1 mol/L ammonium acetate solution (pH = 4.8). Elemental concentrations in extracted solutions were determined by the Atomic Absorption Spectrophotometer (AAS-3, Carl Zeiss Jena, Germany). Application of AAS technique for analysis of extracted solutions is limited to a narrow range of detectable concentrations. To determine the total metal concentrations in soil samples (0.1-1.0 g) were digested by treatment with concentrated nitric acid and hydrofluoric acid. After mixing and heating up to 95 ^{o}C the solution was digested with concentrated perchloric acid, and after cooling it was treated with hydrochloric acid with weak heating for 30 min. After cooling, the solution was diluted up to 50 ml with deionized water, mixed thoroughly and placed in a polyethylene bottle. The solution was analyzed with the inductively coupled plasma-mass spectrometry (Perkin Elmer, ELAN 9000). Determination of mercury was carried out with a flameless atomic absorption method (cold vapor). Concurrent analysis of standard reference materials were conducted necessarily for every set of samples.

The list of chemical agents, included in the chemical analysis program of soil samples, and number of measurements above the limit of detection are presented in Table 1. The pollutants are determined according to the routine ecological monitoring program and justified by their potential danger even in trace quantities (Motuzova et al., 2007).

3. Results and Discussion

In most specimens, the concentration of soluble forms of chromium, cobalt, nickel, copper and zinc and total arsenic, cadmium and mercury appeared to be below the limit of detection of the methods used for chemical analysis (Table 1). Soluble forms of heavy metals leached out of alluvial-humus podzols (Kabata-Pendias et al., 2001).

The correlation matrix was constructed for chemicals with significant concentrations in specimens of regular samples. Figure

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Table 1. *List of characteristics and chemical agents, included in chemical analysis*

Chemical agents	Form	Designation	Level of detection	Number of measurement results above level of detection
Hydrogen ion exponent	-	pH	1 pH unit	103
Chromium	soluble	Cr_AAB	2 mg/kg	0
Chromium	total	Cr_TF	20 mg/kg	103
Manganese	total	Mn_TF	20 mg/kg	103
Cobalt	soluble	Co_AAB	1 mg/kg	4
Cobalt	total	Co_TF	1 mg/kg	103
Nickel	soluble	Ni_AAB	1 mg/kg	23
Nickel	total	Ni_TF	2 mg/kg	103
Copper	soluble	Cu_AAB	2 mg/kg	4
Copper	total	Cu_TF	1 mg/kg	103
Zinc	soluble	Zn_AAB	2 mg/kg	45
Zinc	total	Zn_TF	5 mg/kg	103
Arsenic	total	As_TF	1 mg/kg	19
Cadmium	total	Cd_TF	0.1 mg/kg	21
Mercury	total	Hg_TF	0.05mg/kg	4
Lead	total	Pb_TF	1 mg/kg	103
Phenol	-	C_6H_5OH	0.005 mg/kg	83
Mineral oil products	-	Oil	0.005 mg/kg	103
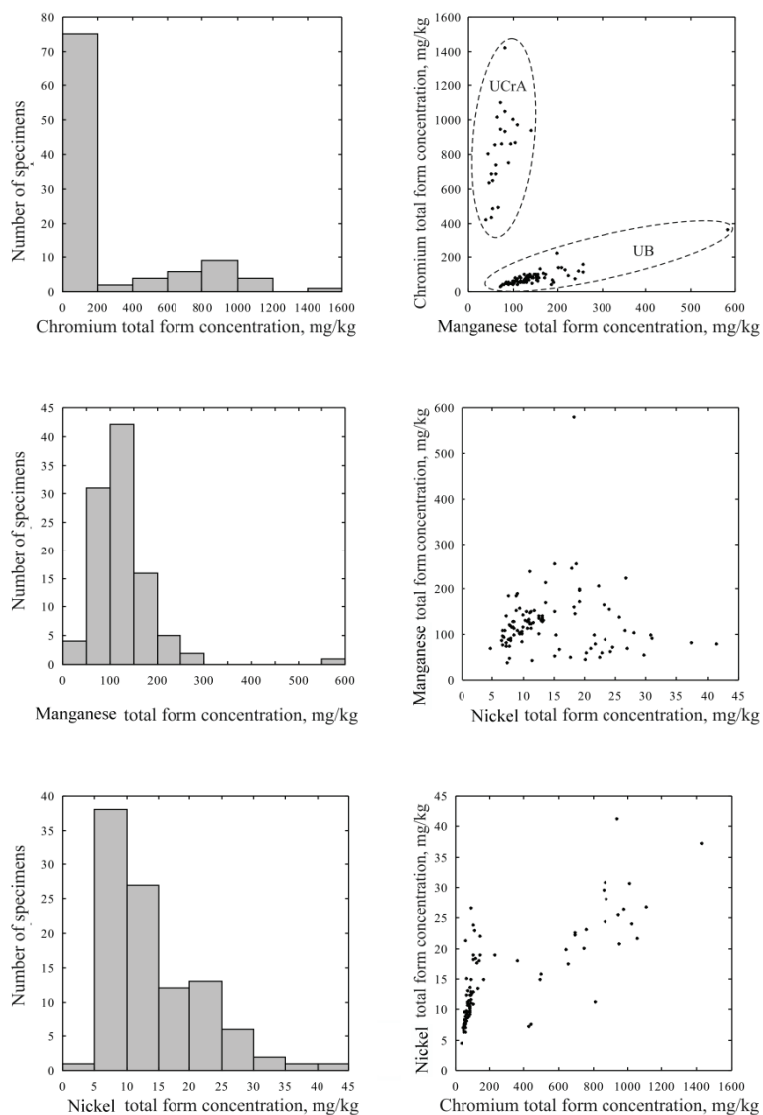
Figure 2. *Correlation scatter plots and histograms of distribution of chemical agents' concentration for regular sample.*

2 shows correlation scatter plots and histograms of distribution of chemicals (i.e., total chromium, total manganese, total nickel). Two clusters are clearly noticeable on the scatter plot of total chromium versus total manganese. Moreover, it was found that concentration distribution for total chromium was bimodal.

On the basis of comparison of the correlation scatter plots (Figure 2) and spatial distribution (interpolation by Ordinary Kriging) of total chromium concentration in soil (Figure 3) and total nickel (Figure 4), the regular samples were divided into urban background subgroup UB (Urban Background – 77 specimens) and urban chromium anomaly subgroup UCrA (Urban Chromium Anomaly – 24 specimens). In spite of bimodal distributions, we have used the geostatistic analysis module of ESRI ArcGIS software, with default ordinary Kriging parameters for construction of only qualitative spatial distribution without the variogram analysis (Dmitriev, 2008).
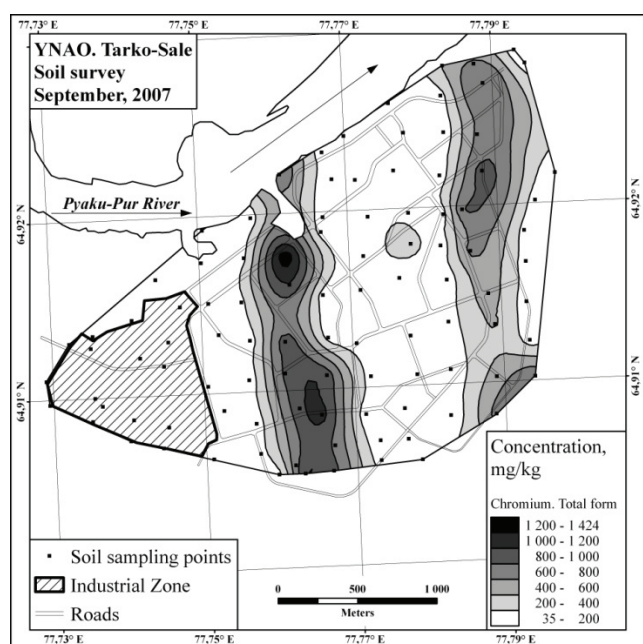

Figure 3. Spatial distribution of total chromium on schematic map of city.

It should be mentioned that the regular sample division according to both spatial distribution of variable total chromium and clusters on correlation scatter plots of total chromium versus total manganese appeared to be essentially equal.

Table 2 presents the results of Kolmogorov-Smirnov two-sample test calculation that was done for comparison of UB and UCrA subgroups. For the most variables, the difference is significant ($p < 0.001$). The results proved that the regular samples were divided to UB and UCrA subgroups correctly.

The most significant difference was observed for the total chromium. Mean concentration of total chromium in UCrA subgroup is ten times higher than in the UB subgroup (Table 2). Comparing with both background total chromium concentrations in the Ural Region of Russia (Ural Clarke) and in world soils (World Clarke) it can be seen that the total chromium concentration in UB subgroup does not exceed the reference values, while the total chromium in UCrA subgroup is 2.5 times higher than Ural Clarke (Vojtkevich et al., 1977; Saet et al., 1990).

Total chromium contents in podzols in particular are known to range from 2.6 to 34 mg/kg in Canada (Frank et al., 1976) and from 3 to 200 mg/kg in USA (Shacklette et al., 1984).
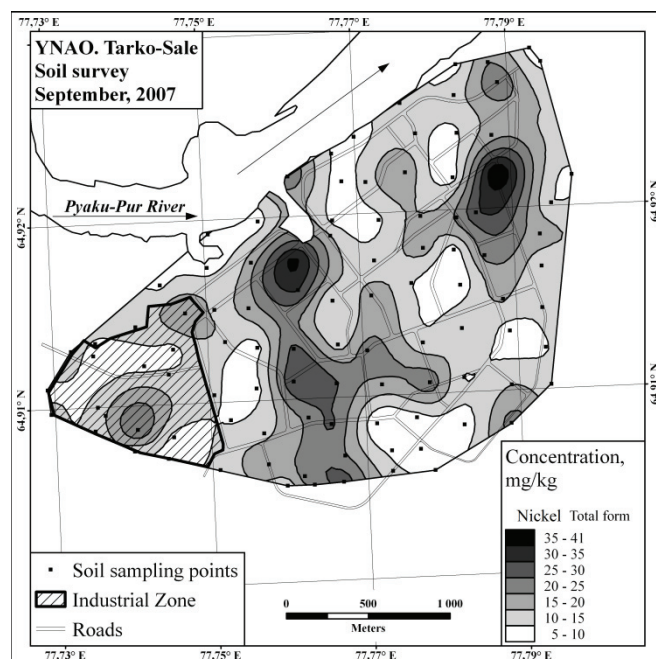

Figure 4. Spatial distribution of total nickel on schematic map of city.

The UCrA subgroup on the map plotted with total chromium values (Figure 3) forms two spots stretched in meridian direction. Two spots with the same location appeared on the map plotted with total nickel values (Figure 4). However, the division corresponding to the west and east spots of UCrA subgroup could not be found on scatter plots (Figure 3). That indicates a similar chemical composition and origin of the spots.

Spearman correlation coefficients for UB and UCrA subgroups are presented in Table 3. As can be seen from Table 3, total chromium, total manganese, total cobalt, and total nickel are closely correlated. The highest correlation coefficients in both UB and UCrA subgroups are found for a pair of total chromium versus total copper, 0.93 and 0.80, respectively. It should be noted that all significant correlation coefficients are positive. However, if the average values are compared (Table 2), it could be seen that UCrA average values are higher than UB ones only for total chromium and total nickel.

Several hypotheses can be suggested on either natural or anthropogenic origin of chromium anomaly spots (Perelman, 1989; Baralkiewicz et al., 1999). The natural concentrations of chromium in the parent rocks forming the soils vary greatly. High concentration of chromium in soil can appear at sites of outcropping of chromium ores. Hypotheses on anthropogenic origin of soil chromium anomaly could be considered as feasible. The important sources of chromium emissions to the environment are associated with industrial use of chromium: refractory insulation (fire-bricks), electroplating, leather tanning, wood preservation, painting, and textile printing. The aerosols, liquid and solid wastes are generated as a result of these processes. Soil pollution by chromium is possible through atmospheric deposition, direct pollution due to waste discharge. Sometimes materials with relatively high chromium content (e.g. crushed brick) are used for land-filling for house and road construction. The land-filling practice is common in northern wetlands such as the territory under the investigation.

Table 2. Kolmogorov-Smirnov two-sample test for comparison UB and UCrA subgroups

Sub-group	Parameter	Concentration, mg/kg								
		pH	Cr_TF	Mn_TF	Co_TF	Ni_TF	Cu_TF	Zn_TF	Pb_TF	Oil
	p-level	>0.100	<0.001	<0.001	<0.001	<0.001	<0.010	>0.100	>0.100	<0.050
	Mean	6.6	83	142	3.7	12	16	17	8.9	51
UB	Median	6.5	73	129	2.8	10	14	8.9	6.1	15
	SE	0.1	5.1	7.6	0.5	0.5	0.8	2.5	1.2	9.2
	Mean	6.5	821	72	3.6	23	11	19	7.2	14
UCrA	Median	6.6	864	68	2.1	3	12	13	5.1	7.7
	SE	0.1	48.1	5	0.8	1.7	0.6	4.4	1.1	4.1
Ural Clarke (Saet et al., 1990)			300	800	10	20	50			
World Clarke (Saet, et al., 1990)			200	850	13	40	30			

Table 3. Spearman correlation coefficients for UB and UCrA subgroups (the underlined correlations are statistically significant, p <0.01)

		pH	Cr_TF	Mn_TF	Co_TF	Ni_TF	Cu_TF	Zn_TF	Pb_TF	Oil
		UB subgroup (n=77)								
pH		1	0.07	-0.15	-0.08	0.23	0.07	0.29	0.26	<u>0.50</u>
Cr_TF		0.45	1	<u>0.75</u>	<u>0.88</u>	<u>0.86</u>	<u>0.93</u>	0.28	<u>0.37</u>	0.13
Mn_TF		0.46	<u>0.69</u>	1	<u>0.84</u>	<u>0.67</u>	<u>0.76</u>	<u>0.38</u>	<u>0.46</u>	0.15
Co_TF	UCrA subgroup (n=24)	0.17	<u>0.75</u>	<u>0.76</u>	1	<u>0.82</u>	<u>0.86</u>	0.26	<u>0.37</u>	0.18
Ni_TF		0.39	<u>0.73</u>	<u>0.75</u>	<u>0.73</u>	1	<u>0.83</u>	<u>0.37</u>	<u>0.50</u>	<u>0.39</u>
Cu_TF		0.43	<u>0.80</u>	<u>0.75</u>	<u>0.64</u>	<u>0.79</u>	1	<u>0.35</u>	0.39	0.20
Zn_TF		0.04	0.29	<u>0.64</u>	0.49	0.44	<u>0.55</u>	1	<u>0.62</u>	<u>0.42</u>
Pb_TF		0.08	0.04	0.47	0.14	0.31	0.19	0.45	1	<u>0.51</u>
Oil		0.15	0.11	0.31	0.16	0.16	0.35	0.26	0.30	1

All available data obtained during the soil survey were analyzed in order to choose a hypothesis that reliably explains the origin of soil chromium anomaly.

The soil survey data are not enough to draw a conclusion on the presence of chromium ores in the underlying bedrock. Other natural processes of soil formation such as sedimentation can be analyzed using data on elevation of investigated sites. However, a correlation between surface height (altitude differences) and concentration of total chromium in soil was not found.

Table 2 shows that the average phenol concentration in UCrA is two times lower than the average phenol concentration in UB, and the average mineral oil products concentration in UCrA is three times lower than the average mineral oil products concentration in UB. In other words, the spots of chromium anomaly are less contaminated by phenol and mineral oil products. There are also lower concentration of total of manganese and copper. Thus, the atmospheric deposition could not be the only reason for such a spatial distribution of chemical agents.

In order to further investigate the atmospheric origin of chromium anomaly a simple calculation was performed. The observed difference between the average value of chromium total concentration in UB subgroup and in UCrA subgroup is about 737 mg/kg. Having the area of 0.0184 m² and specimen mass of 1.5 kg the chromium surface concentration is estimated as: 737 mg/kg x 1.5 kg/0.0184 m² = 60 g/m² (for a layer with a thickness of 0.05 m). The rough estimate of the total area of chromium anomaly is 1 km². Thus, the excess mass of chromium in the anomaly reaches to approximately 60 t. The question is, could such a mass of chromium could be deposited from the atmosphere? If one assumes that chromium have been deposited permanently and evenly from the atmosphere on the surface of

the anomaly, starting from the foundation of the city until the soil sampling (75 years since 1932), then the average daily intensity of chromium deposition would be (60 g/m²)/27 400 days = 2.2 mg/(m².day).

According to our results of the snow surveys of industrial cities in the neighboring region, the average values of total chromium deposition intensity for the about 100 days winter period since permanent snow cover onset were 0.037 mg/m².day in Novouralsk city (2003-2004) and 0.016 mg/m².day in Ekaterinburg city (2007–2008), Russia. These values are about two orders of magnitude lower than the calculated value above for the chromium anomaly. Moreover, the assumed long-lasting chromium deposition could not have formed an apparent spot. The spot of such intensity is possible only under conditions of acute chromium emission from a point source and a stable wind. In this case, the intensity of chromium deposition could be up to 60 g/m² within a short period (e.g. few days). Thus, taking into account above consideration it can be concluded that the chromium anomaly does not only have an atmospheric origin.

4. Conclusions

According to the results of soil survey of the urban territory an anomalously high total chromium concentration was found. Measured concentrations of total chromium in soil considerably exceeded the typical regional and global values. Chromium anomaly appeared on a background of relatively low concentration of nickel, cobalt and other heavy metals that are common pollutants at the urban territory.

The analysis allowed specifying the anomaly of high total chromium concentration, which is shaped with two stretched spots on the map. Since the anomaly is placed far from the industrial

zone but within the residential zone of urban territory, it can be concluded that the chromium anomaly is not associated with industrial activity. As the simple calculations confirm, the origin of this anomaly could not be explained by only atmospheric deposition. There is reason to believe that detected chromium anomaly is related to land-filling. Further research to determine the origin of the anomaly is necessary.

Acknowledgements

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