Magnetic properties and concentration of heavy metals in soils and street dust

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Abstract. Magnetic susceptibility values of different dust fractions were determined by the kappametry method for the Mezhdurechensk city territory (Kemerovo oblast) exposed to coal mining enterprises. The mineral composition of the dust was studied. The magnetic susceptibilities of soil samples were determined as reference values. The analysis of iron group elements in road dust (size fraction < 1 mm) showed the positive noticeable correlation between the dust magnetic susceptibility and amount of Fe, Co, Cr contained in it. The measurement of the road dust magnetic susceptibility by the kappametry method allows quick assessment of pollution with the heavy metals of the iron group and can be recommended for monitoring.

1 Introduction

The main factor of the atmospheric air pollution in urban areas is the presence of dust. Studying dust in a snow cover allows tracing the input of contaminant components in winter, which is relevant for regions with a long period of snow cover presence [1-4]. In this period the incoming of the lithogenous component of rocks and soils into a snow cover is impossible. At present the pollution of the urbanized area topsoil with heavy metals is one of current interest problems. Heavy metals in soils are closely related to magnetite, maghemite and other ferrimagnets, which allows the methods of studying the soil cover magnetic properties to be applied for the soil contamination diagnosis. Measurement of the magnetic susceptibility (MS) is one of the most common methods for determination of the soil magnetism characteristics [5-7]. The theoretical basis of research was the ideas and principles of the ecological and geochemical assessment of soils developed by M.A. Glazovskaya [8], V.V. Dobrovolsky [9], etc., and it also took into account the results of magnetic geochemical studies of E.A. Molostovskii [10]. Along with studying MS of soils, the interest in studies of road dust as the special environmental object of a complex composition, when monitoring ecological and geochemical characteristics, increases. Values of MS represent the level of air dust pollution and can be important for detecting sources of dust incoming into the air [11,12].

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The article present study of MS characteristics of the road dust and topsoil of Mezhdurechensk area, Kemerovo region, in relation to their mineral-substance and element composition

Research procedures. In the summer period (July-August), 2020, 29 road dust samples of spots located at equal distances from each other (M: 1:25000) were taken on the territory of Mezhdurechensk where the maximum accumulation of dust emissions is possible. The dust was carried from of coal mining objects during drilling-blasting operations towards the city and emitted by objects of steam power industry shown in Figure 1. When choosing the pick-up spots the effect of vehicles was tried to be avoided. The material for analysis was taken by sweeping up asphalt areas with clean plastic brushes of rigid pile according techniques described in [13-14].

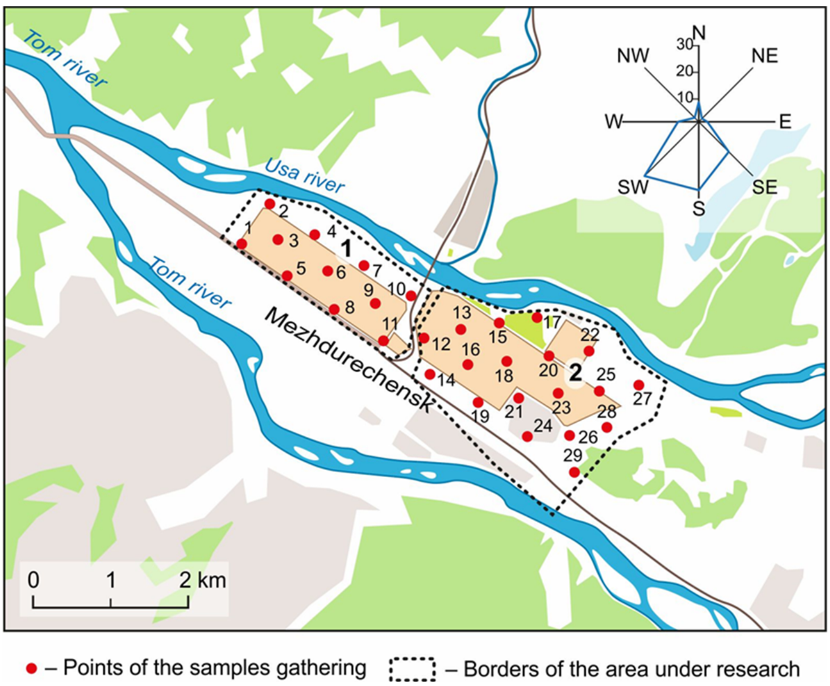


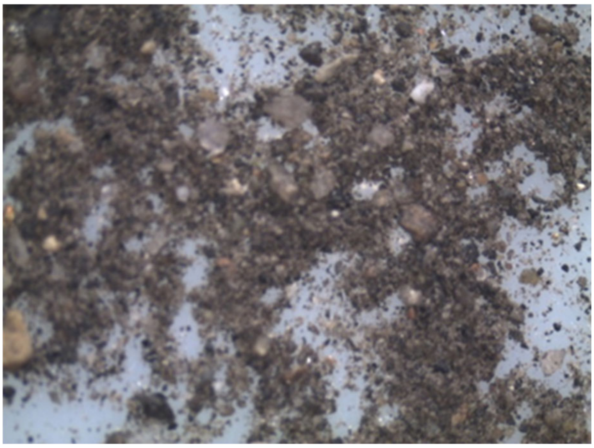
Fig. 1. Schematic map of point test sampling of road dust and soils on Mezhdurechensk area. 1and 2 denote the west part and the east part respectively.

Collected samples, weighing at least 500 g each, were placed in solid polyethylene packages then were dried at room temperature and were sifted through a sieve with a mesh cell dimension of 1 mm for separating the sample substance from the street debris. Selected samples of the road dust were exposed to the mesh screen analysis and then each fraction was analyzed. in fractions of less than 1 mm. The content of iron group elements was determined by the Inductively Coupled Plasma mass-spectrometer (ICP-MS) at the Chemistry-Analytical Center “Plasma”, Tomsk.

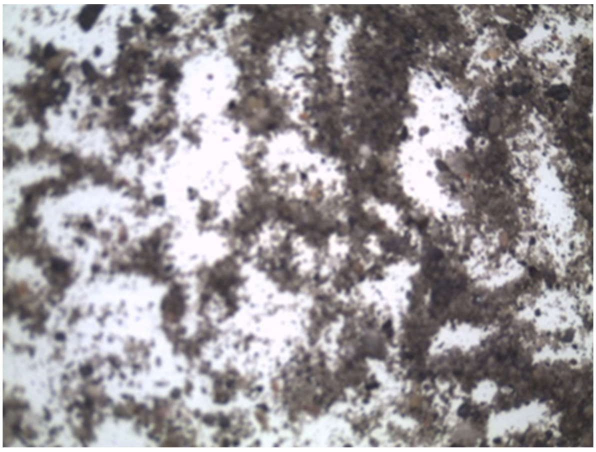
MS was measured by MS meter KM-7 at scientific center "Uranian Geology" of Tomsk Polytechnic University using the patented method contained in Patent of RF No. 2133487. The cuvette made of non-magnetic material kept steady the sample volume during the tests in order to make the comparison of experimental results correct. For working out the methodological issues, sample measurements of MS were carried out for the bulk sample and its fractions with particle dimensions less and more than 1 mm. The weight was determined for each sample and then MS values were determined for the whole sample and separately for each fraction. The measurement was made three times to avoid errors and the average value was taken by the result. The processing and interpretation of the results were performed together for all point taking account of the area landscape features and locations of coal mining enterprises. MS values of soil samples taken at these pointes were determined earlier in 2015. The mineral-substance composition of the road dust was determined by optical microscopy methods using binocular microscope Leica EZ4D and X-ray diffraction analysis methods using diffractometer Bruker D2 Phaser at the premises of educational and scientific laboratory "Uranium Geology".

2 Results

The road dust contains naturally occurring particles and industry-related ones of different size so the substance structure is inhomogeneous as shown in Figure 2(a). The fraction of particles with a size < 1 mm is more homogeneous and presented mainly by natural formations as seen in Figure 2(b).



a)



b)

Fig. 2. Photographs of road dust specimens of Mezhdurechensk area: a) fraction particles > 1 mm, amplification 16^x; b) fraction particles < 1 mm, amplification 16^x (were made on optical microscope Leica EZ4D).

According to results of X-ray diffractometry the road dust substance contained largely quartz (34.5%) and albite (30.7%). There are also ferromagnetic and paramagnetic ore minerals represented by magnetite, ilmenite, chromite and hematite. The mineral composition is presented in Table 1.

Table 1. The road dust mineral composition obtained by X-ray diffractometry methods.

Mineral	Formular	Percentage,%
quartz	SiO_2	34.5
dolomite	$CaMg(CO_3)_2$	11.1
albite	$Na(AlSi_3O_8)$	30.7
kaolin	$Al_4(OH)_8(Si_4O_{10})$	3.5
calci-spar	$Ca(CO_3)$	3.4
orthoclase	KSi_3AlO_8	6.0
muscovite	$KAl_2(Si,Al)_4O_{10}(OH)_2$	9.1
ilmenite	$FeTiO_3$	0.6
chromite	$(Fe_{0.5}Mg_{0.5})(Cr_{1.64}Fe_{0.28}Ti_{0.02}Al_{0.06})O_4$	0.3
magnetite	$Fe_{2.75}Ti_{0.25}O_4$	0.3
hematite	Fe_2O_3	0.4

The volume MS value of the road dust bulk samples of Mezhdurechensk is in the range (158.3 - 564.8) $\cdot 10^{-5}$ at the average value of $295.0 \cdot 10^{-5}$, whereas for the fraction samples with the particle dimension less than 1 mm from it is in the range (137.6 - 475.4) $\cdot 10^{-5}$ at the average value of $273.8 \cdot 10^{-5}$ and for the dimension larger than 1 mm - (85.6 - 1037.6) $\cdot 10^{-5}$ at the average value of 259.8 $\cdot 10^{-5}$. The values of MS for different parts of the city do not significantly change as shown in the Table 2.

Specific MS values were compared with data on MS of the soils widely represented in scientific literature [15, 16]. Perm area (Russia) and soils of urban forests of Upper Silesia (Poland) have background MS values in the range (50-60) $\cdot 10^{-8}$ m^3/kg what is considered typical values for unpolluted soils. Some China province soils have values of the specific MS of 914 $\cdot 10^{-8}$ m^3/kg (Hangzhou), 1128 $\cdot 10^{-8}$ m^3/kg (Luoyang) and 1959 $\cdot 10^{-8}$ m^3/kg (Shanghai). The high values of specific MS of 1271 $\cdot 10^{-8}$ m^3/kg and 656 $\cdot 10^{-8}$ m^3/kg were found at certain points near the boiler houses of Kuzbass area where coals are mainly used for the heat energy production. The specific and volume MS values vary within the city insignificantly and the difference between values for the western part and eastern part of the city is small. The average values of percentage element contents in soils also differ slightly between the two parts of the city. This is explained by the fact that the territory is small and anthropogenic sources of pollutants (coal dust of closely located enterprises, burning coal products) exert their effects by similar ways.

The simultaneous analysis of the MS and the bulk content of the iron group elements allowed estimating the relationship between these characteristics. Some numeric data are presented in Table 3. In dust samples taken in the city the average percentage of iron, cobalt, chromium and nickel defined by the ICP MS method amounted to 3.86 ± 0.07% (Fe), 104.4 ± 3.2 mg/kg (Cr), 15.5 ± 0.4 mg/kg (CO) and 19.5 ± 1.7 mg/kg (Ni) respectively.

Statistical values of MS, the sampling variance of MS of the dust and percentage of elements Cr, Fe and Co do not change beyond 35% of their average value. The distribution of Ni percentage within the area is not so uniform. The values of the sampling variance were 29.7% (specific MS), 9.3 % (Fe), 16.6 % (CR), 14.5 % (CO) and 47.9 % (Ni).

Table 2. Average weight, volume MS and specific MS for different fractions of road dust samples.

Magnitude	City	West part of the city (1)	East part of the city (2)
Number of sampling point	29	11	18
Bulk sample, dust			
$\frac{m_{sample}}{m_{max} \div m_{min}}$	$\frac{99.2 \pm 2.4}{130 \div 60}$	$\frac{103.8 \pm 2.5}{1116 \div 88}$	$\frac{96.4 \pm 3.5}{130 \div 60}$
$\frac{\mu_{vol}}{\mu_{vol.max} \div \mu_{vol.min}}$	$\frac{295.0 \pm 18.1}{564.8 \div 158.3}$	$\frac{310.8 \pm 26.2}{522.8 \div 199.0}$	$\frac{285.4 \pm 24.6}{564.8 \div 158.3}$
$\frac{\mu_{spec}}{\mu_{spec.max} \div \mu_{spec.min}}$	$\frac{291.0 \pm 15.6}{425.8 \div 159.4}$	$\frac{293.9 \pm 23.8}{474.4 \div 185.7}$	$\frac{289.2 \pm 21.1}{570.6 \div 159.4}$
Fraction particle dimension < 1 mm. dust			
$\frac{m_{sample}}{m_{max} \div m_{min}}$	$\frac{93.8 \pm 2.2}{116 \div 60}$	$\frac{97.1 \pm 2.9}{116 \div 83}$	$\frac{91.7 \pm 3.0}{116 \div 60}$
$\frac{\mu_{vol}}{\mu_{vol.max} \div \mu_{vol.min}}$	$\frac{273.8 \pm 15.1}{475.4 \div 137.6}$	$\frac{275.9 \pm 18.1}{355.3 \div 172.1}$	$\frac{272.5 \pm 22.0}{475.4 \div 137.6}$
$\frac{\mu_{spec}}{\mu_{spec.max} \div \mu_{spec.min}}$	$\frac{285.7 \pm 13.4}{457.4 \div 163.5}$	$\frac{280. \pm 18.9}{347.0 \div 168.0}$	$\frac{289.1 \pm 18.7}{457.4 \div 163.5}$
Fraction particle dimension > 1 mm. dust			
$\frac{m_{sample}, g}{m_{max} \div m_{min}, g}$	$\frac{78.7 \pm 4.7}{113 \div 31}$	$\frac{85.1 \pm 7.0}{108 \div 47}$	$\frac{74.8 \pm 6.2}{113 \div 31}$
$\frac{\mu_{vol}}{\mu_{vol.max} \div \mu_{vol.min}}$	$\frac{259.8 \pm 31.2}{1037.6 \div 85.6}$	$\frac{251.6 \pm 24.4}{333.1 \div 85.6}$	$\frac{264.8 \pm 48.7}{1037.6 \div 122.7}$
$\frac{\mu_{spec}}{\mu_{spec.max} \div \mu_{spec.min}}$	$\frac{345.0 \pm 40.2}{1271.1 \div 167.9}$	$\frac{304. \pm 38.2}{545.8 \div 171.2}$	$\frac{369.5 \pm 60.8}{1271.1 \div 167.9}$

Note: $m_{samples}$, m_{max}, m_{min} – average, maximum and minimum weights of samples (g), relatively; μ_{vol}, $\mu_{vol.max}$, $\mu_{vol.min}$ – average, maximum and minimum values of the volume MS ($\cdot 10^{-5}$ SI units) relatively; μ_{spec}, $\mu_{spec.max}$, $\mu_{spec.min}$– average, maximum and minimum values of specific MS ($\cdot 10^{-8}$ m^3/kg) respectively.

The average specific MS of the fraction with the particle dimension < 1 mm of the soil samples taken at the same points was measured $264.7 \pm 16.8 \cdot 10^{-5}$ SI units. The average values of the following element contents 3.66±0.15% (Fe), 116.9 ±4.9 mg/kg (Cr), 17.0±0.6 mg/kg (Co), 39.3±1.7 mg/kg (Ni) were determined by ICP-MS method. The ranges limiting these contents variations from minimum to maximum values differ insignificantly as Table 3 shows. Although MS values vary slightly, as mentioned already, some points had elevated MS and element contents. This indicates the local nature of technogenic effects.

Table 3. Comparable parameters of MS and percentage of iron group elements in road dust and soils.

Object, year, method	$\frac{\mu_{vol}}{\mu_{vol.max} \div \mu_{vol.min}}$	$\frac{c_{sample}}{c_{max} \div c_{min}}$			
		Fe, %	**Cr, mg/kg**	**Co, mg/kg**	**Ni, mg/kg**
Road dust, 2020, ICP MS, 29 samples	$\frac{273.7 \pm 15.1}{475.4 \div 137.6}$	$\frac{3.86 \pm 0.07}{4.80 \div 3.17}$	$\frac{104.4 \pm 3.2}{141.3 \div 68.4}$	$\frac{15.5 \pm 0.4}{21.0 \div 11.0}$	$\frac{19.5 \pm 1.7}{47.0 \div 3.0}$
Soil, 2015, INAA*, 29 samples	$\frac{264.7 \pm 16.8}{524.0 \div 112.9}$	$\frac{3.66 \pm 0.15}{4.70 \div 0.97}$	$\frac{116.9 \pm 4.9}{197.6 \div 51.9}$	$\frac{17.0 \pm 0.6}{22.7 \div 5.3}$	$\frac{39.3^{**} \pm 1.7}{48.4 \div 30.0}$

Note: * instrumental neutron activation analysis;
** the nickel content of soils according to ICP MS (10 samples).

The plots demonstrating correlation between the dust MS values and contents of Fe, Cr, Co and also between the MS values of dust and soils are presented in Figure 3. They show the MS depends on contents of iron group main elements because there are noticeable positive correlations between MS and contents of Fe (R = 0.72) and Cr (R = 0.54).

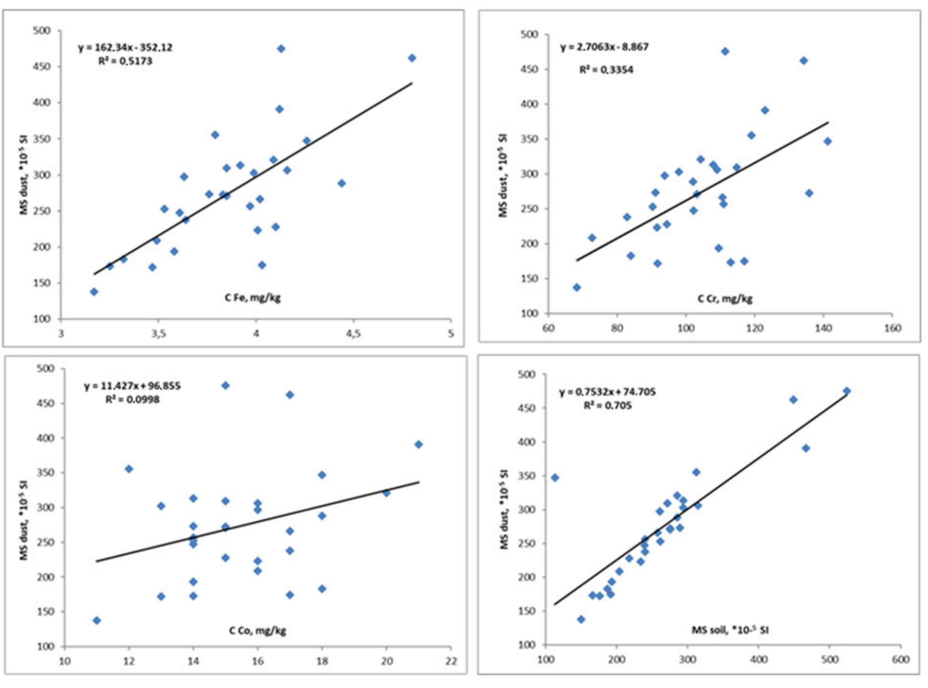


Fig. 3. MS of the samples plotted against the road dust element contents and MS of soils.

It was noted [16] the character of relations between the sample MS and contents of some elements can be different from strong positive to negative ones. No correlation between the MS and the Co content is logical in the study because specific sources of Co pollution were not in the area and its contents in the samples are of trace amount level.

Substantial positive correlations between the MS of soils and dust (R = 0.84) have a dual explanation. First, the soil components constitute a large part of road dust content and, then, it is affected by the long-term tendency of the area soil formation. The steady non-critical pollution of the city area with heavy metals is observed years long, for the last five years no new polluting sources were found. The area distribution of MS and contents of Cr, Fe and Co in road dust and soils is presented in Figures 4 and 5, diagrams illustrate that the area distributions of the variables are similar.

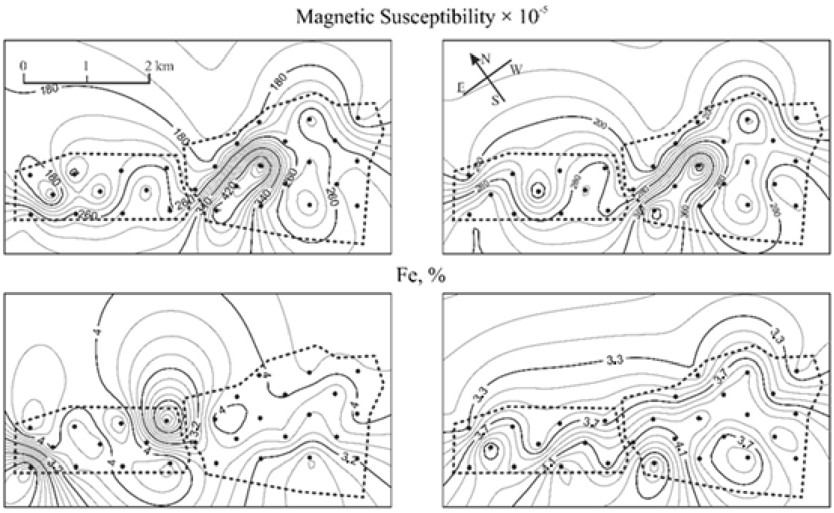


Fig. 4. Distribution in area of MS and contents of Fe in soils (left) and road dust (right) of Mezhdurechensk.

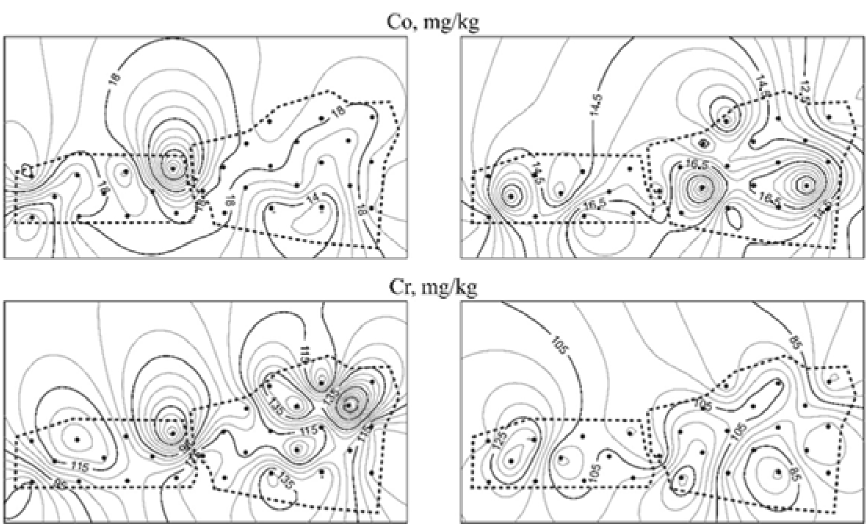


Fig. 5. Distribution in area of Co and Cr in soils (left) and road dust (right) of Mezhdurechensk.

3 Conclusion

The MS values for road dust samples of different fractions in the area of Mezhdurechensk were determined. The analysis of the iron group chemical elements in road dust (fraction particle dimension < 1 mm) revealed positive substantial correlation between the MS and contents of Fe, Cr and Co. The main ferromagnetic minerals are represented by magnetite, ilmenite and chromite. The dust obtained parameters correlate with the corresponding ones of the soil samples taken in 2015; the MS and contents of Cr, Fe, Co and Ni of the samples have similar area distribution pattern. The city area is exposed to the long-term non-critical pollution with heavy metals. For the five-year period, no new sources of pollution were detected. Thus, the measurements of the magnetic susceptibility of road dust samples give quick and informative estimate of the pollution with the iron group heavy metals of the city area and can be recommended for monitoring activities.

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