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Andrei Vasiliev¹, Mikhail Razinsky², Svetlana Gorokhova³

APPLICATION OF MAGNETIC SUSCEPTIBILITY MEASUREMENT FOR MAPPING AND ASSESSMENT OF ECOLOGICAL QUALITY IN URBAN TOPSOILS

ABSTRACT

The article presents the results of geostatistical mapping of the magnetic susceptibility of the urban top soil. Soil magnetometry is well suited for rapid monitoring of pollution in urban areas due to its high sensitivity, ease of measurement, rapidity, high reproducibility of analysis, and low cost. This method allows obtaining large datasets with high resolution. The purpose of the study: spatial modeling of magnetic susceptibility and ecological-geochemical assessment of the top soil of Kudymkar city. The research area covers a section of the city with a total area of 32 km². Spatial modeling was carried out by the geostatistical method based on 51 soil samples. The background magnetic susceptibility of the soils of the city is 3–4 times higher than the magnetic susceptibility of the soils of the non-contaminated regional background. Soils with high and very high magnetic susceptibility occupy more than 30 % of the city area. Anomalous zones of soil magnetic pollution or magnetic "hot spots" formed near industrial facilities, heating boilers, on roadside soils with heavy traffic. A scale for the volumetric magnetic susceptibility of soils was developed on the centile analysis of the data. Strongly magnetic soils contain elevated concentrations of Zn, Cu, and Ni. The concentrations and names of pollutant metals in urban soils depend on the techno-geochemical specialization of cities. It can be recommended that the Environmental Services of cities use measurements of the magnetic susceptibility to monitor the ecological and geochemical state of soils and identify areas of city soils contaminated with heavy metals.

KEYWORDS: magnetic susceptibility, soil heavy metals pollution, geostatistics, ecological valuation

INTRODUCTION

The formation of local soil-geochemical anomalies is an actual environmental problem of urbanized territories [Kapička, 1999; Magiera, 2006; Vasiliev, 2011; Vodyanitsky, 2017; Eremchenko, 2018; Nikiforova, 2021; Świdwa-Urbańska, 2021]. Over the past decades, a number of scientists have done a lot of work to study the geochemical state of soils using the results of kappametry [Vodyanitsky, 2008; Mikov, 1995; Chevychelov, 2021]. A study of the relationship between magnetic susceptibility and heavy metal (HM) pollution was carried out in large industrial cities of Russia, such as Moscow [Gladysheva, 2007], Saratov [Reshetnikov, 2009], Perm [Vasiliev, 2015], etc. As of 2020, there are 809 small towns on the territory of the Russian Federation (population is <50,000 people), which is 71 % of the total number of cities in the country [Regions of Russia..., 2020]. It determines the high importance of conducting ecological and geochemical research. The relationship between the magnetic susceptibility of soils and HM in small towns is not well studied [Vasiliev, 2020].

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¹ Perm State Agro-Technological University, Faculty of Soil Science, Agrochemistry, Ecology and Commodity Research, Petropavlovskaia St., 23, 614990, Perm, Russia, *e-mail:* a.a.vasilev@list.ru

² Perm State Agro-Technological University, Faculty of Soil Science, Agrochemistry, Ecology and Commodity Research, Petropavlovskaia St., 23, 614990, Perm, Russia.

³ Perm State Agro-Technological University, Faculty of Soil Science, Agrochemistry, Ecology and Commodity Research, Petropavlovskaia St., 23, 614990, Perm, Russia, *e-mail*: **gorohova.s@hotmail.com**

The city of Kudymkar is the administrative center of the Kudymkarsky municipal District of the Perm region (Figure 1). Kudymkar has the status of regional significance and an urban district; it is the administrative, business, cultural, educational, industrial center of the Komi-Permsky District. In 2020, more than 30,400 people live in Kudymkar [Regions of Russia..., 2020].

The ecological situation on the territory of Kudymkar is assessed by regional environmental organizations as a hotspot [On the state and protection ..., 2020]. The main stationary sources of *HM* in the territory of Kudymkar for several decades were local heating plants, OJC "Kudymkarsky mechanical repair plant", LLC "Electrical Appliance Plant". The chemical composition of river waters is an indirect indicator of the ecological and geochemical state of the top soil of the city. In the period from 2014 to 2019, the quality of river water in the river Inva in the area of Kudymkar city varied between "polluted" (2016, 2019) and "very polluted" (2015, 2017–2018). Average annual concentrations of *HM* in river water exceeding the maximum permissible concentrations were observed for Mn, Fe, Cu, Zn.

The ecological and geochemical state of soils is satisfactory for agricultural landscapes adjacent to the city, according to the Perm State Center of Agrochemical Service. The average content of elements Cu is 23 ppm, Zn 47 ppm; Cd 0.87 ppm; Pb 26 ppm in arable soils of the Kudymkar region [State annual report "The state …", 2013]. This is above or at the level of the clarke of chemical elements in the upper part of the continental crust according to K.H. Wedepohl [*Wedepohl*, 1995]: $KK_{Cu} = 1.6$; $KK_{Zn} = 0.9$; $KK_{Cd} = 8.5$; $KK_{Pb} = 1.5$. But they do not exceed the hygienic standards established for soils in Russia.

The purpose of the study: spatial modeling of magnetic susceptibility and ecological-geochemical assessment of the top soil of Kudymkar.

MATERIALS AND METHODS

Research area. Kudymkar city (N 59°01'00" N, 54°40'00" E) locates in the northwest part of the Middle Cis-Urals (Figure 1).

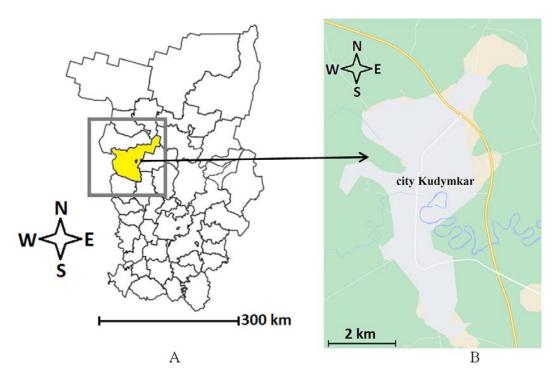


Fig. 1. Research area: A-Kudymkarsky District is in the Map of Perm region; B-Kudymkar city

The distance to the regional center of Perm is 201 km. The Perm–Kudymkar–Gayny–Syktyvkar highway passes through the city of Kudymkar. The study area is characterized by a moderate continental climate [*Ogureeva*, 2020]. The relief of the research area is smooth-widewavy, complicated by river valleys. The geological foundation of the territory is composed of red clays with interlayers of marl and limestones of the Capitanian, Wordian and Roadian stages of the Guadalupian series of the Perm period [*Vasiliev*, 2014]. The vegetation of natural land-scapes in the vicinity of the city is represented by southern taiga fir-spruce forests [Decree of the Governor.. Forest plan of the Perm region for 2018–2027, 2018]. Podzolic and sod processes of soil formation are leading *in vivo*. According to a study by N.Ya. Korotaev [1962], natural top soil of the Kudymkarsky's region is heavy loamy Umbric Albeluvisols Abruptic [IUSS Working Group WRB, 2015]. A distinctive feature of it is the combination of industrial and residential areas on a relatively small area – 32.24 km². The main territory of the city is dominated by 1–2-storey wooden manor buildings.

Site description and sampling strategy

Soil sampling sites covered the following territories of the city of Kudymkar: inside residential areas, roadside areas, in the vicinity of industrial enterprises and boiler houses, in a forest park zone (Figure 2).

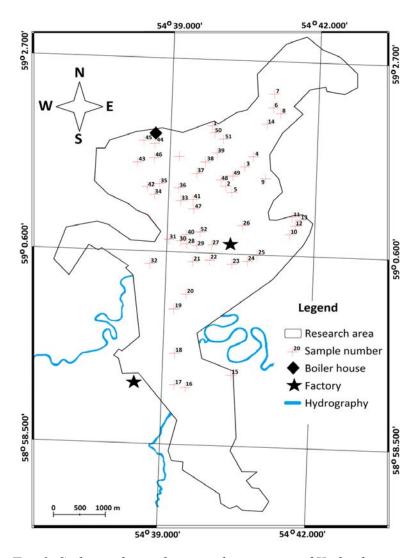


Fig. 2. Soil sampling scheme in the territory of Kudymkar city

The objects of study on the territory were urbo-sod-podzolic soils, urbanozem, and replantozem [Aparin, 2015]. The location of the sampling sites was recorded using GPS, with a record of the surrounding conditions. We took 51 combined soil samples from the 0–10 cm layer. Each (combined) soil sample weighing 1.2-1.5 kg was obtained by mixing five to six subsamples within one 10 m^2 site. The combined soil samples were homogenized, roots removed, air dried, crushed and sieved through a 1.0 mm nylon sieve. The elemental chemical composition was determined in soil samples with a particle size d < 1.0 mm.

Analytical methods

Magnetic susceptibility (K) was measured using Kappameter KT-6 (StatisGeo, Czech Republic) at the Soil Science Department of the Perm State Agro-Technological University. The sensitivity of the equipment was 1×10^{-5} SI units, and the measurement ranges varied from -9.99 to 99.99×10^{-5} SI units. Parameter was determined at three points on each site. A total of 153 single measurements K were carried out.

The bulk content of Cu, Zn, Ni, and Cr in 7 samples of high-magnetic soils was analyzed by atomic absorption spectroscopy using a Savant AA spectrometer (GBC Scientific Equipment, Australia). Analysis was carried at the FBUZ Center for Hygiene and Epidemiology in the Perm region. Soil samples were disaggregated using an agate mortar and pestle. Three times, 5 g of each of these composite samples were treated with a concentrated solution of ethylenediamine tetraacetic acid (EDTA) and topped up with distilled water (40 ml). The digested soil solutions were cooled to room temperature, filtered and transferred to plastic vials prior to metal analysis; the splitting was carried out in accordance with the working manual for the analysis [PND F 16.1:2.2:2.3:3.36-2002, 2011].

Geostatistical analysis

The assessment of the spatial inhomogeneity of the *K* included the selection of the optimal interpolation parameters. A preliminary analysis of the *K* data in the sample is carried out, which included: an assessment of the statistical distribution of indicators; determination of the presence of global trends; semivariogram analysis and modeling; cross-validation of interpolation accuracy. The ArcGIS Geostatistical Analyst was used as software.

With normal (Gaussian) data distribution, the Ordinary kriging method was used – this is one of the most commonly used interpolation methods in geostatistics [Yost, 1982].

The optimal parameters for creating a schematic map of the magnetic susceptibility of soils in the city Kudymkar were selected by the geostatistical method of conventional kriging [Chashchin, 2020]. The identification of classes (groups) of soils on the K map of soils of the city Kudymkar was carried out by the method of natural intervals. The groups (classes) of the magnetic susceptibility of soils are selected in such a way as to group similar in K values.

Construction of a map of magnetic susceptibility and analysis of areas of soils with different magnetic susceptibility

The formation of raster values for calculating areas by groups of intervals of soil properties is carried out by reclassifying geostatistical layers. For this, the continuous values of the indicator were replaced by the interval in which they fall. The interval itself was denoted by an integer. Ranges of magnetic susceptibility were selected from the raster according to the formula written in the "Raster calculator" of the GIS application:

«ok_Clip11@1» – geostatistical raster of soil magnetic susceptibility. After perclassification, the areas of groups with different levels of magnetic susceptibility were calculated for the resulting rasters.

Ecological and geochemical analysis

For a geochemical assessment of the state of soils, the following formulas were used: Geoaccumulation index (Igeo) [*Muller*, 1979]:

$$I_{geo} = log_2 \frac{C}{1.5C_R} \tag{2}$$

C – concentration of the i-th chemical element in the soil component (soil, magnetic phase), ppm;

 $C_{\rm \it B}$ – concentration of the *i*-th chemical element in the background soil, ppm [Bakharev, 2012];

1.5 – constant is used as a coefficient to minimize possible variations in background values due to lithogenic effects.

The contamination categories based on the I_{geo} are classified as below: uncontaminated $(I_{geo} \leq 0)$; uncontaminated to moderately contaminated $(0 < I_{geo} \leq 1)$; moderately contaminated $(1 < I_{geo} \leq 2)$; moderately to heavily contaminated $(2 < I_{geo} \leq 3)$; heavily contaminated $(3 < I_{geo} \leq 4)$; heavily to extremely contaminated $(4 < I_{geo} \leq 5)$; and extremely contaminated $(I_{geo} > 5)$.

Coefficient of concentration relative to the clarke of lithosphere according to K.H. Wedepohl (KK_w) [Wedepohl, 1995]:

$$KK_{w} = \frac{C}{C_{w}} \tag{3}$$

 C_w – clarke of the *i*-th chemical element of the lithosphere according to K.H. Wedepohl, ppm [Wedepohl, 1995].

Contamination factor (CF) [Hakanson, 1980]:

$$CF = \frac{C}{C_R} \tag{4}$$

Coefficient of concentration relative to the clarke of soils of residential landscapes according to V.A. Alekseenko (KK_A) [Alekseenko, 2013]:

$$KK_a = \frac{C}{C_a} \tag{5}$$

 C_a – clarke of the i-th chemical element of the soil of residential landscapes in Russia according to V.A. Alekseenko, ppm [*Alekseenko*, 2013].

When using KK_w , CF, and KK_a the soil pollution was classified as follows: x < 1 low contamination, $1 \le x < 3$ moderate contamination, $3 \le x < 6$ considerable contamination, x > 6 very high contamination [Hakanson, 1980].

Statistical analysis

Statistical parameters were calculated in the MS Office 2010 software package using the "Data Analysis" function and according to E.A. Dmitriev [Dmitriev, 2008].

RESULTS

Magnetic susceptibility of soils

Statistical evaluation of the data distribution. Table 1 shows the descriptive statistics of the averaged values (n = 3) of the magnetic susceptibility of the city soils at 51 observation sites. The soils on the territory of Kudymkar are characterized by values of magnetic susceptibility in a wide range: from 0.25 to 8.17×10^{-3} SI. The distribution of **K** values has a weakly pronounced left-sided skewness (Table 1, Figure 3).

Table 1. Descriptive statistics of the magnetic susceptibility of the top soils of Kudymkar, 10^{-3} SI, n = 51

Indicator values			Std. Dev.	Kurtosis	Cleans		
Min	Max	Mean	Median	Siu. Dev.	Kurtosis	Skew	
0.25	8.17	1.67	1.18	1.52	8.25	1.99	

The distribution of soil magnetic susceptibility values is shown in the histograms (Figure 3). The data of magnetic susceptibility were logarithmic (function = log10) (Figure 3). The central values of the data on the magnitude of the logarithmic magnetic susceptibility have close values of the mean and median, which indicates the distribution of properties according to the normal (Gaussian) law.

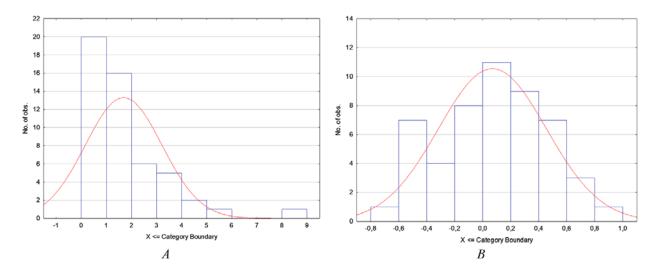


Fig. 3. Histograms of relative frequencies of magnetic susceptibility of the top soils, n = 51: A – magnetic susceptibility, 10^{-3} SI; B – logarithmic magnetic susceptibility

The **K** values in the sample correspond to the normal (Gaussian) distribution and are suitable for further processing by the ordinary kriging method, without performing the transformation over them using the normal labels method. There is no need to optimize the curve for the data values.

Trend analysis. The magnetic susceptibility of urban soils is often influenced by an external anthropogenic factor; therefore, for correct interpolation of **K** data for the entire territory of Kudymkar, a check was made for the absence of global trends. The test results showed the absence of global trends (Figure 4).

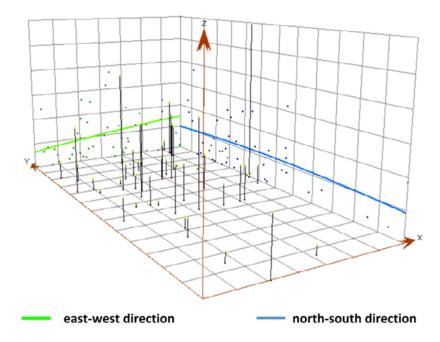


Fig. 4. Trends in the spatial distribution of magnetic susceptibility of the top soils, n = 51

Analysis of semivariograms. The relationship between the magnetic susceptibility of soils and their spatial distance from each other is described by a variogram. The model variogram showed a weak spatial dependence of the magnetic susceptibility (Figure 5).

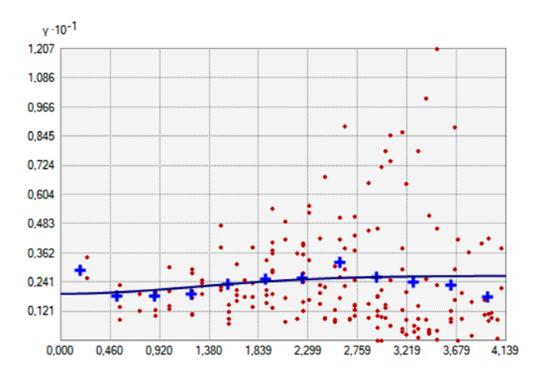


Fig. 5. Variogram of magnetic susceptibility of the top soils, n = 51

Correct interpolation should be based on an optimal semivariogram model. It was fitted automatically using the Semivariogram Optimization feature of the Geostatistical Analyst.

Figure 6 shows the result of the classification of the magnetic susceptibility of soils in the city Kudymkar by the method of natural boundaries. According to the magnitude of the magnetic susceptibility of soils on the variogram, 5 grades were identified (Figure 6). The 1st grade includes K values in the range from 0 to 1.34×10^{-3} SI. The first grade differs in the breadth of the range of intervals from other grades. The second grade includes K values from 1.34 to 1.52×10^{-3} SI. Third grade is from 1.52 to 1.73×10^{-3} SI. This grade includes the arithmetic mean value of K for the entire sample of the K values of the soils of the city. The rest of the grades unite soils that occupy significantly smaller areas on the map of the K of soils of the city (Figure 6).

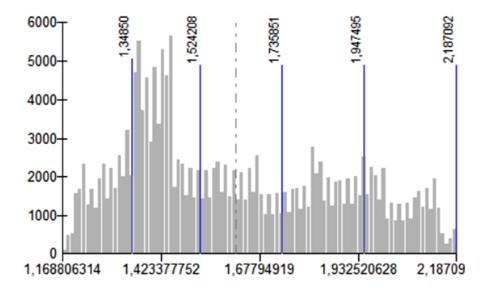


Fig. 6. Grouping by the "natural intervals" method of the values of the magnetic susceptibility of the top soils, n = 51

Based on the obtained distribution, the gradations of the magnetic susceptibility of soils were formed (Table 2). In accordance with the scale K, the structure of the top soils of Kudymkar had the following appearance: with low K-271.9 ha (14.2 % of the city area), medium K-608.4 ha (31.9 %), increased K-364.6 ha (19.1 %), high K-347.1 ha (18.2 %), very high K-317.2 ha (16.6 %) (Table 2). The most common in the city were medium-magnetic soils -32 %. The smallest area had low-magnetic soils -14.2 % of the city area (Table 2).

Class	Grade	Magnetia suspentibility 10-3 CI	Area	
		Magnetic susceptibility, 10 ⁻³ SI	ha	%
I	Low	<1.34	271.9	14.2
II	Medium	1.34–1.52	608.4	31.9
III	Increased	1.52–1.73	364.6	19.1
IV	High	1.73–1.94	347.1	18.2
V	Very high	>1.94	317.2	16.6

Elemental chemical composition

The concentrations of the studied elements in the soils of magnetic "hot spots" of Kudymkar varied in wide ranges: Cr 146–331; Zn 41.6–85.3; Cu 20.2–31.6; Ni 34.3–119.0 ppm. The average content of HM was: Cr – 249; Zn – 59.0; Cu – 25.8; Ni – 64.8 ppm (Table 3).

Coefficients of variation of the bulk HM content are estimated as follows: Cu – insignificant, Cr and Zn – medium, Ni – high (Table 3).

Table 3. The bulk content of heavy metals in of the top soils (0–10cm layer), ppm n = 7, P = 0.05

Site No.	Location of the sampling site		Zn	Cu	Ni
2	Stroiteley St., 15/1 District (shopping center area)		82.5	20.2	47.7
16	Sverdlova St., 19 (area of the bridge on the river Olich)		47.5	23.3	103.0
21	Kirov St., 12 (roadside territory)		58.0	31.6	55.0
22	8th March St., 9 (roadside)		43.1	24.9	119.0
27	M. Gorky St., 38 (area of the mechanical repair plant)		85.3	26.0	34.3
33	Danilov St., 8 (roadside territory)		55.3	26.9	54.5
46	Novoselov St., 15 (roadside territory)		41.6	27.8	40.4
	Mean		249.0	59.0	25.8
SE		27	27.0	6.8	1.4
SD		70	70.0	18.0	3.6
SV		49.2	49.2	324.4	12.9
Min		146	146.0	41.6	20.2
Max		331	331.0	85.3	31.6
Variance, %		28.2	28.2	30.5	13.9

DISCUSSION

Areas of low-magnetic soils are confined to the western part of the city, on which land of low-rise residential buildings is located, bordering on agricultural land. Soils with medium magnetic susceptibility are distributed in the meridional direction. Garden and summer cottages and low-rise residential buildings are widespread in this territory. The values of low and medium magnetic susceptibility of soils of Kudymkar are 3–4 times higher than the background of soddy-podzolic soils of the Middle Cis-Urals [Vasiliev, 2011].

The soils of residential areas of the central part of the city had an increased K. Soils with high and very high magnetic susceptibility on the territory of the city belong to the category of magnetic "hot spots" [Magiera, 2006]. The bulk of man-made magnetic particles enter the city's territory from the industrial centers of the Perm Region and the Kirov Region due to transboundary transport at high altitudes of emissions of flue gases and aerosols, as well as from local anthropogenic sources.

Soils with high magnetic susceptibility were formed within the sanitary protection zone of industrial enterprises of the city. Areal areas of soils with a very high magnetic susceptibility were identified in the industrial zone in the north-east of the city, as well as in the east of the city, in the residential area of 4–5-storey buildings with active car traffic (Figure 7).

Until the 80s XX century many residential buildings and administrative buildings of the city were supplied with heat carriers from numerous heating boilers that fired coal from the Kizelovskoye deposit [Shishkin, 2009]. Coal of the Kizelovsky coal deposit has a high ash content, sulfur content and is saturated with trace elements (Be, Ti, V, Co, Ni, Cu, Ga, Zr, Ag). Sulfur is in the form of FeS₂, FeSO₄ [Maksimovich, 2006].

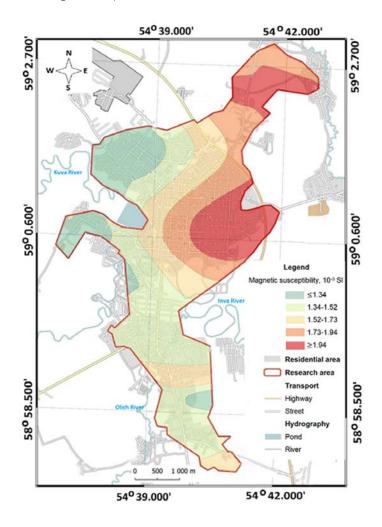


Fig. 7. Map of magnetic susceptibility of the top soils of Kudymkar city by ordinary kriging method

Geochemical assessment of the elemental chemical composition of soils

Ecological-geochemical analysis of soils with abnormally high magnetic susceptibility showed that the bulk content of Zn, and Cu exceeds background soils; the clarke of lithosphere according to K.H. Wedepohl. Soils are enriched in Ni relative to the geoaccumulation index; background soils; the clarke of the lithosphere according to K.H. Wedepohl, and the clarke of residential landscapes in Russia according to V.A. Alekseenko (Figure 8). However, soils are not contaminated with Cr with respect to all geochemical constants, which confirms the concept of the relationship between the concentration and name of pollutant metals in urban soils and the technogeochemical specialization of cities.

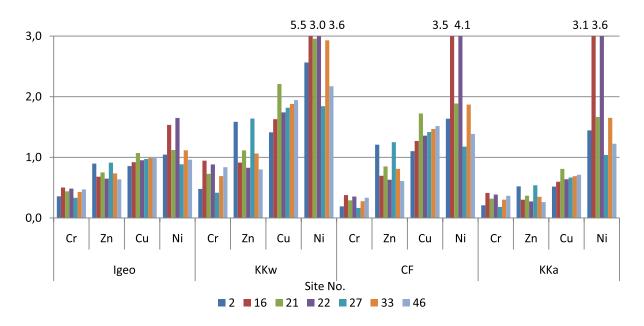


Fig. 8. Pollution indexes of top soils of Kudymkar

CONCLUSION

On the territory of the city of Kudymkar, soil areas high and very high, relative to the local background, magnetic susceptibility were formed. Abnormal zones of magnetic soil contamination or magnetic "hot spots" have formed near industrial facilities, heating boilers, on roadside soil with heavy traffic and occupy more than 30 % of the city's space. The scale of volumetric magnetic susceptibility of soils was developed on the basis of centile data analysis. Highly magnetic soils contain elevated concentrations of heavy metals: Zn, Cu, and Ni. It can be recommended that the Environmental Services of cities use measurements of the magnetic susceptibility of soils to monitor the ecological and geochemical state of soils and identify areas of city soils contaminated with heavy metals.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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