

Geostatistical and geospatial assessment of soil pollution with heavy metals in Pavlograd city (Ukraine)

Mykola M. Kharytonov^{1,*}, Sergey A. Stankevich², Olga V. Titarenko²,
Helena Doležalová Weissmannová³, Iryna I. Klimkina⁴, Liliya A. Frolova⁵

¹Dnipro State Agrarian and Economic University, Dnipro, Sergey Efremov str., 25, 49600, Ukraine, e-mail: kharytonov.m.m@dsau.dp.ua

*corresponding author's e-mail: kharytonov.m.m@dsau.dp.ua

²Scientific Centre for Aerospace Research of the Earth, NAS of Ukraine, Kiev, O. Gonchar str., 55-b., 01054, Ukraine

³University of Technology, Brno, Purkyňova str. 115, 61200, Czech Republic

⁴Dnipro University of Technology, Dnipro, Dmytro Yavornytskiy Av. 19, 49005, Ukraine

⁵Ukrainian State University of Chemistry and Technology, Dnipro, Gagarin av. 5, 49008, Ukraine

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Abstract. This paper presents the result of studies of the geostatistical and geospatial assessment heavy metal pollution in soils caused by various technogenic sources to assess the environmental impact of industrial agglomeration activity in the Pavlograd city. The main sources of technogenic pollution in the Pavlograd city and suburban areas are industrial enterprises, coal-fired plants, mine dumps and other. The vast number of analyzed soil samples with weakly acidic pH values from 6.3 to 6.8 is characterized as loam (63 %), the rest are sand (33 %) and clay soils (4 %). The correlation matrix of metals data indicates positive correlation with correlation coefficient $r^2 > 0.5$ among texture – Ni (0.705) and Pb – Zn (0.695) within the Pavlograd city area. In the case of Cu (2.73) and Cd (4.27), the geoaccumulation index indicated “moderately to strongly” and “strongly to extremely” polluted soils accordingly. Means of pollution index (PI) for heavy metals were between uncontaminated ($P \leq 1$) and of moderate contaminated soils ($P \geq 1$). The results of this study show that industrial enterprises' activities lead to heavy metal contamination in the topsoil of the studied sites and close to the background values. Similar properties were confirmed by principal component analysis (PCA) and cluster analysis. The PCA and cluster analysis results indicate that Cd, Ni, Pb, Cu, Zn and Mn in topsoil were affected by the technogenic activity. The spatial distribution characteristics of Cu, Pb, Cd and Zn in the geochemical maps are also similar. Highlighted are some of the halos in Pavlograd of high density of total soil contamination with heavy metals. The metals come from anthropogenic sources, mainly produced with four industrial enterprises in Pavlograd city. Mostly they are concentrated in the Southeast and West of the city and suburban areas of the Pavlograd district. Therefore, it is necessary arrangements to predict of the development of ecologically dangerous state of environmental pollution within the area of industrial enterprises of city.

Keywords: Environmental state, technogenic pollution, soil, heavy metals.

1. Introduction

The social, logistic, medical, urban heat and air quality consequences of urbanization and large industrial cities' development create numerous problems (Karnaukh & Lugovskoy, 2008; Crutzen, 2004). The air basin of industrial

agglomerations is extremely polluted in spite of the permanent convection and inter-boundary transfer (Parrish et al., 2011; Dufour et al., 2004).

High level of air pollution is connected with various economic activities. As a result, the air quality is very low. The large number of industrial enterprises in the Dnieper

natural-economic region leads to the formation of technogenic anomalies of atmosphere pollution (Babiy et al., 2003). Consequently, the inhabitants adjacent to industrial enterprises, as well as residential areas are "hostages" of a certain number of mining and metallurgical industry, fuel-energy complex and patterns of functioning vehicles (Masaitis & Miller, 2014; Ghorani – Azam et al., 2016). The level and character of airborne soil pollution depend on different reasons: quantity and quality of industrial and traffic emissions, type and intensity of physical and chemical atmospheric processes, land surface etc (Maas et al., 2010; Joshi & Balasubramanian, 2010; Johansson et al., 2009). The main reasons, which determine the air quality, are volume and composition of industrial emissions (Biliavie et al., 2017).

The main pollution sources in the southeastern part of Ukraine are facilities of metallurgy, power industry, mining and petrochemical industries. One of the most polluting industries in Pre-Dnieper region is the ferrous and non-ferrous metallurgical production plants. The steel industry originally developed because of plentiful and high quality local resources of iron and coal in Krivbass and Western Donbass mining regions. The majority of the sector is related to steel production. Structural issues, poor energy efficiency and environmental problems are intertwined in this industry (Voitiuk et al., 2014).

General maintenance and housekeeping are poor. The technologies used in much of the industry are outdated and energy inefficient. Last decade there are modern sections founded in some plants built in Dnipro city (e. g. InterPipe metallurgical plant).

The chemical industry is more diverse in terms of production and its process technologies, on average, are not as old as those used in the steel industry (Babiy et al., 2003). The large number of industrial enterprises of Western Donbass coal mining region leads to the formation of technogenic anomalies of atmosphere pollution caused with dust emissions of coal-fired heat-and-power objects (Kolesnik et al., 2018). The coal and mine rocks contain significant amounts of heavy metals and rare-earth elements. Settling on the land's surface, they form insoluble compounds and accumulate in the upper parts of the soil cover.

The study objective is environmental assessment of soil technogenic pollution in the area of industrial enterprises within the Pavlograd city area.

2. Materials and methods

The Pavlograd city is located between Samara and Vovcha rivers. The investigated area belongs to the North-East slope of the Ukrainian crystalline massif and extends along the South-Western side of the Dnieper-Donets basin. From the South to the North of the city crossed with Vovcha river

(over 2.85 km). Samara river is a natural boundary from the North-East. Two small rivers entitled as "Gnyzdka" (3.9 km) and "Kocherga" (2.9 km) cross the territory of the city of Pavlograd as well. The most common soils are typical black and meadow soils. Underground fresh and mineral water are essential to the life of the city.

The climate is the Atlantic-continental, not humid, characterized by hot summers, with the thaw, dry. The average temperature for the year is 4.4°C. The Number of dry days is approx. 80 (April-October). The priority direction of the wind: during the warm season – West (18% of the days); during the coldest season – East (23% of days). Forest area both around and within the city are presented with large tracts of pine trees. Investment potential of the city is characterized, in particular, for existing production facilities relating to various forms of ownership. More than one thousand real estate objects belong to communal property of the city territorial community. The numerous sources of soil pollution in Pavlograd city and suburban territories are four industrial enterprises, mine tailings, heat supply companies and transport. There are 32 industrial enterprises with more than 600 organized sources and emit more than 1,000 tons of pollutants (including more than 350 tons of carbon monoxide, 130 tons of oxides of nitrogen, 280 tons of suspended solids) in the Western Donbass region. Main industrial emission sources of air pollution in Pavlograd city are following: Pavlograd chemical plant (PCP), Pavlograd mechanical plant (PMP), Pavlograd machine factory (PMF) and Pavlograd foundry plant (PFP). Soil samples were taken to determine the effect of airborne technogenic pollution in Pavlograd (Fig. 1). Soil samples were collected in the vicinity of each enterprise to detail the impact of the main environmental pollutants in Pavlograd city. Soil sampling was performed by the method of "envelope". The total number of samples is 60. The soil samples were collected in the depth 0-10 cm, mass of each sample was 800-900 g. After that, soil samples were dried at room temperature and powdered, have been removed impurities and particles using sieves with holes of different diameter from 5 to 1 mm. The shredded material is thoroughly mixed and scattered smooth a thin layer in the form of a square, was divided into four sectors to reduce the mass of the sample. The content of the two opposite sectors was discarded, and the remaining two were again mixed.

After multiple repetitions, the sample remained was dried to obtain extracts from the soil. The definition of the content of acid-soluble forms of heavy metals in the collected samples was performed using atomic absorption spectrophotometry method. Assessment of soils ecological quality was given by the degree of soil contamination with HM regarding exceeding the maximum permissible concentrations (MPC) of pollutants established by Ukrainian legislation (Fedoniuk et al., 2020). In order to assess heavy metal contamination of soils the following pollution

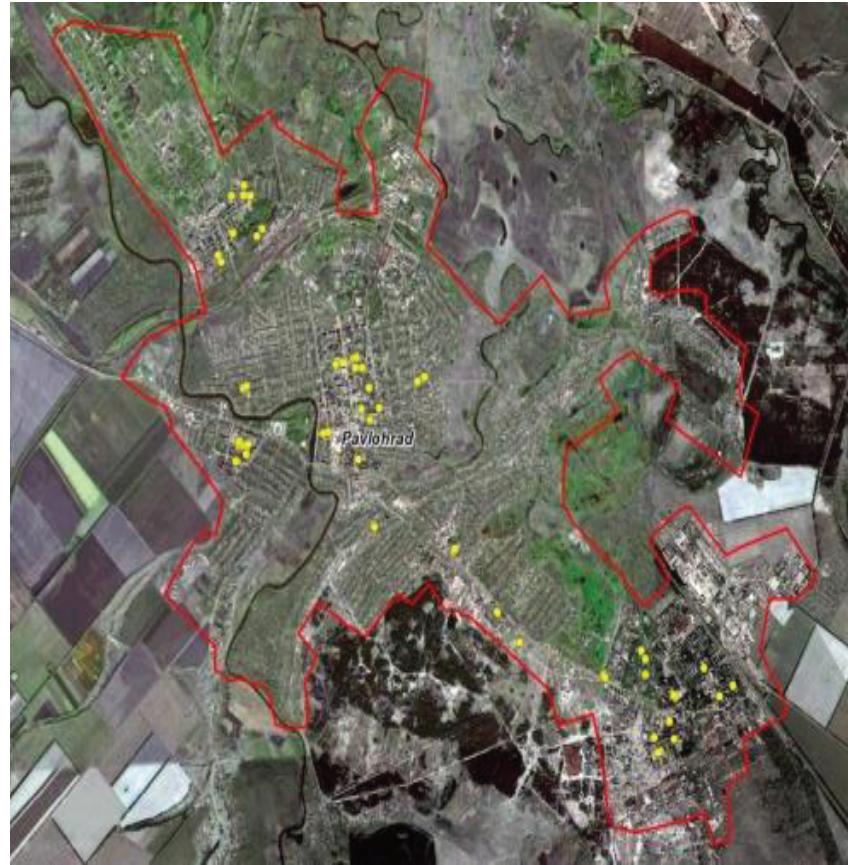


Figure 1. Soil sampling locations

three indices were calculated. Geoaccumulation index (I_{geo}) enables the estimation of pollution by comparing current and preindustrial concentrations (Müller, 1969; Khalilova & Mammadov, 2016).

$$I_{geo} = \log\left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

where C_n is the measured concentration of the element in soil; B_n is the value of background concentration (BC) of element n , and 1.5 is the background matrix correction factor due to lithogenic effects (the constant 1.5 is introduced to minimize the effects of possible variations in the background values that may be attributed to lithologic variations in soils). The I_{geo} was classified into six categories: $I_{geo} < 0$ (practically unpolluted, $I_{geo} = 0$), $0 < I_{geo} < 1$ (unpolluted to moderately polluted, $I_{geo} = 1$), $1 < I_{geo} < 2$ (moderately polluted, $I_{geo} = 2$), $2 < I_{geo} < 3$ (moderately to strongly polluted, $I_{geo} = 3$), $3 < I_{geo} < 4$ (strongly polluted, $I_{geo} = 4$), $4 < I_{geo} < 5$ (strongly to extremely polluted, $I_{geo} = 5$) and $I_{geo} > 5$ (extremely polluted,

$I_{geo} = 6$). The PI of each heavy metal (PI_i) was evaluated with pollution index according to the method of (Lee et al., 1998), calculated as the ratio between the metal concentration (C_i) in sample and maximum permissible concentration (MPC). Maximum permissible concentrations (MPC) of pollutants were established by Ukrainian legislation as reference value-national criteria of the metal and were taken as S_i values. It was expressed as stated below:

$$PI = \frac{C_i}{S_i} \quad (2)$$

Classification of PI values for each HM contaminated soil was characterized on the basis of criteria such as practically uncontaminated soils ($P \leq 1$), moderate contaminated soil ($1 < P \leq 3$) or high contaminated soil ($P > 3$). Assessment of soils ecological quality was given by the degree of soil contamination with HM regarding exceeding the MPC. The descriptive statistical analyses were performed using Microsoft Excel spreadsheet and Statistica software by TIBCO Inc. The multidimensional statistical

methods were applied for the analysis of the environment pollution state within the selected contamination sources of emission: method of PCA and cluster analysis. Satellite radar interferometry (InSAR) digital elevation model (DEM) was used to build a map of terrain elevation changes map in Pavlograd city. Density map of the total soil contamination with copper, zinc, manganese, cadmium, lead and nickel has been created using the 3D Analyst program module of ArcGIS software package by ESRI Corp.

3. Results and discussion

Elevation map were acquired to extract the features of the terrain during three years from 2015.11 to 2017.05 using Sentinel 1A satellite InSAR data product.

Terrain elevation maps was acquired using the satellite InSAR based on the two pairs of Sentinel-1A images for the November 2015 to May 2017 time spans. The terrain elevation dynamics for this period of the study area are described by data of Table 1.

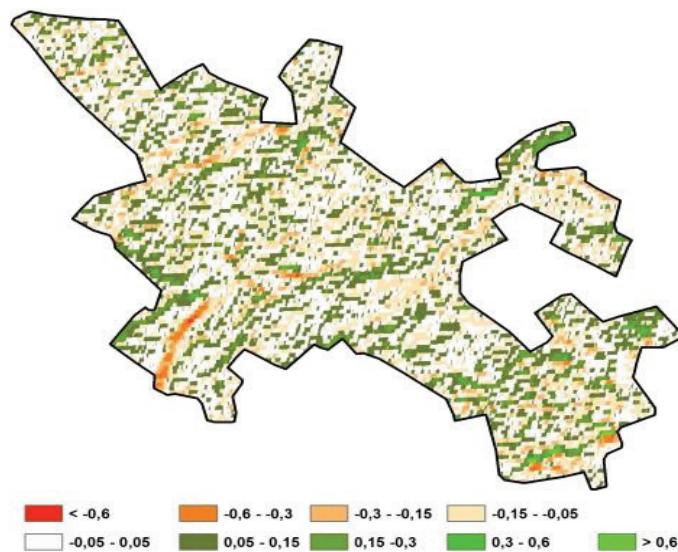


Figure 2. Terrain elevation changes map within the Pavlograd city area

Table 1. Terrain elevation changes in Pavlograd city

Code	Color	Class	Difference	Percent
0	Black	Unclassified	no data	0.000
1	Red	Very Strong Down	< -0.6	0.676
2	Orange	Strong Down	-0.6 .. -0.3	3.107
3	Light Orange	Moderate Down	-0.3 .. -0.15	8.970
4	Yellow	Weak Down	-0.15 .. -0.05	17.900
5	White	No Change	-0.05 .. 0.05	34.127
6	Dark Green	Low Rise	0.05 .. 0.15	22.785
7	Medium Green	Medium Rise	0.15 .. 0.3	10.132
8	Light Green	High Rise	0.3 .. 0.6	1.946
9	Dark Green	Very High Rise	> 0.6	0.357

The relationships among metals concentrations are important information on hazardous metal resources and their pathways in the environment (Johansson et al., 2009; Manta et al., 2002). The details of the correlations matrix are presented in Table 2. The correlation matrix of metals data indicates positive correlation with correlation coefficient $r^2 > 0.5$ among texture – Ni (0.705) and Pb – Zn (0.695) in Pavlograd city. The results metals contaminations of soils within the Pavlograd city were verified and exactly evaluated with the Geoaccumulation index (I_{geo})

and PI. Geoaccumulation index (I_{geo}) for heavy metals ranged from unpolluted to strongly polluted soil quality (Fig. 3 and Table 3). Soils were moderately polluted by Pb (1.32), Mn (1.37), Ni (1.44), Zn (1.96) based on geoaccumulation index. In the case of Cu (2.73) and Cd (4.27), the geoaccumulation index indicated “moderately to strongly” and “strongly to extremely” polluted soils accordingly. The details of the metal I_{geo} correlations matrix are presented in Table 4.

Table 2. The correlation coefficient matrix between metals in soil samples (significance level $\alpha = 0.05$, $p < 0.001$)

Variable	Color map of correlations (data in Pavlograd), N=60; (Case wise deletion of missing data)							
	pH	texture	Cd	Mn	Cu	Ni	Pb	Zn
pH	1.000	-0.064	0.300	0.118	-0.009	0.037	0.291	0.201
texture	-0.064	1.000	-0.117	-0.011	0.139	0.705	0.056	-0.012
Cd	0.300	-0.117	1.000	0.170	0.056	-0.124	0.308	0.215
Mn	0.118	-0.011	0.170	1.000	0.038	-0.021	-0.028	-0.002
Cu	-0.009	0.139	0.056	0.038	1.000	0.178	0.221	0.254
Ni	0.037	0.705	-0.124	-0.021	0.178	1.000	0.289	0.171
Pb	0.291	0.056	0.308	-0.028	0.221	0.289	1.000	0.695
Zn	0.201	-0.012	0.215	-0.002	0.254	0.171	0.695	1.000

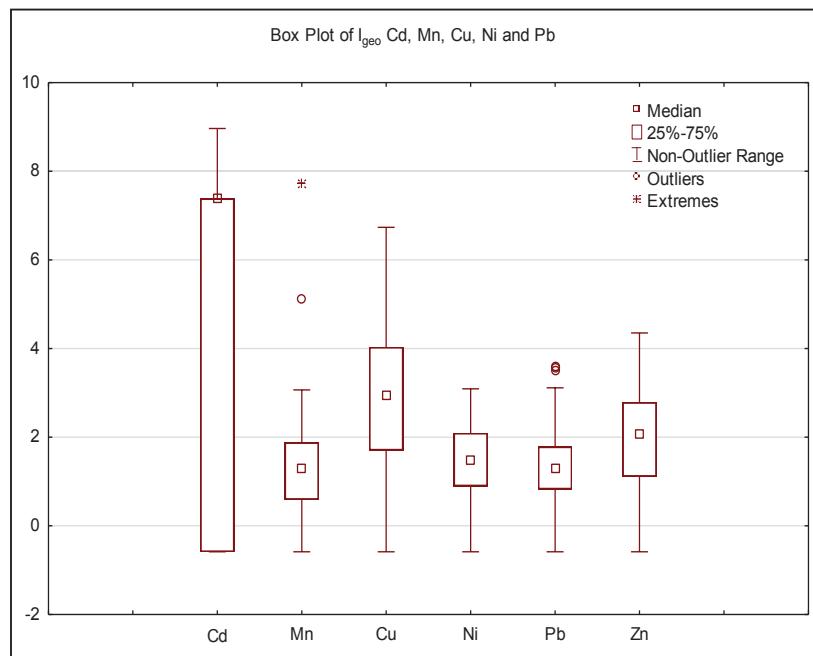


Figure 3. Means of I_{geo} for heavy metals

The each parameter correlation matrix data indicate positive correlation with correlation coefficient $r^2 > 0.5$ among texture – Ni (0.72) and Pb – Zn (0.65) in region of Pavlograd.

It was fixed also closed to 0.5 interval correlation coefficient $r^2 > 0.45$ among Mn – Pb (0.45), Cu – Ni (0.45) and Cu – Ni (0.46). Mean of PI increases in the following order 0.2 (Cd), 0.28 (Ni), 0.33 (Cu),

Table 3. I_{geo} values

Variable	Valid N	Mean	Median	Min.	Max.	Lower	Upper	Std.Dev.
pH	60	6.530	6.500	5.800	7.000	6.500	6.600	0.167
texture	60	2.567	3.000	1.000	5.000	1.000	4.000	1.307
Cd	60	4.272	7.381	-0.585	8.966	-0.585	7.381	4.158
Mn	60	1.371	1.293	-0.585	7.727	0.595	1.880	1.306
Cu	60	2.732	2.937	-0.585	6.737	1.708	4.030	1.763
Ni	60	1.439	1.485	-0.585	3.093	0.900	2.093	0.830
Pb	60	1.319	1.290	-0.585	3.611	0.830	1.784	0.998
Zn	60	1.959	2.078	-0.585	4.354	1.115	2.784	1.146

Table 4. The correlation coefficient matrix between pH, texture and I_{geo} for heavy metals

Variable	Color map of correlations							
	pH	texture	Cd	Mn	Cu	Ni	Pb	Zn
pH	1.000	-0.064	0.252	0.133	0.119	0.054	0.227	0.156
texture	-0.064	1.000	-0.125	0.379	0.394	0.720	0.206	0.037
Cd	0.252	-0.125	1.000	-0.030	0.024	-0.022	0.076	0.162
Mn	0.133	0.379	-0.030	1.000	0.401	0.452	0.182	0.099
Cu	0.119	0.394	0.024	0.401	1.000	0.452	0.450	0.330
Ni	0.054	0.720	-0.022	0.452	0.452	1.000	0.463	0.361
Pb	0.227	0.206	0.076	0.182	0.450	0.463	1.000	0.645
Zn	0.156	0.037	0.162	0.099	0.330	0.361	0.645	1.000

Table 5. PI index for heavy metals

HM	Valid N	Mean	Median	Minimum	Maximum	Lower	Upper	Std.Dev.
Cd	60	0.200	0.250	0.001	0.750	0.001	0.250	0.199
Mn	60	0.965	0.351	0.095	30.287	0.216	0.526	3.901
Cu	60	0.334	0.209	0.018	2.909	0.091	0.446	0.430
Ni	60	0.279	0.247	0.059	0.753	0.165	0.376	0.152
Pb	60	0.451	0.344	0.094	1.719	0.250	0.485	0.370
Zn	60	0.413	0.331	0.052	1.600	0.170	0.540	0.346

0.41 (Zn), 0.45 (Pb), and 0.96 (Mn), as shown in Table 5 and Figure 4.

The reason of this contamination is fact that industrial works emissions and traffic emission are the different in Pavlograd city and district. Maximum PI values were constant for manganese (30.3) and copper (2.9). The details of the metal PI correlations matrix are presented in Table 6.

The correlation matrix data indicate positive correlation with correlation coefficient $r^2 > 0.5$ among texture – Ni (0.7) and Pb – Zn (0.695) in city. PCA outputs are described by the Table 7.

The first two principal components of the Table 7 determine the 54.74 % of total contribution into covariance matrix.

The projection of metals concentration's distribution onto principal components plane is shown in Fig. 5.

The projections of the distribution of pH, texture, metals I_{geo} and PI on the principal components plane are shown in Figure 6

The PCA was used to identify the sources of contamination (Fachinelli et al., 2001). All of the elements are consequently well represented by these two principal compo-

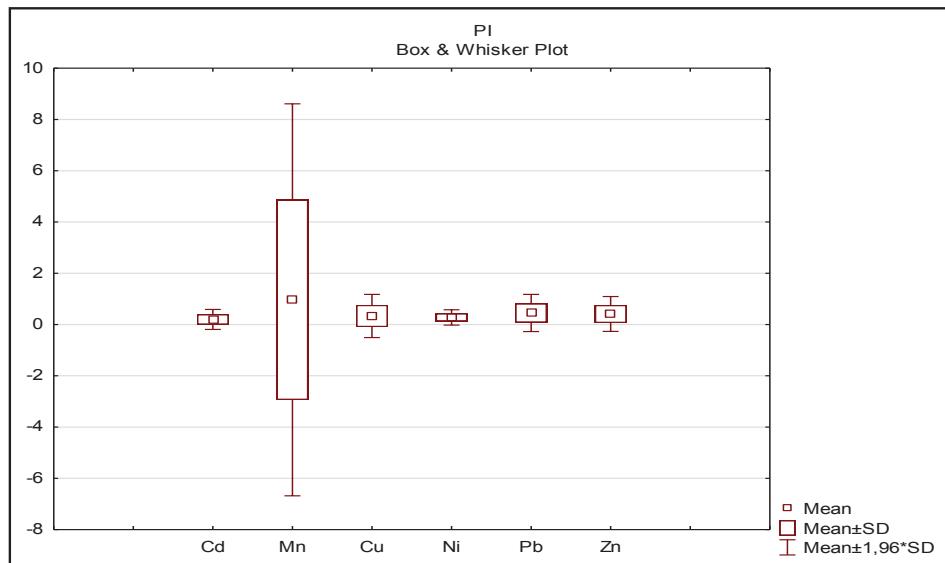


Figure 4. Means of PI for heavy metals

Table 6. The correlation coefficient matrix between pH, texture and PI for heavy metals

Variable	pH	texture	Cd	Mn	Cu	Ni	Pb	Zn
pH	1.000	-0.067	0.300	0.118	-0.009	0.038	0.291	0.201
texture	-0.067	1.000	-0.117	-0.011	0.139	0.705	0.056	-0.012
Cd	0.300	-0.117	1.000	0.170	0.056	-0.124	0.309	0.216
Mn	0.118	-0.011	0.170	1.000	0.038	-0.021	-0.028	-0.002
Cu	-0.009	0.139	0.056	0.038	1.000	0.178	0.221	0.254
Ni	0.038	0.705	-0.124	-0.021	0.178	1.000	0.290	0.171
Pb	0.291	0.056	0.309	-0.028	0.221	0.290	1.000	0.695
Zn	0.201	-0.012	0.216	-0.002	0.254	0.171	0.695	1.000

Table 7. Total variance of explained and component matrices

Variable	Factor coordinates (PC) of the variables				Eigen values of matrix	
	PC 1	PC 2	PC 3	PC 4	Eigen value	Total, %
Cd	-0.413	-0.718	0.159	0.035	2.060	34.328
Mn	-0.051	-0.567	-0.739	-0.265	1.225	20.409
Cu	-0.478	0.187	-0.448	0.727	0.984	16.404
Ni	-0.408	0.594	-0.369	-0.440	0.821	13.681
Pb	-0.883	0.003	0.198	-0.160	0.636	10.603
Zn	-0.843	-0.010	0.191	-0.032	0.275	4.575
*pH	-0.275	-0.215	0.047	-0.118		
*texture	-0.167	0.437	-0.329	-0.267		

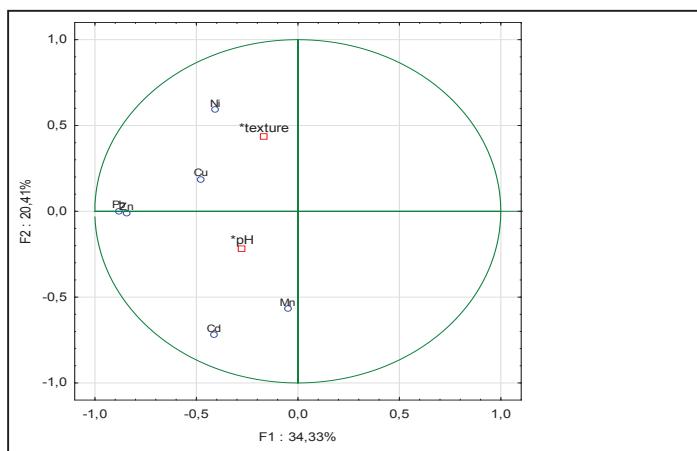
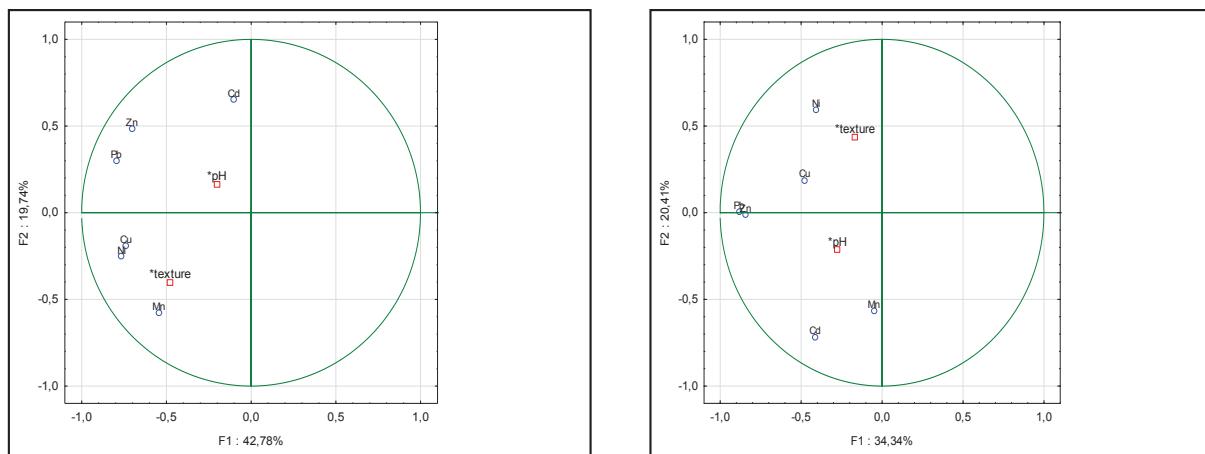


Figure 5. The first two principal components distribution

Figure 6. The principal component analysis for I_{geo} (left) and PI (right) indices

nents. Total variances explained by first two principal components are in Tables 8 and 9.

The first two principal components of the Table 8 determine the 62.5% of total contribution into covariance matrix. First PC is in negative relation with correlation coefficient $r^2 > 0.5$ for Cu (-0.738), Ni (-0.766), Pb(-0.796). Second PC is in positive relation with Cd (0.651) and negative relation with Mn (-0.578). Next two principal components determine the 24.3 % of total variance contribution. Third PC is in negative relation with correlation coefficient $r^2 > 0.5$ for Cd (-0.747). Fourth PC is in negative relation with Cu (-0.622) and Mn (-0.578). The first two principal components of the Table 9 determine the 54.75% of total contribution into covariance matrix. First PC is in negative relation with Pb (-0.883) and Zn (-0.843). Second and third PCs are in negative relation with Cd (-0.717) and Mn (-0.738). Fourth PC is in positive relation with Cu (0.727).

Thus the metals in the PC 1- 4 probably come from anthropogenic sources, mainly produced with four industrial enterprises in Pavlograd city. 3D surfaces and contour plot of Cd, Mn, Cu, Ni and Pb against pH and texture were built to show and to analyze corresponding distributions (Figs. 7 and 8).

Cluster analysis was performed to divide the clusters of pH, texture and 6 heavy metals and to analyze possible sources within the Pavlograd city area (Fig. 9). Ward method was chosen to determine the Euclidean distance as the most common technique applied for the distance metric. The cophenetic correlation coefficient (CC) was applied to verify the results obtained. The pH, texture and Cd are forming one independent cluster. Cd is mainly from the mining and smelting of non-ferrous metals. It is known that coal combustion is also important source of cadmium (Guan et al., 2014).

Table 8. Total variance of explained and component matrices for heavy metals I_{geo}

Variable	PC 1	PC 2	PC 3	PC 4	Eigen value	Total, %
Cd	-0.102	0.651	-0.747	0.016	2.567	42.783
Mn	-0.545	-0.578	-0.425	0.173	1.184	19.735
Cu	-0.738	-0.189	-0.103	-0.622	0.900	14.995
Ni	-0.766	-0.252	-0.034	0.357	0.561	9.344
Pb	-0.796	0.301	0.284	0.003	0.458	7.632
Zn	-0.704	0.485	0.261	0.125	0.331	5.511
*pH	-0.202	0.165	-0.171	-0.014		
*texture	-0.477	-0.403	-0.072	0.142		

Table 9. Total variance of explained and component matrices for heavy metals PI

	PC 1	PC 2	PC 3	PC 4	Eigen value	Total, %
Cd	-0.414	-0.717	0.160	0.034	2.060	34.337
Mn	-0.051	-0.568	-0.738	-0.265	1.225	20.411
Cu	-0.478	0.187	-0.449	0.727	0.984	16.396
Ni	-0.408	0.594	-0.369	-0.441	0.821	13.684
Pb	-0.883	0.003	0.198	-0.160	0.636	10.600
Zn	-0.843	-0.010	0.191	-0.031	0.274	4.572
*pH	-0.276	-0.215	0.048	-0.118		
*texture	-0.167	0.437	-0.330	-0.268		

The Pb, Ni and Cu are of similar characteristics and are forming one cluster. As usual Pb and Cu associated with traffic, combustion, waste incinerators, pipes, cables, paints, and colors (Biasioli et al., 2006; Van Bohemen & Janssen van de Laak, 2003). Both clusters are associated with Zn. The last cluster includes Mn only. Two clusters analysis for pH, texture, I_{geo} and PI for heavy metals were made for comparative assessment of Euclidean distances (Fig.10).

Cluster of Figure 10 were used to classify all contamination parameters. The smaller the value on the distance cluster, the more significant the association (Luo et al.,

2007). pH, texture indices and 6 heavy metals, were classified and merged into three distinct clusters in the Figure 10 a. The first cluster include Zn, Pb and Ni are most likely associated with Mn. The second cluster included Cu and texture and the third one included pH and Cd. Accordingly to the Figure 10 b Zn and Pb are in the first cluster. These two elements are in positive relation with $r^2 = 0.695$ (Table 5). Cd, Ni and Cu are in the second cluster. Both clusters are highly likely associated with texture. pH and Mn are last vertexes of this dendrogram. Soil texture distribution map is shown in Figure 11.

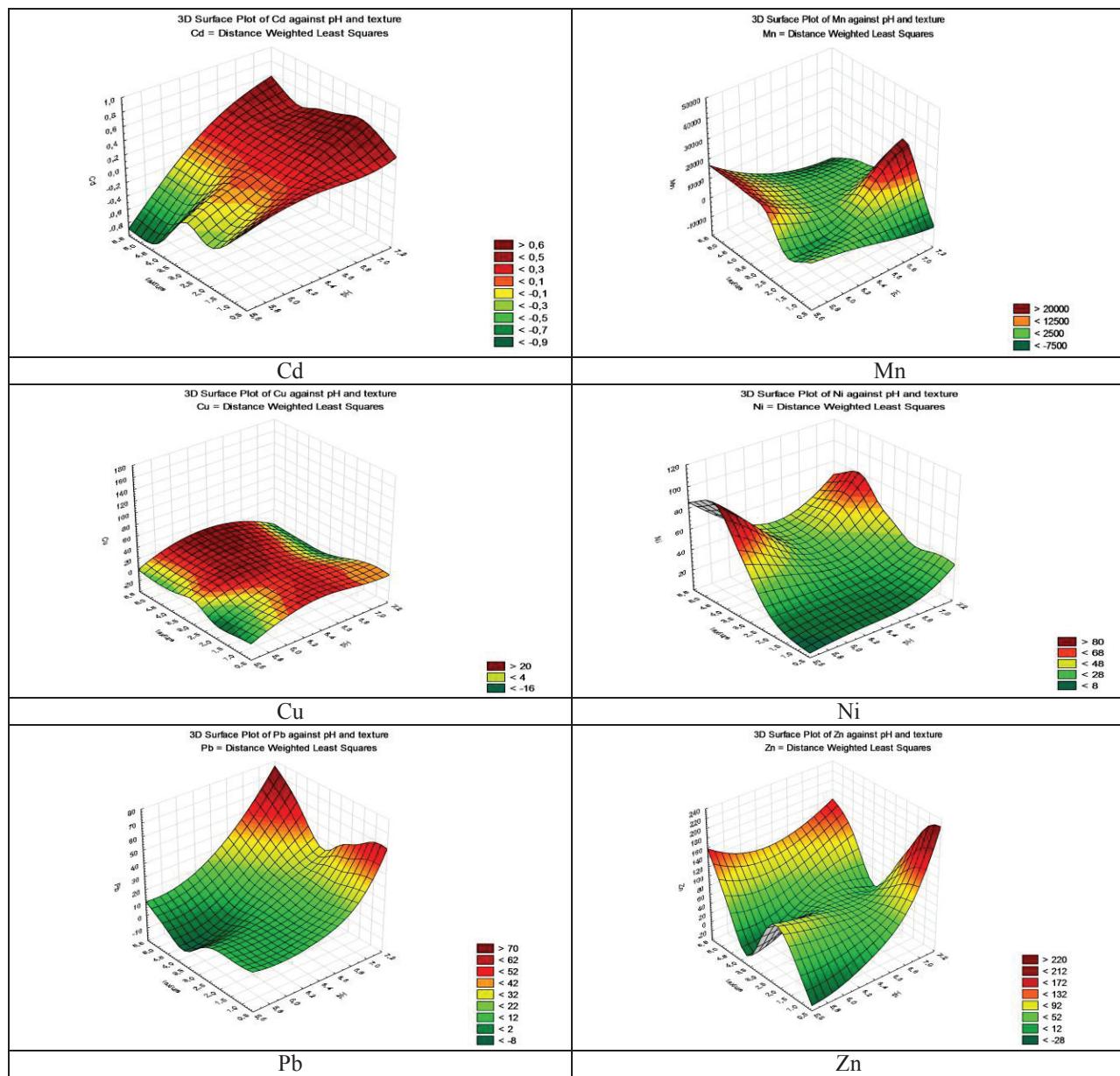


Figure 7. 3D surfaces of Cd, Mn, Cu, Ni and Pb against pH and texture

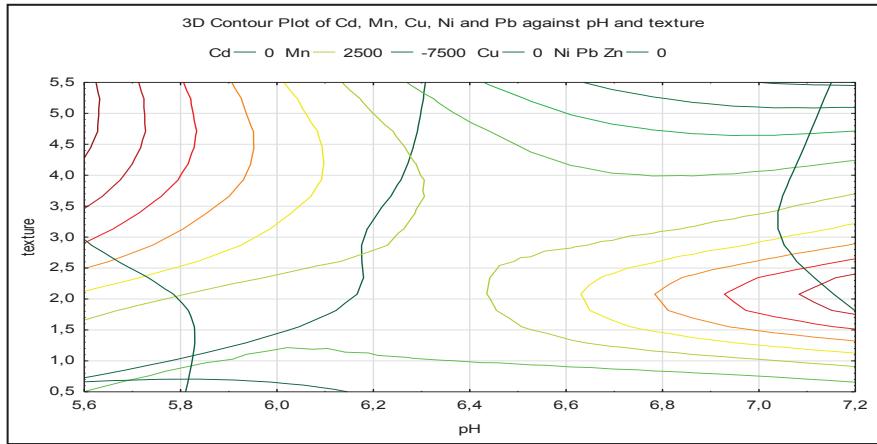


Figure 8. The contour plot of Cd, Mn, Cu, Ni and Pb against pH and texture

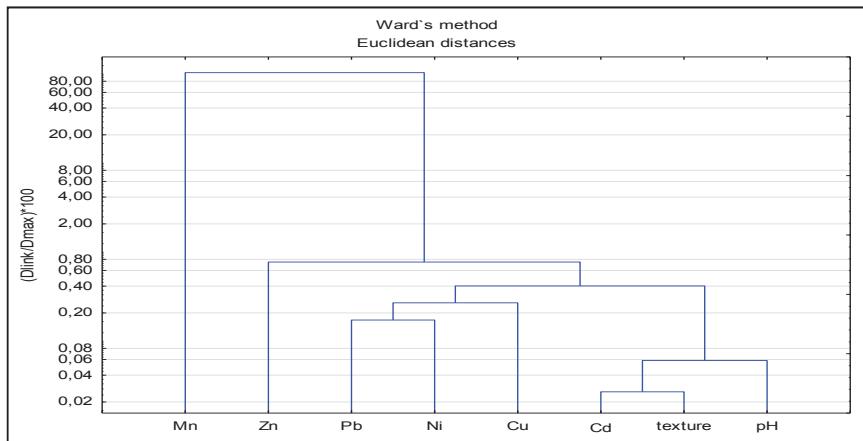


Figure 9. Clusters' dendrogram of 8 contamination parameters

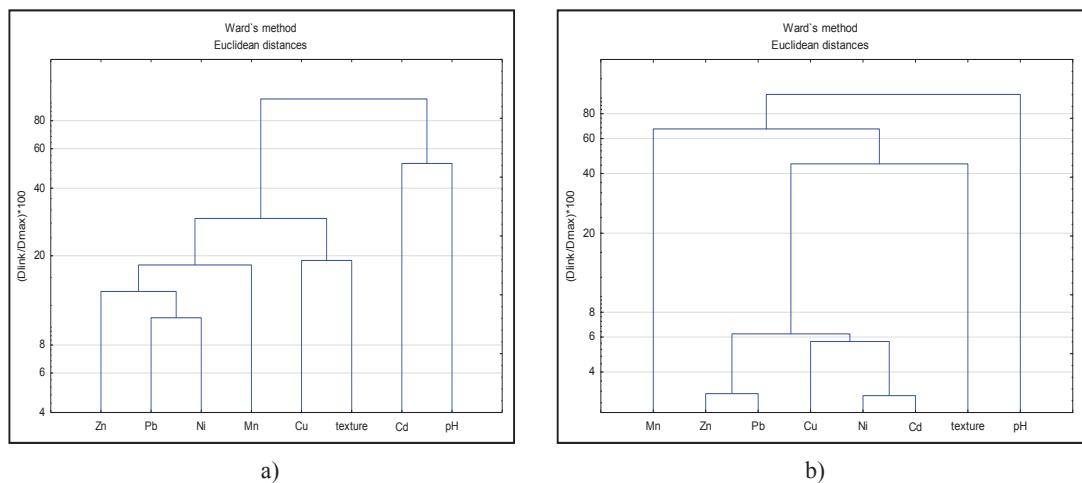


Figure 10. Clusters' dendrograms of pH, texture, metals I_{geo} (a) and PI (b)

According to the results of determination of texture the vast number of analyzed soil samples (63 %) is characterized as loam. The rest are sand (33 %) and clay soils (4 %). Data percentage distribution map of soil samples according to their pH is shown in Figure 12.

As a result of consistent mapping of pollution within the Pavlograd city area with six heavy metals were obtained corresponding distributions' maps (Fig.13).



Figure 11. Locations of soil samples according to their texture composition

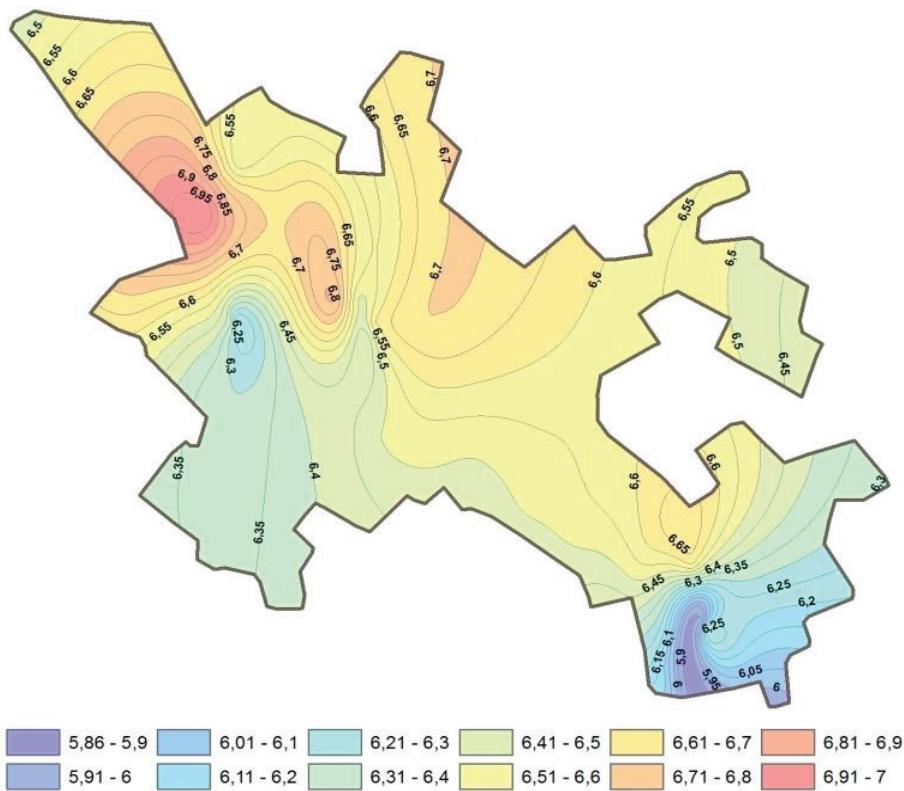


Figure 12. The map of the soil pH distribution

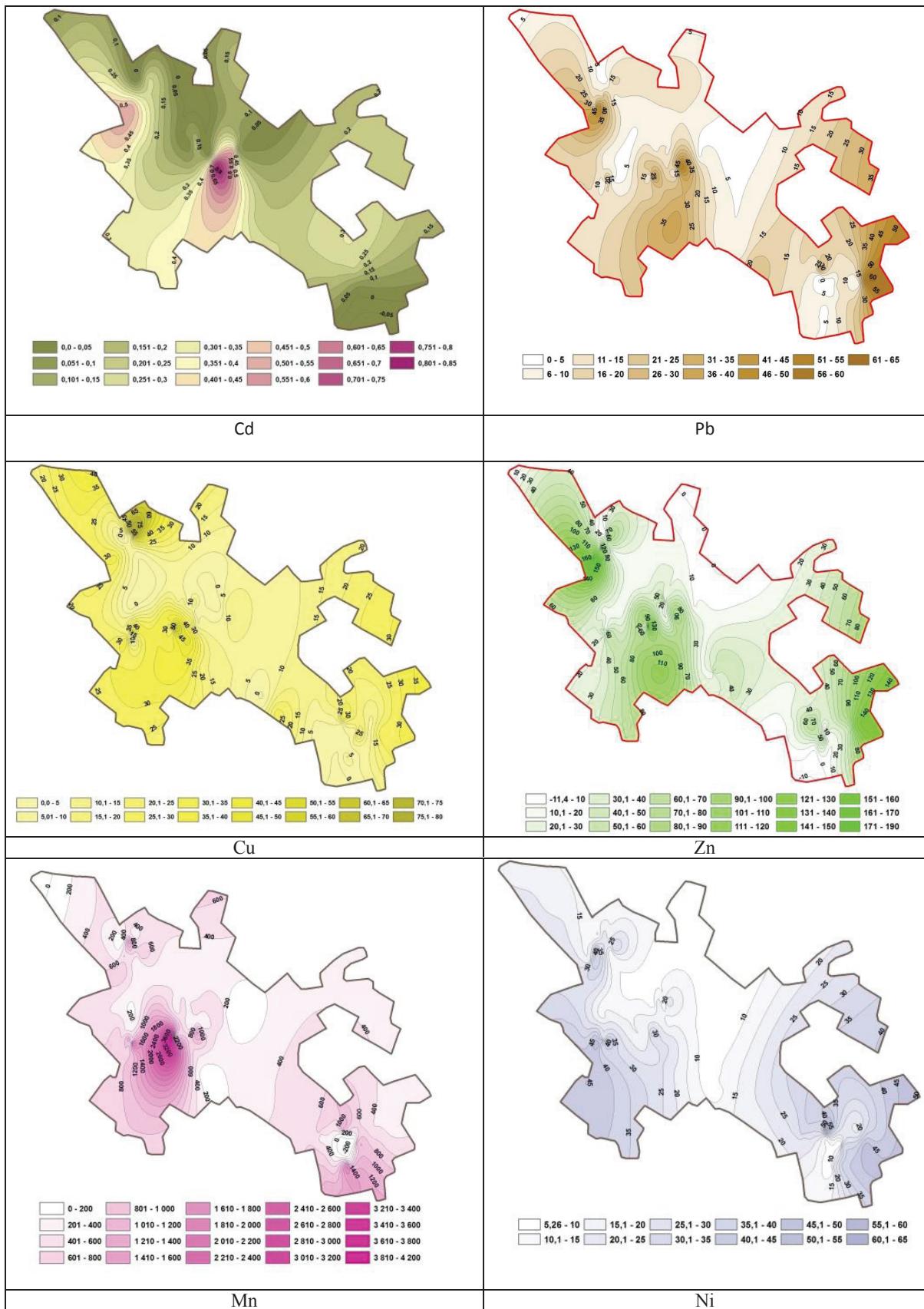


Figure 13. Heavy metals distributions in topsoil within the Pavlograd city area, mg/kg

The metal ions are injected into soil cover from main industrial facilities, coal-driven power plants, municipal and private waste refuses as well as form motor transport in Pavlograd city terrain. Sources of heavy metals emission in the South – Eastern part of city are caused by foundry and two machine building enterprises. The high density of soil contamination with Cd, Pb, Mn and Ni in the west of the city can be associated both with the activities of the Pavlograd chemical plant and the weathering process of coal mine heaps (Biliaiev & Kharytonov, 2013; Kharytonov & Kroik, 2011). Several case studies have demonstrated also that the combination of environmental mapping and multivariate geostatistical analysis can be an appropriate tool to characterize spatial distribution of heavy metals and to determine their sources (Luo et al., 2008; Li & Feng, 2012; Yuan et al., 2013). Two Cd – hallows with range 0.4-05 and 0.45 – 0.65 were fixed in the western and south-west parts of city. High polluted with Mn hallow (1210 – 3610 mg/kg) was selected in the south-west parts of city as well. Similar character of spatial distribution was fixed for Pb, Zn, Cu and Ni. In this case it is possible to see at least 4 – 5 hallows in the east, south east, north and south west parts of studied city areas.

4. Conclusion

The vast number of analyzed soil samples in Pavlograd is characterized as loamy and have a weakly acidic pH at 6.3 and 6.8. The correlation matrix of metals data indicate positive correlation with correlation coefficient $r^2 > 0.5$ among texture – Ni (0.705) and Pb – Zn (0.695) in Pavlograd city. In the case of Cu (2.73) and Cd (4.27), the geoaccumulation index indicated “moderately to strongly” and “strongly to extremely” polluted soils accordingly. Means of PI for heavy metals were between uncontaminated ($P \leq 1$) and of moderate contaminated soils ($P \geq 1$). The results of this study show that industrial enterprises activities lead to heavy metal contamination in the topsoil of the studied sites and close to the background values. Similar properties were confirmed by PCA and cluster analysis. The PCA and cluster analysis results indicate that Cd, Ni, Pb, Cu, Zn and Mn in topsoil were affected by the technogenic activity. The spatial distribution characteristics of Cu, Pb, Cd and Zn in the GIS geochemical maps are also similar. The metals come from anthropogenic sources, mainly produced with four industrial enterprises in Pavlograd city. Highlighted are some of the halos in Pavlograd of high density of total soil contamination with heavy metals. Mostly they are caused with impact of the industrial enterprises, which are localized in the South-East and in the West of the Pavlograd city. This study demonstrated that the combination of geostatistical and geospatial analysis are an appropriate tool

to select emissions sources and to create GIS maps to characterize soil pollution with heavy metals in industrial city. It is necessary arrangements to predict of the development of ecologically dangerous state of environmental pollution within the area of industrial enterprises of the city.

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