Multivariate Statistical Characterisation of Soil Quality in the Lower Danube River Riparian Areas

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Increasing anthropogenic influences on the environment has caused negative changes in natural ecosystems and soil contamination with potentially toxic metals has become a worrying issue at global level, due to the negative impact on the environment and human health. For the purpose of assessing soil contamination in the riparian areas of the Lower Danube River, a number of 144 soil samples were collected twice a year, in the period of June 2013 – December 2016, from 9 monitoring locations, from 0.05 m and 0.3 m depths, and the following indicators: Cr, Cu, Mn, Ni, Pb, Zn, including Ca, Mg, C_{org}, SO_4^{2-} *and humus content have been monitored. The soil was sampled, conserved and analysed according to the European standards in force. Metal concentrations were determined using flame (FAAS) and graphite furnace (GFAAS) atomic absorption spectrometry after "aqua regia" digestion of dried, homogenised and 0.5 mm sieved soil sub-samples. Comparing the average concentration values of the analysed potentially toxic metals, a decreasing tendency following the order Cr>Pb>Ni>Cu>Zn>Mn was observed and by reporting the average values at the normal limits, the order Zn>Cu>Mn>Ni>Pb>Cr of magnitude was obtained. To investigate possible correlations and interdependencies of potentially toxic metals content in the riparian soil, multivariate statistical methods were used. After applying Principal Component Analysis (PCA), 3 main components were identified, with a combined share of about 74 % of the original data-set variance. It was observed that during the monitoring period the average values of the all monitored elements from the studied soils were slightly below the normal reference values, according to the national legislation.*

Keywords: heavy metals, soil pollutants, statistical analysis, Danube River

In the last years, the scientific community has focused on the soil research as this is a significant component of the ecosystem, being a complex heterogeneous environment (aqueous, gaseous and solid components) containing mineral constituents, organic matter and constituting a support for the living organisms [1-4]. Soil pollution has become a major environmental issue, because of industrialization and fast economic growth, both aspects favouring the increase of pollutants emitted into the environment [5-10]. The development of human activities (industry, agriculture, etc.), as well as human intervention in changing the environmental conditions led to irreversible degradation of the quality of environmental components, including soil, and consequently to an intense pollution [11-14].

Globally, soil pollution with potentially toxic metals, such as Cr, Cu, Mn, Ni, Pb, Zn, is of particular interest due to their long-term toxicity and persistence in ecosystems, their reactivity and mobility in the soil, and due to leakage of these metals to underground water [15-20]. Potentially toxic metals in soil may occur both from natural sources (rocks and minerals) and as a result of anthropogenic contamination – habitually as compounds with greater mobility than ones from natural sources [21, 22]. The ecological importance of potentially toxic metals in soil is closely linked to human health due to their high potential for ecological transfer [5, 22]. Soil contamination with toxic metals can potentially be easily transferred to food products and therefore to the consumers [23-25]. Metals can reach the human body through ingestion of contaminated dust, dermal contact or inhalation, the prolonged exposure to them causing harmful effects to the organism [1, 26]. Prolonged exposure to toxic metals in concentrations that exceed specific toxicological thresholds may lead to pulmonary, kidney and liver problems, cancer, etc. [22, 23].

In order to avoid the occurrence of these environmental and health problems caused by the potentially toxic metals, it is recommended to carefully evaluate the quantitative data regarding the levels of heavy metals in soils. Therefore, the use of simple and precise methods for heavy metals monitoring has a great importance in the environmental studies [22]. The assessment of soil quality can be performed initially by reporting the determined values at reference values mentioned in the current legislation but more information can be obtained by applying statistical methods, pollution indices, geo-accumulation indices, GIS techniques etc.

This study was focused on assessment of soil quality in the riparian areas of the Lower Danube River, between Calarasi (km 375) and Braila (km 175), where hydro-technical constructions were carried out to improve navigation conditions [27]. In this area, in order to ensure the commercial navigation continuity even in drought periods, sediment dredging and embankments were carried out. This type of anthropic interventions required monitoring also because dredging of polluted sediment in the environment is associated to risks of uncontrolled dispersion of pollutants, both in dissolved state and in particle state [28]. Also, the Danube River due to its large drainage basin (over 800,000 km^2) receive relative high intensity anthropic inputs of potentially toxic metals [29]. The assessment of potentially toxic metals pollution was performed both using multivariate statistical methods and through comparison to the national legislation [30]. The obtained results can constitute a useful tool for monitoring the level of soil pollution and also can serve as a reference

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database for authorities with competences in environmental protection field for a better management of environmental pollution.

Experimental part

The monitoring sites are located along the lower area of the Danube River (Fig. 1), between Calarasi (km 375) and Braila (km 175), where hydro-technical works were carried out to meet the recommendations of the Danube Commission to maintain minimum navigation water depths during dry seasons [27]. Hydro-technical works included dredging, embankments and construction of bottom sills and the re-suspended sediments accumulated along the banks may have a potential impact on the environment.

The soil samples were collected twice a year, between June 2013 - December 2016, at two depths (0.05 m and 0.3 m), from 9 locations represented in figure 1 with the following GPS coordinates (table 1).

During the study, 144 samples were collected in labelled polyethylene bags and transported to the laboratory. Soil was sampled with a Burkle Mole device, after removal of the superficial layer (vegetal soil). The samples were air dried at room temperature, homogenized and sieved in order to remove roots and stones. The fraction smaller than 2 mm was crushed in a ceramic mortar and sieved through 150 µm. About 0.5 g soil from the homogenized fraction of 150µm was mineralised with Aqua Regia (HCl : HNO$_3$ in ratio 3:1) using a microwave digestion method. The concentration of pseudo-total (only Aqua Regia leached, without total silicates dissolution in HF) content of potentially toxic metals (Cu, Cr, Mn, Pb, Ni and Zn) were determined using a Thermo Solaar M5 atomic absorption spectrometer with flame and graphite furnace modules.

The organic carbon content was extrapolated from the volumetric determination of unspent oxidant after the sample thermal treatment in the presence of a known quantity of potassium bichromate and sulphuric acid oxidant mixture. The organic carbon content were converted to humus percentages considering a natural humus distribution.

The *p*H, conductivity and soluble salts of calcium, magnesium and sulphates of the soil samples were determined from the 1:5 (soil weight: distilled water) aqueous extract. The pH and electrical conductivity were determined using a CONSORT C833 multi-parameter. Calcium and magnesium ions were volumetrically determined through complexometric titration, and the sulphates ions were gravimetric determined after precipitation with barium chloride.

All reagents used in this study were of analytical grade and the all laboratory glassware used was pre-washed according to each method's prescription and rinsed with double distilled or ultra-pure water before use.

Approximately 1900 analyses were performed for the following quality indicators, according to the current standard methods: total chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), *p*H,

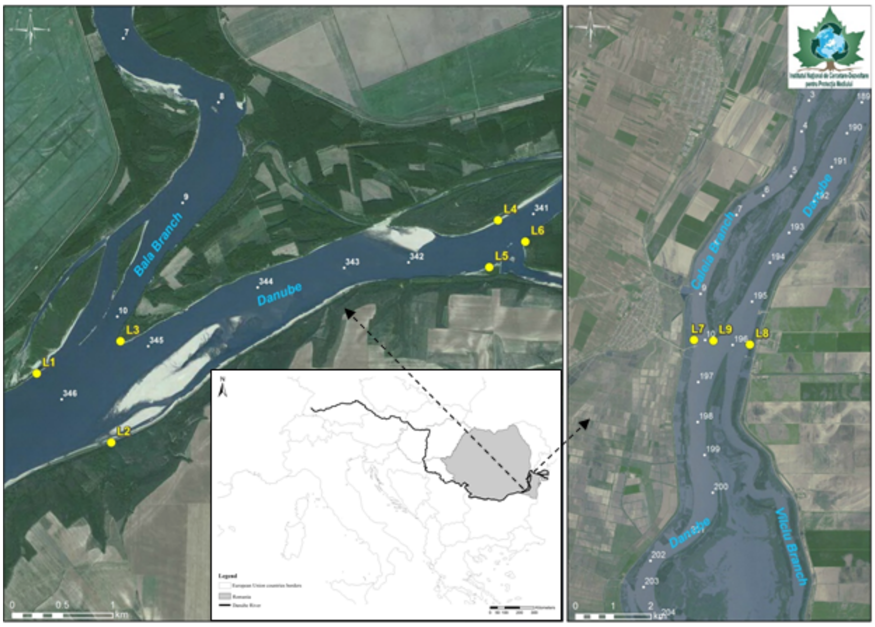


Fig. 1. The study area (*L1* - Danube km 346 from the left bank, *L2* - Danube km 346 from the right bank, *L3* - Turcescu Island km 345, *L4* - Danube km 341.5 left bank, *L5* - Danube km 341.5 right bank, *L6* - Epura°u Island km 341, *L7* - Caleia km 10 branch left bank, *L8* - Danube km 196 right bank, *L9* - Lupu Island km 196)

Table 1

THE EXACT POSITIONING OF THE SAMPLING LOCATIONS

Locations	River km	Geographical coordinates			
		Latitude	Longitude	Stereo_X	Stereo_Y
L1	Danube km 346.1	44°11'21.96"N	27°33'37.27"E	704804.3	302089.9
L2	Danube km 345.9	44°10'59.14"N	27°34'09.62"E	705545.1	301408.6
L3	Bala Branch Km 10 (Danube km 345.3)	44°11'31.38"N	27°34'15.22"E	705637.7	302407.4
L4	Danube km 341.3	44°12'06.02"N	27°37'06.01"E	709394.8	303598.0
L5	Danube km 341.5	44°11'51.13"N	27°37'01.46"E	709308.8	303135.0
L6	Danube km 341.2	44°11'58.89"N	27°37'17.90"E	709666.0	303386.4
L7	Caleia Branch km 10 (Danube km 196)	45°04'09.65"N	27°54'02.95"E	728496.8	400746.5
L8	Danube km 196	45°04'04.05"N	27°55'10.55"E	729981.1	400627.5
L9	Caleia Branch km 10 (Danube km 196)	45°04'08.53"N	27°54'26.49"E	729012.8	400730.7

conductivity, calcium (Ca), magnesium (Mg), sulphates (SO_4^{2-}), organic carbon (C_{org}) and humus. Additional information regarding the sampling areas and the quality indicators may be accessed on the monitoring project homepage stated in the Acknowledgements section.

This paper presents an overview of the soil quality indicators and a descriptive analysis regarding behaviour of potentially toxic metals in the riparian soil of the Lower Danube River. Finally, a multivariate statistical analysis was performed using the Principal Component Analysis (PCA) and Cluster Analysis (CA) in order to identify correlations between potentially toxic metal concentrations in soil and to obtain information on possible sources responsible for the presence of the respective potentially toxic metals.

Results and discussions

The average values of the quality indicators monitored in the riparian soil along the Lower Danube River are presented in Table 2. The obtained data was compared with the reference values from the national legislation [30] and highlighted that the monitored indicators are below normal values and the humus content ranges from low (about 1 %) to medium (about 10 %).

Table 3 presents a descriptive analysis of the potentially toxic metal concentration using several variables: minimum, 10 % percentile, median, 90 % percentile, maximum, mean, standard deviation, standard error and reference values according to the applicable legislation.

The results showed that all 6 metals (Cr, Cu, Mn, Ni, Pb and Zn) were situated below the normal values from the national legislation. Generally, Mn has the highest concentration, while Cr has the smallest one. The order of absolute average values observed in this study is Cr> Pb> Ni> Cu> Zn> Mn, while the order of the relative average values at the normal limits is Zn> Cu> Mn> Ni> Pb> Cr.

For an overall assessment of the potentially toxic metals concentrations in the studied area, multivariate statistical analysis techniques were applied to the data obtained during the monitoring program using the PCA and the CA procedures from the statistical software package JMP 10. Principal Component Analysis was performed to reduce the dimensionality of the data set using a matrix composed of the concentrations obtained for each metal. Table 4 shows the matrix of correlation coefficients between the potentially toxic metal concentrations.

Table 2

THE AVERAGE VALUE OF THE QUALITY INDICATORS IN SOIL

Indicators Locations	L1	L2	L3	L4	L5	L6	L7	L8	L9
Cr (mg/kg)	2.18	4.94	3.22	4.76	3.87	2.67	2.67	2.94	2.67
Cu (mg/kg)	15.02	14.40	5.15	9.46	5.64	6.60	6.50	6.02	7.24
Mn (mg/kg)	188.24	320.41	189.34	265.62	354.51	142.50	174.89	195.71	288.43
Ni (mg/kg)	2.49	5.58	6.12	4.00	2.47	3.01	3.70	5.32	3.86
Pb (mg/kg)	5.20	3.59	4.96	2.95	4.22	1.95	2.61	3.02	4.50
Zn (mg/kg)	44.64	79.39	53.86	45.29	45.83	46.40	45.24	37.73	37.07
SO_4^{2-} (mg/kg)	75.11	274.69	83.46	148.22	113.85	58.85	124.16	71.13	149.61
Ca (mg/kg)	127.32	133.76	51.60	74.61	78.76	36.00	120.86	156.13	80.60
Mg (mg/kg)	33.49	36.67	30.08	31.81	36.09	24.45	28.19	52.48	34.47
C_{org} (%)	1.39	4.79	1.08	5.08	3.09	1.28	3.01	5.56	2.60
Humus (%)	2.39	8.27	1.86	8.76	5.33	2.21	5.19	9.59	4.63

Table 3

STATISTICAL ANALYSIS OF POTENTIALLY TOXIC METALS IN SOIL

	Cr	Cu	Mn	Ni	Pb	Zn
Min	1.41	2.83	99.70	1.44	1.06	22.70
10 % percentile	2.15	4.98	145.90	2.39	2.10	31.75
Median	3.11	7.05	211.95	3.77	3.47	46.20
90 % percentile	5.00	15.29	339.50	6.25	5.58	69.50
Max	6.12	19.62	410.20	8.15	7.32	91.40
Mean	3.33	8.45	235.83	4.06	3.68	48.35
St Dev	1.08	3.80	74.03	1.48	1.37	14.38
Normal values*	30	20	900	20	20	100

*Normal values according to Order 756/1993 [30]

Table 4

CORRELATION MATRIX FOR WATER QUALITY PARAMETERS

	Cr	Cu	Mn	Ni	Pb	Zn
Cr	1.0000					
Cu	**0.2512**	1.0000				
Mn	**0.5890**	0.1720	1.0000			
Ni	**0.3197**	-0.0217	0.0011	1.0000		
Pb	0.0587	**0.2967**	0.2373	0.1623	1.0000	
Zn	**0.4571**	**0.3979**	0.2370	**0.3272**	0.0658	1.0000

Pearson correlation coefficients for potentially toxic metal concentrations from the soil samples (table 4) showed a direct relationship between most metals. These statistical values have highlighted the pronounced heterogeneous nature of metals concentrations dispersion at the soil level in the monitored area because the correlations were predominantly low, with only a few statistically more significant correlations.

Table 5 contains selected significant loading values for the first 3 Principal Components (PC). The results of the loading matrix on the principal components showed that the first component comprised the variability of Cr, Cu, Mn, Zn and Ni data sets, the second component took over the variability of Pb, Cu and Ni and the third component was associated with Mn, Pb and Ni as main constituents.

In table 5 it can be seen that the pronounced non-uniformity of the values does not seem to indicate other major common sources of contamination, the first component being associated with common alluvial intake for the entire region.

Figure 2 shows the eigenvalues associated with the principal components and the percentage of variability accounted by each PC.

Table 5

LOADING MATRIX

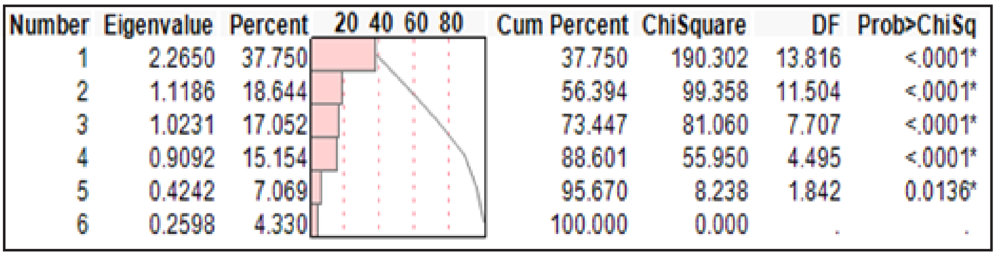
Parameters	PC1	PC2	PC3
Cr	0.8080		
Zn	0.7242		
Mn	0.6610		-0.5733
Cu	0.5613	0.5124	
Ni	0.4320	-0.6175	0.5250
Pb		0.5689	0.4639

The first principal component represents 37.8 % (fig. 2) from the variability of the entire data set, the second principal component supplemented by 18.6 % the coverage of the original variance and the third principal component contributed with 17.05 %. This fact indicated that the first component collected much of the information from the samples, which contained potentially toxic metals from the common source of alluvia supplied by the river. All the three principle components accounted for approximately 74 % of the entire variability of the data set, highlighting the major trends of the monitored ecosystem. The relative slow decay rate of the variability contribution of each individual PC may be another indication of the mostly uncorrelated evolutions of the monitored indicators caused by a high degree of heterogeneity both at soil type coverage and concentration levels.

The plots between the first 3 PC (fig. 3) show the slight emergence of groups of aggregated data, being useful in the identification of underlying trends such as common pollution sources superimposed on common geochemical make up.

These relationships could serve to identify artificial sources caused by different human activities, depending on the specificity of the association between metals. By testing the correlation of the potentially toxic metal groups studied with other general parameters, significant correlation between Cr, Mn and Zn levels with SO_4^{2-} content and Zn levels with Ca content were observed (table 6).

Evaluation of the correlations between the total content of potentially toxic metals and some soil properties (table 6) showed that the content of organic carbon and the soluble salts are generally low or not correlated with the concentration of the heavy metals with the exception of Cr, Mn and Zn with sulphates, Zn with calcium and Cr with organic carbon. Soil *p*H only showed more statistically significant relationships with Mn and Zn concentrations.



Number	Eigenvalue	Percent	20 40 60 80	Cum Percent	ChiSquare	DF	Prob>ChiSq
1	2.2650	37.750		37.750	190.302	13.816	<.0001*
2	1.1186	18.644		56.394	99.358	11.504	<.0001*
3	1.0231	17.052		73.447	81.060	7.707	<.0001*
4	0.9092	15.154		88.601	55.950	4.495	<.0001*
5	0.4242	7.069		95.670	8.238	1.842	0.0136*
6	0.2598	4.330		100.000	0.000	.	.

Fig. 2. Eigenvalues and percentage of data variability accounted by each PC

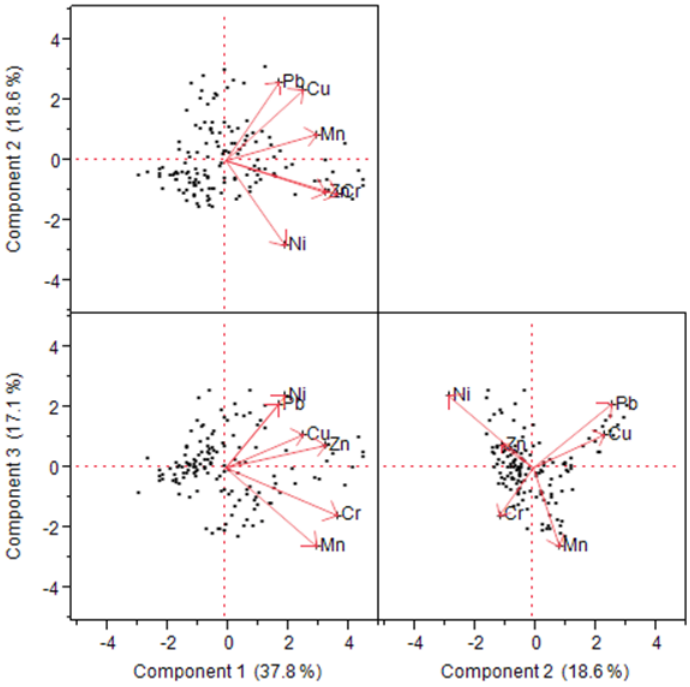


Fig. 3. Loading plots of the first three components influenced by geochemical variation of soils

Table 6

CORRELATION COEFFICIENTS MATRIX OF THE TRACE ELEMENTS TOGETHER WITH OTHER SOIL PROPERTIES, WITH P < 0.01(*) AND P < 0.001(**) SIGNIFICANCE LEVELS.

Parameters	pH	Conductivity	SO_4^{2-}	Ca	Mg	C_{org}	Humus
Cr	0.3671	0.3193	0.6453**	0.0100	0.1737	0.5032*	0.4998
Cu	0.1680	0.3386	0.4722	0.3962	0.0332	0.1228	0.1213
Mn	0.5637*	0.4603	0.6252**	0.0972	0.2400	0.4013	0.4044
Ni	0.0760	0.1882	0.3284	0.1736	0.2880	0.2887	0.2832
Pb	0.1880	0.1606	0.0584	0.0353	0.2076	-0.2384	-0.2325
Zn	0.4339	-0.0211	0.6022**	0.6022**	-0.0850	0.0956	0.0892

In order to identify natural and anthropic sources of contamination an exploratory hierarchical cluster analysis of the metal concentrations was performed. The results are illustrated by a hierarchical dendrogram as shown in figure 4. It is known that as value on the group of distances is lower, the more important the association is.

Depending on the degree of association between metals, two distinct clusters could be identified (fig. 4): the first group includes Cr, Pb and Ni, supporting the hypothesis of a common origin and the second group formed by Cu, Zn and Mn, which probably derives from anthropogenic activities. Overall, the clusters seemed to indicate the presence of both natural and anthropogenic potentially toxic metal sources of origin.

The statistical distribution of the data was compared to an equivalent normal distribution, with an average

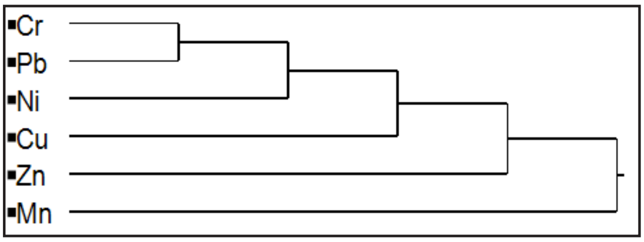


Fig. 4. Dendrogram of potentially toxic metals

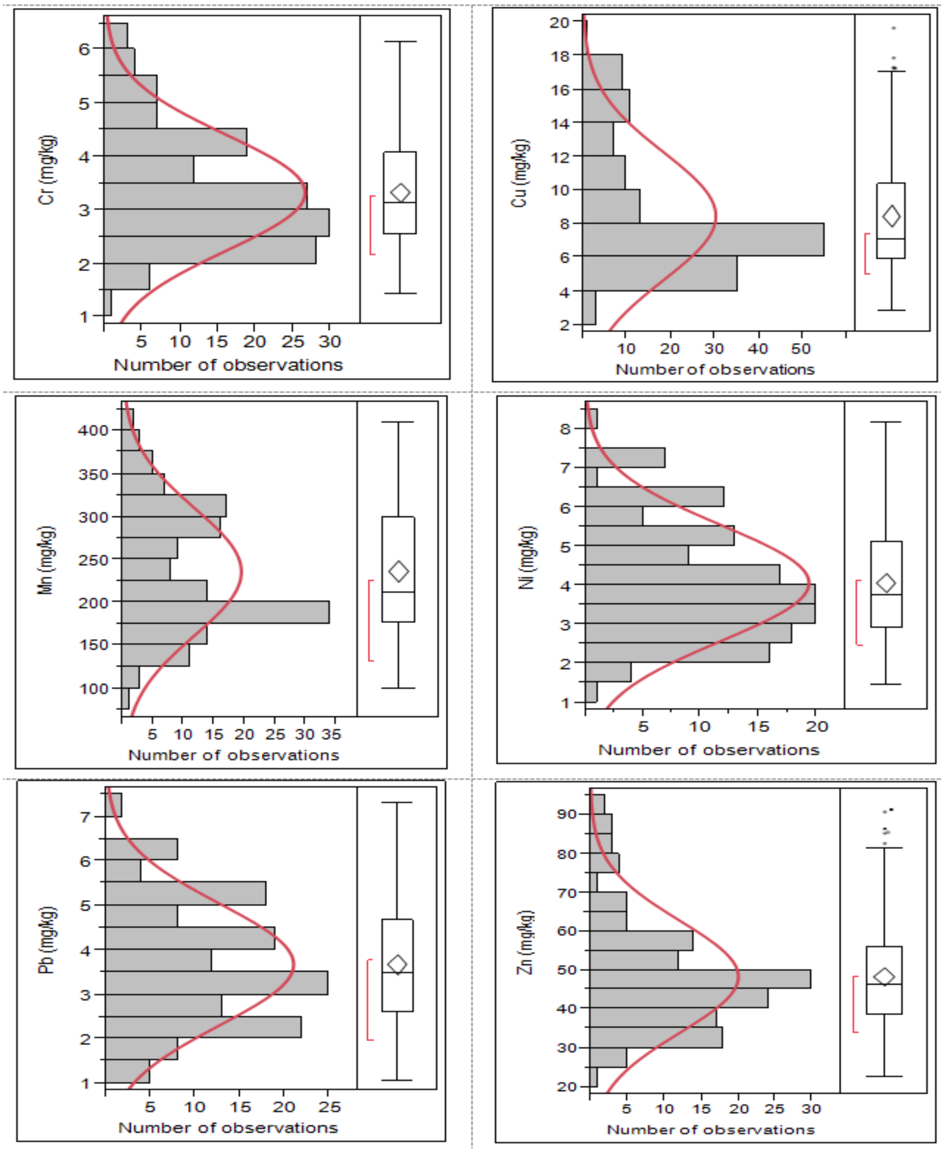


Fig. 5. Histograms of Cr, Cu, Mn, Ni, Pb, Zn concentrations

confidence level of 95 %. Histograms for concentration of Cr, Cu, Mn, Ni, Pb and Zn are shown in figure 5. The assessment of histogram confirmed that the original data sets for the analysed potentially toxic metals are normally distributed.

The obtained information can be useful both in exploring possible accidental pollution and in the effort to assess the overall quality of ecosystems that depend on the local environmental factors.

Conclusions

The average values of the potentially toxic metals present in the soil from the monitored locations do not exceed the normal values from the national legislation, which means that no major pollution problems were identified.

Multivariate statistics prove to be a useful tool to identify the main factors that underlies the variability of soil quality data and to provide a new insight in interpreting environmental quality based on large database of measurement results. After PCA, 3 principal components were identified with a combine share of approximately 74 % of the original variability, and the statistical distribution of potentially toxic metals represented by histograms confirmed that the original data sets are normally distributed.

Comparing the average values of the analysed potentially toxic metals, a decreasing tendency in the order of Cr>Pb>Ni>Cu>Zn>Mn was observed and by reporting the average values at the normal limits the order Zn>Cu>Mn>Ni>Pb>Cr was obtained, Zn being the closest to the normal limit. The humus content ranges from low (about 1%) to medium (about 10%), being directly proportional to the amount of organic matter.

The obtained results can be useful as a comparison base for authorities with competences in environmental protection for identifying environmental pollution and acting accordingly to decrease it. Moreover, the application of multivariate statistical methods can provide logistical support for the detection of pollution in case of accidental contaminations.

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