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PRELIMINARY DATA CONCERNING THE SPATIAL VARIABILITY OF HEAVY METAL DISTRIBUTION IN THE TOPSOIL FROM IAŞI MUNICIPALITY, ROMANIA

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Abstract

Establishing the model of spatial variability is an essential condition for monitoring the heavy metal pollution of urban soils. We have collected 171 samples from the topsoil of Iaşi Municipality, thus determining the contents of Zn, Cu, Fe, Mn, Pb, Cd, Co, Ni and Cr. The abundance of heavy metals found in these soils has decreased as it follows: Fe>Mn>Zn>Pb>Cu>Cr>Ni>Co>Cd. The mean values of Zn, Cu, Pb, Ni and Cr were higher than the critical values of the Romanian soil quality standard. All these data have followed normal or lognormal distribution. Local background levels have exceeded in soils the normal values in the case Zn, Cu, Pb, Ni and Cr. The correlation distance of heavy metals from soil ranged from 300 m to 6732.198 m, nine heavy metals having a moderate to strong spatial dependence. The spherical model was fitted to the semivariograms of Zn, Cu, Fe, Mn, Pb, Ni, Cr, while Cd and Co were fitted to the exponential model.

Key words: soils, heavy metals, spatial variability, Iaşi, Romania

Introduction

Urban soil pollution with heavy metals is a major environmental problem. Heavy metals are very persistent in the environment and therefore, accumulate toxic levels. In urban soils, heavy metals can result from human activities, such as industrial production, coal and fuel combustion, as well as construction. The ingestion of atmospheric dust and

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soil particles can have a direct influence on human health. Soils used for urban agriculture is another way of exposure to heavy metals by means of rhizosphere.

Material and methods

1. Environmental Information

Situated in north-eastern Romania, at 47.1^{o} N and 27.3^{o} E, Iaşi Municipality has an area of 9361 ha and a population of 308,843 inhabitants and over 60,000 students (according to the National Institute of Statistics, 2009; City Hall of Iaşi, 2009).

The capital of Moldavia between 1564 and 1859, Iaşi was one of the two capitals of the Romanian Principalities during 1859 and 1862 and capital of Romania during 1916-1918.

Known as the city of the seven hills, Iaşi has heights varying between 40 m and 400 m and is crossed by Bahlui, Nicolina and Şorogari rivers.

The climate has a significant continental character.

Being highly industrialized during 1945-1990 (chemical, pharmaceutical, metallurgical and heavy machine industries, textile, food, energetic and furniture industries), Iaşi County has recorded a slow decrease in the industrial activity during 1991-2009.

Geologically, the area of Iaşi Municipality is situated in the Moldavian Platform, which consists of a crystalline basement and a sedimentary cover, ranging from Neoproterozoic to Neogene, according to Ionesi (1994).

Investigations on some aspects concerning the geochemistry of heavy metals from soils of Iaşi County were conducted by Lăcătuşu et al. (2005, 2008), Apostoae et al. (2007), Iancu and Buzgar (2008), Apostoae and Iancu (2009).

2. Sample Collection

A number of 171 soil samples were collected at depths of 0.00 – 0.25 m from the nodes of a square network with the side of 500 m. The weight of one sample varies between 1.5 and 2.5 kg.

Once the samples were air-dried and crumbled into fragments < 0.2 mm, they determined the total heavy metal content through the atomic absorption spectroscopy (AAS Solar type), in air-acetylene flame, in the hydrochloric solution obtained after digestion with a concentrated nitric and perchloric acid mixture (ICPA-Bucureşti methodology).

3. Spatial Structure Analysis

Soil heavy metals are typical regionalized variables (Webster and Olivier, 2007). The experimental semivariogram measures the average degree of dissimilarity between sampled values and a nearby data value, and thus autocorrelation at various distances can be depicted (Isaaks and Srivastava, 1990; Goovaerts, 1997). The value of the experimental semivariogram for a separation distance of h is half of the average squared difference between the value at $Z(x_i)$ and at $Z(x_i+h)$:

$$\gamma(h) = \frac{1}{2} Var[Z(x+h) - Z(x)]$$

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2$$

Where: *N(h)* is the total number of pairs of sample points separated by the lag distance *h*;

Z(xi) is the measured sample value at point *i*;

Z(xi + h) is the measured sample value at point *i + h*

The variogram model is chosen from a set of mathematical functions that describe spatial relationships. The appropriate model is chosen by matching the shape of the curve of the experimental variogram to the shape of the curve of the theoretical function. The fitted model provides information about the spatial structure as well as the parameters, such as nugget, slope at the origin, range and sill.

Results

1. Statistical Descriptive Parameters

For the evaluating of the raw data, the statistical parameters of soil heavy metals are shown in table 1. The mean values of heavy metal content are higher than the normal values in soils in the case of Zn, Cu, Pb, Ni and Cr and lower in the case of Mn, Cd and Co. The values of the variation coefficient vary between 0.171 (Mn) and 2.450 (Pb). The coefficient of variation values shows, especially in the case as of Zn, Pb and Cd, the highest possibility of being influenced by the extrinsic factors, such as human activities. The Kolmogorov-Smirnov normality test shows the presence of normal distribution only in the case of Cr. Zn, Cu, Fe, Mn, Pb, Cd, Co and Ni followed a lognormal distribution.

The Pearson correlation coefficients, which measure the linear relationship between the heavy metal content, are illustrated in table 2. A significant positive correlation was noticed between Zn and Cu, Cd; Cu and Fe, Mn, Pb, Cd, Ni, Cr; Fe and Mn, Cd, Co, Ni, Cr; Mn and Co, Ni; Cd and Cr; Co and Ni. They speculated that these pairs of heavy metals originated from the same soil parent material.

The values calculated for local background exceed the normal values of the Romanian soil quality standard in the case of Zn, Cu, Pb, Ni and Cr (tab. 1).

2. Spatial Structure of Soil Heavy Metals

Semivariograms were used for the establishing of the degree of spatial continuity and the range of spatial correlation. The experimental semivariogram represents the variance of the sample value at various separation distances. Experimental semivariograms can be described mainly based on three parameters: nugget, sill and range (Armstrong, 1998; Pan and Harris, 2000).

The obtained experimental semivariograms for heavy metal content from soils of Iaşi Municipality have shown that the theoretical spherical model was in agreement with these data (Zn, Cu, Fe, Mn, Pb, Cd, Cr); only Co and Ni were fitted to the exponential model (fig. 1; tab. 3).

The highest nugget effect of Zn (C_0 = 16960) indicated a strong random variance at short distance. The lowest nugget effect of Cd (C_0 =0.636) showed that the relative variance and the sampling density were adequate to reveal the spatial structures.

The range of heavy metal content varied from 300 m (Ni) to 6732,198 m (Co). Co and Cd had the largest ranges, 6732,198 m and 5202,697 m, respectively, suggesting that the two chemical elements were correlated and depended on the soil parent material. Ni had the smallest range, 300 m, which implies that the length of the spatial autocorrelation is smaller than the sampling interval of 500 m.

Cambardella et al. (1994) assessed that the ratio $C_0/(C + C_0)$ was a classification criterion of the spatial dependence of soil properties. If this ratio is less than 25%, the variable has strong spatial dependence. If it is between 25% and 75%, the variable has moderate spatial dependence. If the ratio is greater than 75%, the variable shows only weak spatial dependence. According to this criterion, Zn, Cu, Fe, Mn, Pb, Ni and Cr have a strong spatial dependence of soil properties, which may be attributed to intrinsic factors, among which the most important one is soil formation. Cd and Co show moderate spatial dependence, suggesting that the anthropogenic factors have changed their spatial correlation because of industrial production, vehicle emissions and urbanization factors.

Tab. 1 Univariate statistics of heavy metals

Element / Statistics	Zn	Cu	Fe	Mn	Pb	Cd	Co	Ni	Cr
Mean	224.474	46.277	19621.539	590.305	63.970	0.879	8.390	37.694	43.465
Geometric Mean	141.992	40.991	19019.290	582.673	40.772	0.570	8.201	34.350	40.362
Median	119.526	37.462	19168.350	572.579	39.487	0.594	7.907	32.576	45.409
Mode	85.000	32.900	-	593.000	22.900	0.250	7.600	30.800	47.000
Standard Deviation	479.589	26.629	5418.205	100.984	156.703	1.554	1.959	25.536	14.114
Kurtosis	96.482	13.733	12.382	7.190	137.736	52.950	4.291	71.404	0.624
Skewness	9.019	3.314	2.536	1.789	11.230	6.733	1.809	8.148	-0.598
Minimum	14.912	20.639	8090.000	331.050	7.362	0.020	5.200	18.807	0.000
Maximum	5624.000	234.800	54111.180	1148.000	1995.432	15.440	17.967	334.200	77.366
Coefficient of Variation	2.136	0.575	0.276	0.171	2.450	1.768	0.233	0.677	0.325
Local Background *	112.566	40.952	17280.250	361.396	43.755	0.841	11.802	34.472	48.665
Normal value **	100	20	-	900	20	1	15	20	30
Distribution	lognormal	lognormal	lognormal	lognormal	lognormal	lognormal	lognormal	lognormal	normal

* calculated according to the methods indicated by Reimann et al. (2005), Oulette (2007)
** according to Order no 756/1997 of the Ministry of Waters, Forests and Environment Protection

Tab. 2 Matrix of the correlation coefficients of heavy metals

Element	Zn	Cu	Fe	Mn	Pb	Cd	Co	Ni	Cr
Zn	1								
Cu	0.14670*	1							
Fe	0.08121	0.34443*	1						
Mn	-0.03026	0.17694*	0.59708*	1					
Pb	0.06968	0.20242*	0.07883	-0.01223	1				
Cd	0.19217*	0.23069*	0.17721*	0.01469	0.07049	1			
Co	-0.02632	0.04274	0.54578*	0.54087*	-0.01697	0.06819	1		
Ni	0.07602	0.36364*	0.24072*	0.14206*	0.08894	0.00443	0.16046*	1	
Cr	0.05396	0.19104*	0.14640*	0.01391	0.09777	0.12378*	-0.04779	0.11775	1

* $p < 0.05$, $n = 200$

Tab. 3 Semivariogram models and parameters of soil heavy metals

Parameter / Heavy metal	Model	Nugget (Co)	Sill (C+Co)	Co/(C+Co) (%)	Range (m)
Zn	Spherical	16960.000	231700.000	7.320	1020.000
Cu	Spherical	75.365	681.700	11.055	480.000
Fe	Spherical	10000.000	29820000.000	0.034	910.000
Mn	Spherical	1060.000	9910.000	10.696	890.000
Pb	Spherical	4961.200	23625.360	20.999	1167.583
Cd	Exponential	0.636	2.367	26.869	5202.697
Co	Exponential	1.074	3.833	28.020	6732.198
Ni	Spherical	75.000	658.200	11.395	300.000
Cr	Spherical	5.400	199.200	2.711	770.000

Conclusions

- Using soil sampling on a relatively large scale, a number of nine heavy metal concentrations in Iaşi Municipality were tested;
- The abundance of heavy metals measured in the topsoil of Iaşi Municipality decreases as it follows: Fe > Mn > Zn > Pb > Cu > Cr > Ni > Co > Cd;
- High mean values of contents (Zn, Cu, Pb, Ni, Cr) and the coefficient of variation values (Zn, Pb, Cd) suggest the possibility of being influenced by the anthropic activity;
- All these data followed normal or lognormal distribution;

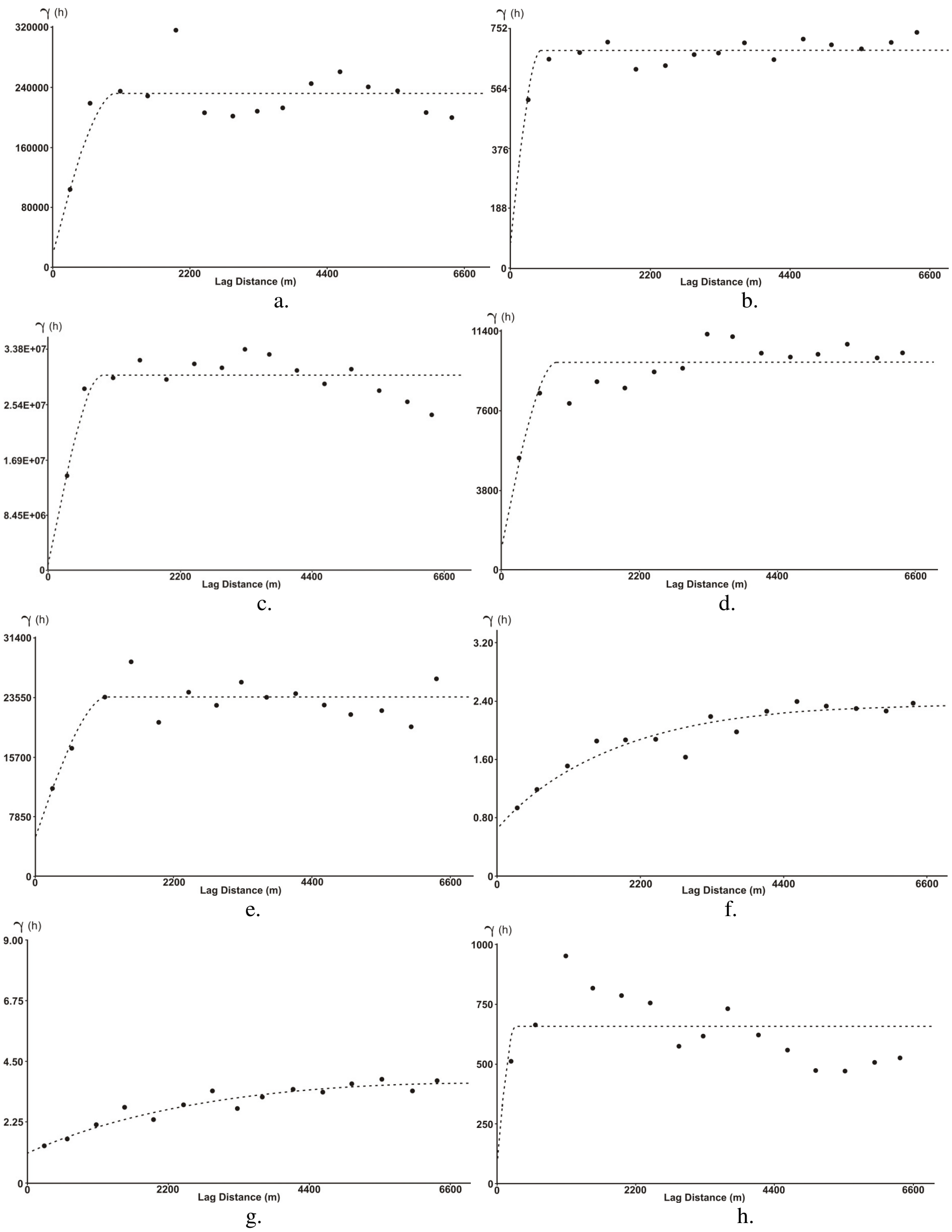

Fig. 1 Semivariogram model of soil heavy metals: a-Zn; b-Cu; c-Fe; d-Mn; e-Pb; f-Cd; g-Co; h-Ni

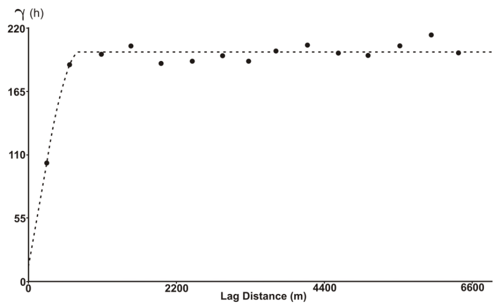

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Fig. 1 Semivariogram model of soil heavy metals: i-Cr

- The significant correlation coefficient, noticed between Zn and Cu, Cd; Cu and Fe, Mn, Pb, Cd, Ni, Cr; Fe and Mn, Cd, Co, Ni, Cr; Mn and Co, Ni; Cd and Cr; Co and Ni, indicated that they had the same origin as their soil parent materials and the same soil formation factors;
- The range of Co and Cd suggests that the two chemical elements were correlated and depended on the soil parent material;
- The ratio $C_0/(C + C_0)$ indicates moderate (Cd, Co) to strong spatial dependence (Zn, Cu, Fe, Mn, Pb, Ni and Cr).

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