GEOCHEMICAL ATLAS OF HEAVY METALS FROM THE SOILS OF THE IAŞI CITY AND SURROUNDINGS – PRELIMINARY DATA

Ovidiu Gabriel IANCU[1*], Nicolae BUZGAR[1], Laviniu APOSTOAE[1], Radu LĂCĂTUŞU[1], Emanoil GANDRABURA[1], Ciprian POPA[2,3], Eugen TEODORESCU-SOARE[4], Mihaela LUNGU[5], Oana STAN[1], Cristian PATRICHE[6]

The main goal of this research is the geochemical mapping of the Iasi area and surroundings, for potential polluting heavy elements, trying to discriminate between the local geochemical element trend and possible anthropogenic interference. A preliminary analysis was performed on a number of about 400 samples from the agricultural soils and forests covering the NE (259 samples, 14 alignments from E to W) and SE (136 samples, 7 alignments from E to W) perimeters of the surveyed area, which has shown possible concerning trends for some elements. The current work has established a possible anthropogenic geochemical Ni, Cu anomalies for the entire preliminary research areas and a localized one for Cr, Ni and Pb in the northeastern perimeter and for Cu, Zn and Pb in the southeastern perimeter.

Keywords: urban soil, heavy metals, geochemical maps, AAS

1. Introduction

The basic objective of this study is to pursue a systematic investigation concerning the content and distribution of Zn, Cu, Fe, Mn, Pb, Ni, Cr, Co and Cd, heavy metals commonly found in the urban soils due to anthropogenic activities. This will serve to the soil quality assessment and contamination level prognosis, including the identification of the anthropogenic polluting sources in the Iaşi City area. The proposed perimeter is a square of roughly 16x16 km^2, which encloses the urban Iaşi City and surroundings (Fig. 1). Iasi, the second-largest Romanian city, is an important economic centre in Romania. It has an active trade in metals, medical drugs, textiles and clothing, banking, wine and preserved meat. The city has also become an important IT sector centre, with 5 state and 3 private

[1]Department of Geology and Geochemistry, University "Al. I. Cuza" of Iasi, Romania (*Corresponding author)
[2]Capodimonte Astronomical Observatory, Naples, Italy
[3]International Research School of Planetary Sciences, Pescara, Italy
[4] University of Agricultural Sciences and Veterinary Medicine Iasi, Romania
[5]Research Institute for Soil Science and Agrochemistry ICPA Bucharest, Romania
[6]Romanian Academy, Iasi Branch

universities. Iasi is also an important regional commercial centre. The total population of the Iasi metropolitan area is about 400,000 inhabitants, with a density of 149.6 inhabitants/km^2.

A systematic research of urban soils from Iaşi city started recently [1]. Local studies regarding the heavy metals distribution in soils belonging to certain industrial objectives have been also made by economic agents (S.C. Fortus SA, ELECTROCENTRALE - C.E.T. I, and C.E.T. II, S.C. ASAM, S.C. MITTAL STEEL – TEPRO etc., strictly for the industrial precinct).

2. Pedogeological setting

The soil cover inside Iasi municipality zone mainly consists of anthropogenic modified soils belonging to Protisols. In the frame of this class, dominantly, is Entiantrosol type, with the Urbic and Mixic subtypes (Anhropic Regosols, according to WRB-SR-1998). On small areas, as in Copou, there are Cambic Chernozems (Haplic Chernozems) within the Exposition Park and Cambic Chernozems (Haplic Chernozems) anthropical covered, in Copou Park. In the Bahlui alluvial plane there are Fluvisols with the Gleyic, Vertic and Calcaric subtypes, most them anthropical covered. Sporadically, in these Fluvisols the salinization process occurred.

In the surroundings of Iasi city the soils are usually in their natural state. Belonging to Cernisols class, Chernozems types with the Calcic and Fluvic subtypes prevail. From Phaeozems class there are Haplic Phaeozems and Fluvic Phaeozems. Erodisols and Anhrosols appear on slops and valleys, respectively.

The geological background in the investigated area is represented by Sarmatian sedimentary rocks: sands, silts, clays, sandstones and oolithic sandy limestone [2].

3. Methods

Topsoil samples were collected on a grid of 500 m, from a depth of 0-25 cm, with a 25 cm long hand sampler. The preliminary study was concentrated on a number of about 400 samples from the agricultural soils and forests covering the NE (259 samples, 14 alignments from E to W) and SE (136 samples, 7 alignments from E to W) areas of the surveyed perimeter. The samples weighing between 1.5 and 2.5 kg were dried and sieved to < 1 mm fraction and then randomized and analyzed by Atomic Absorption Spectroscopy (AAS). pH was also determined by using a Corning M-555 pH/Ion Meter. External check was performed on 40 samples (10%) by X-Ray Fluorescence Spectroscopy (XRF) at the University of Wien, Austria and by AAS at the University of Katowice, Poland.

We used a GIS software system to make the interpolation for the available sampled data, and due to the public diffusion ESRI ArcGIS was chosen mainly for two reasons:

1. Its wide compatibility with other software systems (GIS, CAD), making possible to transfer, edit and verify the validity of the data we have interpreted in a widely compatible data format.

2. The availability of a licensed workable workstation provided by the University of Chieti-Pescara, Italy, with the "Geostatistic Analyst" extension.

Due to the way the sampling was planned, a quadratic grid was obtained and an Inverse Distance Weighting Interpolation method was chosen to predict the non sampled areas concentration.

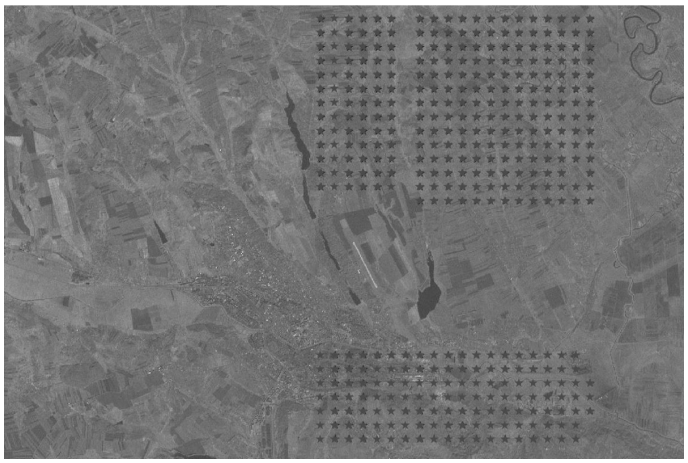

Fig. 1. The surveyed perimeter with the areas sampled (perimeter I – NE, perimeter II - SE); Landsat Image

4. Results

According to Romanian legislation, in the areas investigated in this study the heavy metals contents for the soils (Table 1) may be interpreted as follows:

Northeastern perimeter - soils with sensitive land use:

- has normal values for Fe and Hg;
- has higher than normal values for Ni and Cu for most of the analyzed samples (Fig. 2, Fig. 4);
- has higher than normal values for Zn, Mn, Co, Cd, Pb (Fig. 6) and Cr for localized samples;
- there are local anomalies, higher than alert limit: 1 sample for Zn, 4 samples for Ni and Cr (Fig. 2);
- there ale local anomalies that overcome the intervention limit threshold (1 sample for Pb – Fig. 6, 1 sample for Zn and 3 samples for Ni and Cr - Fig. 2).

Southeastern perimeter - soils with sensitive land use:

- has normal values for Fe;
- global concentrations surpass the normal threshold values for Ni and Cu (Fig. 3, Fig. 5);
- in some cases, they surpass the normal values for Zn, Mn, Co, Cd, Pb and Cr;
- in few cases (1 sample for Mn, Hg and Ni, 3 samples for Pb and Zn, 16 samples for Cu), they surpass the alert limit (Fig. 3, Fig. 5);
- greater than intervention limit threshold (1 sample for Zn, 12 samples for Cu - Fig. 5).

Significant positive correlations (p=99,995%) have been determined for the following chemical elements pairs: Zn-Cu, Zn-Pb, Zn-Cd, Cu-Cd, Fe-Mn, Fe-Co, Ni-Cr, Cd-pH in the northeastern perimeter and Fe-Mn, Fe-Cd, Fe-Ni, Mn-Co, Pb-Cd, Ni-Cr for the southeastern perimeter (Table 2).

- Significant negative correlations for Cd-Co and Co-pH have been determined for the southeastern perimeter.

The soil pH varies between moderately acid and strongly alkaline.

The statistical parameters suggest a mixing of populations for most of the chemical elements investigated in this study (high skewness, kurtosis, standard deviation and coefficient of variation). The heavy metals contents may be used with precaution as local estimators for the geochemical characterization of both perimeters sampled (mean, median, mode, upper and lower quartiles).

Table 1

Qualitative parameters of Iasi soils and surroundings (ppm)

Parameter	Area	Range interval		Average	Normal values*	Normal values**
		Minimum value	Maximum value			
Zn (ppm)	NE	40.10	618.80	72.23	100	150-300
	SE	27.93	1620.30	102.72		
Cu (ppm)	NE	15.70	82.80	27.02	20	50-140
	SE	11.60	702.61	80.97		
Fe (ppm)	NE	7118.00	32586.00	19607.14	-	-
	SE	4214.53	45319.00	19035.33		
Mn (ppm)	NE	50.00	952.00	635.23	900	-
	SE	223.40	1669.00	655.03		
Pb (ppm)	NE	8.20	209.80	18.95	20	50-300
	SE	4.50	91.10	21.65		
Cd (ppm)	NE	0.04	2.37	0.47	1	1-3
	SE	0.03	1.89	0.25		
Co (ppm)	NE	5.70	18.20	9.32	15	10-15
	SE	4.88	18.10	10.44		
Ni (ppm)	NE	23.00	349.60	42.41	20	30-75
	SE	13.50	77.20	36.89		

Cr (ppm)	NE	6.60	591.60	30.40	30	50-200
	SE	7.60	77.37	26.14		
Hg (ppm)	NE	0.06	0.60	0.16	0.1	0.01-5
	SE	0.10	1.80	0.60		
$CaCO_3$ (%)	NE	0.42	8.88	1.88	-	-
	SE	-	-	-		
pH	NE	5.13	9.56	7.44	-	-
	SE	4.07	8.43	7.14		

* As of Romanian legislation (OMAPPM 756/1997)
** As of European Legislation - Directive 86/278/EEC

Table 2

Correlation Coefficients Matrix

	Zn	Cu	Fe	Mn	Pb	Cd	Co	Ni	Cr	Hg	CaCO3	pH
NE Area												
Zn	1											
Cu	+	1										
Fe	+	+	1									
Mn	-	+	+	1								
Pb	+	+	+	+	1							
Cd	+	+	-	+	+	1						
Co	-	-	+	+	+	-	1					
Ni	+	+	+	-	+	+	+	1				
Cr	+	-	+	-	+	-	+	+	1			
Hg	-	-	-	-	-	-	+	-	+	1		
$CaCO_3$	-	-	+	+	-	-	+	-	-	+	1	
pH	+	-	-	-	-	+	-	+	-	+	-	1
SE Area												
Zn	1											
Cu	+	1										
Fe	-	+	1									
Mn	-	+	+	1								
Pb	+	-	+	-	1							
Cd	+	-	+	+	+	1						
Co	-	+	+	+	-	-	1					
Ni	-	+	+	+	+	+	+	1				
Cr	+	-	+	+	+	+	-	+	1			
Hg	-	-	-	-	-	-	+	+	+	1		
$CaCO_3$	*	*	*	*	*	*	*	*	*	*	1	
pH	+	-	+	-	+	+	-	+	+	-	*	1

+ positive correlation, - negative correlation, + - significant positive correlation (p=99,995%), - significant negative correlation (p=99,995), * low sample number

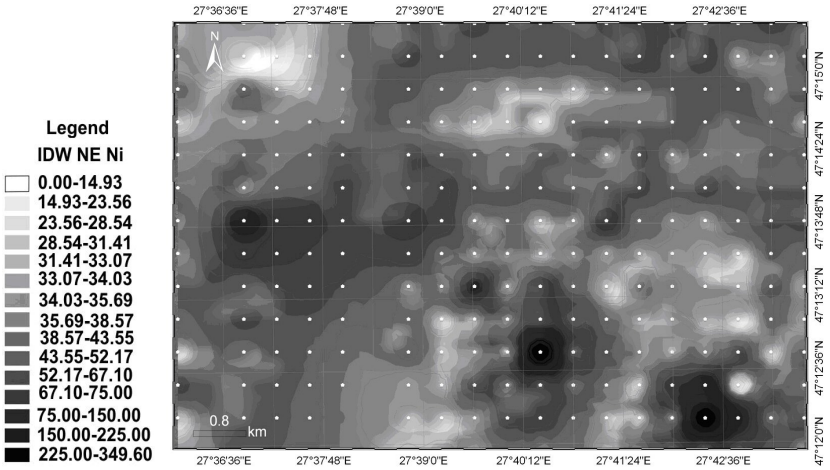

Fig. 2. The geochemical distribution of Ni in the northeastern perimeter

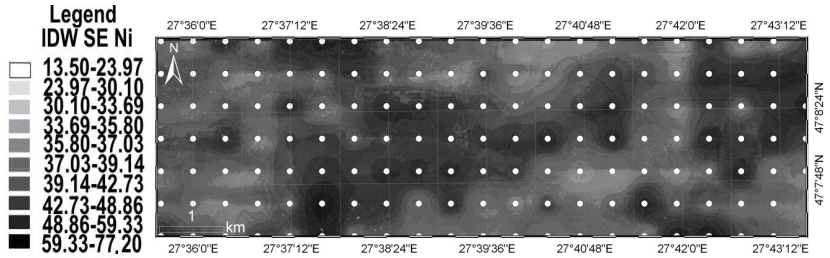

Fig. 3. The geochemical distribution of Ni in the southeastern perimeter

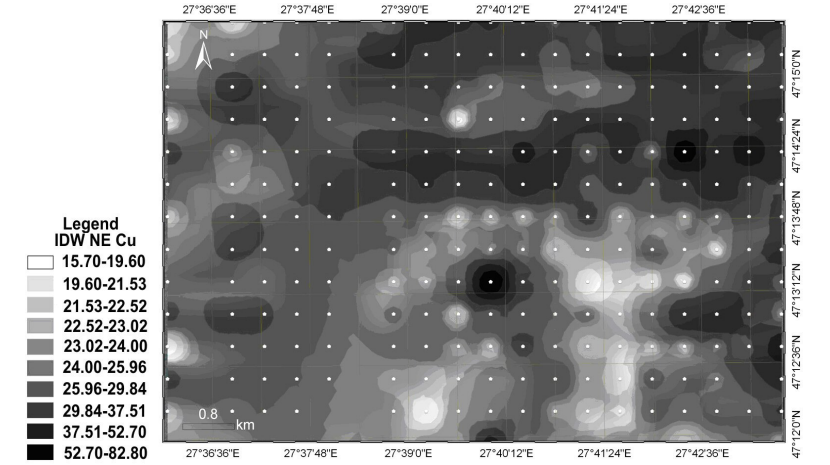

Fig. 4. The geochemical distribution of Cu in the northeastern perimeter

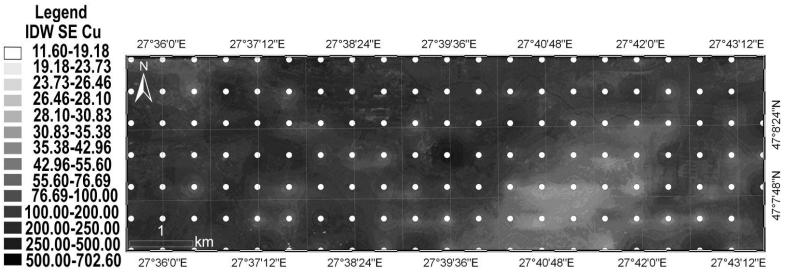

Fig. 5. The geochemical distribution of Cu in the southeastern perimeter

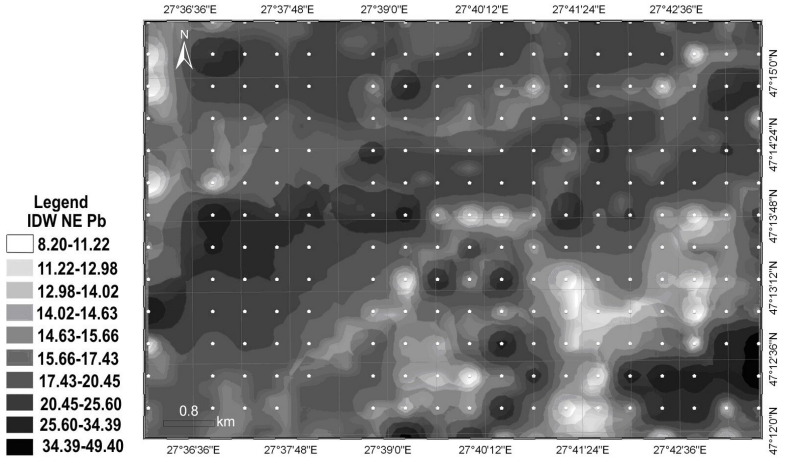

Fig. 6. The geochemical distribution of Pb in the northeastern perimeter

5. Conclusions

Concerning the heavy metals content there is a detectable dominant trend for positive correlations (35) with respect to the negative ones (28) as follows:

- Significant positive correlations (p=99,995%) for the following element pairs: Fe-Mn; Fe-Co; Fe-Ni; Mn-Co; Ni-Cr + Cd-pH

- Significant negative correlations (p=99,995%) for the following element pairs: Cu-Cd; Cd-Co + Cu-pH, Mn-pH, Co-pH.

Heavy metals contents are contrasting, from normal to high values even in the same profile. The current work has established a possible anthropogenic geochemical Ni, Cu anomalies for the entire preliminary research areas and a localized one for Cr, Ni and Pb in the northeastern perimeter and for Cu, Zn and Pb in the southeastern perimeter (Fig. 7).

The possible causes of the anomalies could be caused by the industrial activity in the city [3]: plastic industry (for Cu), steel works (for Cu, Ni, Cr and Pb) electrometallurgy (for Cr), refractory bricks factories, traffic, coal combustion (for Pb and Zn), waste disposal and incineration (for Ni, Cr and Pb), by

agricultural activities in the surroundings P-fertilizers (for Ni and Cr) and fungicide (for Cu) or by traffic (Ni, Zn and Pb).

Acknowledgements

This work was supported by a Grant from the Romanian Ministry of Education, Research and Youth (CEEX – MENER 748/2006). We are grateful to Professor Dr. Friederich Koller from the University of Wien, Austria and to Dr. Jolanda Burda from the University of Katowice, Poland for the external check of the samples in the framework of the CEEPUS program.

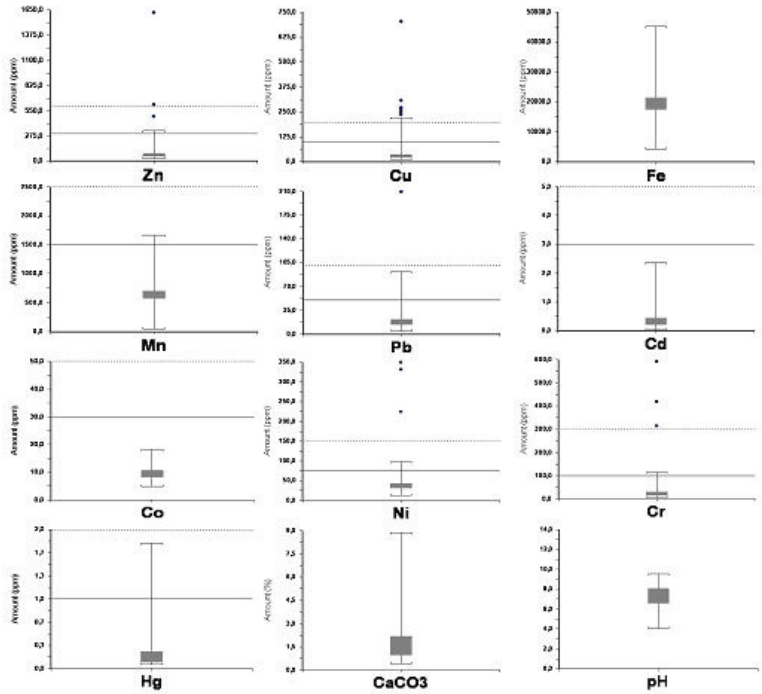

Fig. 7. Box plot of heavy metals concentration, $CaCO_3$ concentration and pH in both studied areas : — alert limit ---- intervention limit threshold (as of Romanian legislation)

REFERENCES

[1] *R. Lăcătuşu, Mihaela Lungu, Beatrice Kovacsovics, Iuliana Gabriela Breabăn, C. Rusu and Rîşnoveanu I.*, "Heavy Metals in Urban Soils of Iassy Municipium" in Hazards and Risks Monitoring, I. Giurma and F. Stratescu (eds.), Ed. Performantica, Iasi, 2005.

[2] *L. Ionesi*, Geologia unităţilor de platformă şi a Orogenului Nord Dobrogean, Ed. Tehnică, Bucureşti, 1994.

[3]. *C. Reimann, P. De Caritat*, Chemical Elements in the Environment, Springer – Verlag, Berlin -Heidelberg – New York, 1998.