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THE DISTRIBUTION OF HEAVY METALS AND As IN SOILS OF THE FĂLTICENI MUNICIPALITY AND ITS SURROUNDINGS

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Abstract: The study of heavy metals **(**Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) and As found in the topsoil (0-25 cm) of the Falticeni municipality and some of its surroundings has generally indicated the presence of contents belonging to the geochemical natural background, with some interferences associated with urban soils and areas covered with orchards or other crops, onto which fertilizers and pesticides are applied intensively. The highest values for Co do not exceed the maximum accepted threshold (MAT) in Romania. For Cd and Cr, there are, in small areas, contents over the MAT in Romanian soils. Some of the concentrations obtained for As, Cu, Ni and Zn exceed the alert threshold, but they are still far below the intervention threshold for sensitive terrains. Pb is the only heavy metal whose maximum content is higher than the intervention threshold for a sensitive terrain; however, only one sample out of the 63 analyzed is over this threshold. It is certainly the case of a punctual contamination with Pb. Along with analyses of the elements, we have determined the pH of the soil samples.

Keywords: urban soils, heavy metals, arsenic, GIS.

1. INTRODUCTION

The study of the geochemical distribution of heavy metals in Romania mainly focused on mining areas and the steel industry (Răuță et al., 1988, Damian et al., 2010), and in to a much lesser degree on urban areas and their surroundings (Bulgariu & Bulgariu, 2007; Iancu & Buzgar, 2008; Lăcătuşu et al., 2008). Extremely high content values, much above the maximum limit allowed, were highlighted for Pb and Zn. The amounts of Pb accumulated in the soils around the main non-ferrous ore processing units in Romania range from 1083 $mg \cdot kg^{-1}$ (Baia Mare), 2248 $mg \cdot kg^{-1}$ (Zlatna) to 3550 $mg \cdot kg^{-1}$ (Copşa Mică); the Zn contents reach the following values: 1378 $mg \cdot kg^{-1}$ (Baia Mare), 400 $mg \cdot kg^{-1}$ (Zlatna) and 2010 $mg \cdot kg^{-1}$ (Copşa Mică) (Răuță et al., 1992).

The current project presents the distribution of the natural geochemical background for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the upper horizon of soils found in the Fălticeni municipality and its surroundings, as well as the anomalies caused by the anthropogenic activities which have led to the spreading of these elements in the soils.

After 1989, the industrial activities registered in Fălticeni have gone through a steady decline as a result of the transition to capitalism. Nevertheless, a series of industrial activities with polluting potential are still practiced in the area: chemical industry (chemical products, pharmaceuticals, paints/dyes, detergents and cleaning products, plastic products); beverage industry (distilled alcoholic and non-alcoholic drinks); wood industry (gross processing of the wood and wood impregnation, furniture production); typographies; construction (building) material industry (glass, BCA, brick); machine-building industry (agricultural and forest machinery, metal constructions); food industry (bakery and pastry products, meat-based products, dairy products, processing and canning of fruits and vegetables, processing and canning of fish and fish products).

The soils are reprezented by the luvisol (preluvosol) and cernisol classes (gleyic and cambic phaeozems). The protisols (urbic entiantrosol) are predominant in the central part of the studied area.

Knowing the distribution of heavy metals in soils constitutes a first phase in the location of potential anomalies caused by the regional anthropogenic factor, thereby the planning of new studies on the necessary interventions and land use in the future.

2. MATERIALS AND METHODS

2.1. Study area

The study area extends over approximately 20 km^2, including the Fălticeni municipality and some areas from its surroundings which are covered with orchards, arable land or grassland (Fig. 1 & 2).

The Fălticeni municipality is placed in a hilly area on the western boundary of the Suceava Plateau, having developed on three terraces, between the Şomuzul Mare brook and the Buciumeni brook.

According to the 2002 census, the population of the Fălticeni municipality is of 29.787, with a density of 1.004 inh./km².

Figure 1. Map of the Suceava county.

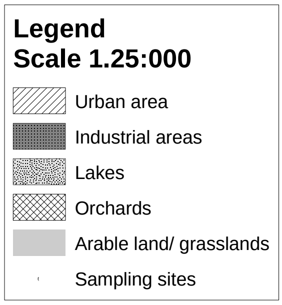

Figure 2. Map of sampling sites and land use in study area.

2.2. Soil sampling and spectrographic analysis

The present study was focused on the analysis of 63 soil samples from the town of Fălticeni and its surrounding areas.

The sampling operation took place in July 2009. The soil samples were collected using a rectangular 500x500m sampling network (Fig. 2), from depths ranging from 0 to 25cm. The approximate weight for each sample was 2 kg.

The samples were dried in a room with a constant temperature and air circulation. Afterwards, the traces of vegetation were removed, then the samples were sieved and fractions smaller than 1 mm were separated. Each sample was homogenized through continuous mixing for 1 hour.

Through halving, a quantity of approximately 30 g was separated out of each sample, which was then mixed using a C_2H_2 binder, at a 4:1 ratio. The mixing was done mechanically, using a Fritsch Planetary Mill Pulverisette 5, for 15 minutes, at a constant speed of 180 rpm. For each sample, 2 powder pressed (at $20t/cm^2$) samples were obtained for XRF analysis, each weighing 9 g. The chemical analysis of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) and As was done through XRF, using an EDXRF Epsylon 5 Spectrometer. The standardization was performed by using 24 soil standards (SO_{1-4}, RT, RTH, GSD and LKSD). The exposure time was 50 s, with the exception of As and Cd, in which case the exposure time was 100 s.

2.3. Statistical analysis

The set of results of the double analysis obtained for 63 soil samples was used to determine statistical parameters with the use of specialized software, namely STATISTICA 8, Surfer 9 and Microsoft Excel (Microsoft Office 2002). Additional software was used in order to identify potential variations of parameters obtained using different software.

The following statistical values were obtained: the arithmetic and geometric mean, the median, the mode, the minimum and maximum values, the lower and upper quartile, the inter-quartile range, the inter-limits range, the variance, the standard deviation, the coefficient of variation, the standard error, the skewness and the kurtosis (Tab. 1).

2.4. SIG methods and graphic representation

For the present study, the SIG platform was used in order to integrate compositional and geographic information so as to identify, through prediction and data interpolation, the noticeable concentration anomalies in the final geochemical distribution maps.

Afterwards, a graphical representation was obtained, consisting of sampling points being laid on a plane surface, corresponding to the geographical coordinates of the sampling points. The Cartesian coordinate system uses default projection – UTM, area 32N, geodesic datum WGS 84.

The widely spread ESRI ArcGIS Desktop platform was used so as to easily import, process and export data.

The distribution histograms were devised by using STATISTICA 8 and other programs. According to Siegel (2002), a Gaussian distribution of a histogram with values within the standard deviation ($x\pm1\sigma$) represents the normal fluctuations of the geochemical background. Values between $x\pm1\sigma$ and $x\pm2\sigma$ represent the immixture of anomalous values with the background, whilst the values higher than $x\pm2\sigma$ represent true geochemical anomalies.

2.5. Data interpolation

A sampling network of 500 m, capable of determining the eventual anomalies of the geochemical background, which may be determined by the industrial activities and the use of fertilizers and pesticides in the nearby orchards and agricultural fields, was established for Falticeni.

For the data interpolation, two of the most widespread methods were used, namely kriging and IDW (Inverse Distance Weight). The kriging method is characterized by the best linear unbiased estimator (BLUE) (Franco et al., 2006). This method of interpolation was used for Co, Cr and Cu. The IDW method uses a certain number of points that are adjacent to the point which is to be interpolated, and is based on the assumption that nearer points possess more characteristics similar to those of the interpolated point. According to this rule, the nearer points have a more pronounced local influence on the interpolated point, an influence that decreases with the increase of the distance to the predicted area. The IDW method was used in data interpolation for the following: Zn, Cd, Pb, Fe, Mn, Ni, As and pH.

3. RESULTS AND DISCUSSIONS

3.1. Total concentration of heavy metals and As

In the investigated soils, concentrations of heavy metals generally present a uniformity that is consistent with the geochemical background of the target area. Only a few of the determined contents show deviations from the background concentrations. Thus, there are overdraws of As, Cu, Ni and Zn, as compared to the alert thresholds for soils with sensitive usage (15 $mg\cdot kg^{-1}$; 100 $mg\cdot kg^{-1}$; 75 $mg\cdot kg^{-1}$; 300 $mg\cdot kg^{-1}$; GEO 756/1997). Nevertheless, the percentage of analyses for Cu, Ni and Zn in which the above mentioned thresholds was exceeded is the same for all metals, namely 1.59%, that is one sample out of 63. In the case of As, the percentage over the alert threshold for sensitive use soils is 9.52%. As far as Pb is concerned, 6.35% of the samples exceed the alert threshold, and 1.59% exceeds the intervention threshold for sensitive use soils. Cd, Cr and Mn register contents over the maximum allowable concentration in soils, but these do not exceed the alert threshold, while the Co concentration does not exceed the MAC in Romanian soils.

Globally, the Cd concentration in soils ranges between 0.06 and 1.1 mg·kg^{-1}, with an average of 0.52 mg·kg^{-1}. The highest concentrations of Cd are recorded near the integrated iron and steel factories, e.g. 1,781 mg·kg^{-1} in Belgium, 270 mg·kg^{-1} in Poland and 1,500 mg·kg^{-1} in the US (Kabata-Pendias & Pendias, 2001). For 840 of the surface soil samples collected during the conduct of the "Geochemical Atlas of Europe," the average content of Cd was of 0.145 mg·kg^{-1} (Salminen et al., 2005). In soils from the city of Iasi and its surrounding areas, the content of Cd ranges from 0.1 to 15.4 mg·kg^{-1} (Iancu & Buzgar, 2008).

In the investigated area, the content of Cd oscillates from 0.20 to 1.34 mg·kg^{-1}, which is a narrow range. Out of the total number of analyzed samples, 98.41% do not exceed the 1 mg·kg^{-1} concentration (MAC in Romanian soils). This interval may be considered the areal geochemical background. One single sample of those analyzed has a concentration higher than 1 mg·kg^{-1} (sample sample no. 29, 1.34 mg·kg^{-1}) and it was collected from the city's industrial area. Cd has a weak correlation with Zn, As, Ni, Pb, Cr and Cu (0.48, 0.45, 0.40, 0.35, 0.32, 0.30) in the studied area.

The world's average content of Co in soil varies between 4.5 and 12.0 mg·kg^{-1}, being higher in loamy soils and lower in sandy and mostly organic soils. For a number of 843 topsoil samples collected during the conduct of the "Geochemical Atlas of Europe," the average content of Co was of 7.78 mg·kg^{-1} (Salminen et al., 2005). The concentrations of Co recorded in soils throughout the city of Iaşi during the conduct of the "Geochemical Atlas of Heavy Metals in the City of Iasi and the Surrounding Area" oscillates between 4.83 and 27.90 mg·kg^{-1} (Iancu & Buzgar, 2008).

For the soils in the town of Fălticeni, contents of Co that vary within a very narrow interval (7.10 – 14.13 mg·kg^{-1}), with an average of 10.50 mg·kg^{-1}, were recorded. With an overwhelming percentage of 80.95%, the contents of Co are between 9 mg·kg^{-1} and 12 mg·kg^{-1}. The recorded values may be considered as representative for the geochemical background of the investigated area, and they are entirely below the MAC for the total content of Co in a soil of Romania. Co has a strong correlation with Fe and Ni (0.93, 0.69), and a weak correlation with Mn and As (0.41, 0.33).

The content of Cr in soil is mainly determined by the parent rock it formed upon. The average content of Cr in soil is set at a value of 54 mg·kg^{-1} (Kabata-Pendias & Pendias, 2001). For 845 samples collected during the conduct of the "Geochemical Atlas of Europe," the average content of Cr was of 60 mg·kg^{-1} (Salminen et al., 2005). The content of Co determined for soils in Iasi varies from the detection limit to 591.6 mg·kg^{-1} (Iancu & Buzgar, 2008).

In the case of the Fălticeni samples analyzed, the content of Cr was between 35.85 and 74.40 mg·kg^{-1}, with an average value of 59.1 mg·kg^{-1}; this narrow gap suggests a natural distribution of Cr in the investigated area. Moreover, 82.94% of the analyzed samples had values between 50 and 70 mg·kg^{-1}. It can be noticed that there are no concentrations that exceed the alert threshold, but all values are higher that the MAC in soil. Cr has a weak correlation with Cd and As (0,32; 0,31).

The average value of the Cu content in soil in the world is set between 20 and 30 mg·kg^{-1} (Alloway, 1995). Nevertheless, there are often values recorded out of this interval, mainly due to the multitude of soil types. For 840 samples collected from surface soils during the conduct of the "Geochemical Atlas of Europe," the average content of Cu was of 13 mg·kg^{-1} (Salminen et al., 2005), and the concentrations of Cu recorded in the soils of Iasi vary between 11.6 and 702.6 mg·kg^{-1} (Iancu & Buzgar, 2008).

For the soils in Fălticeni, the analyses revealed contents of Cu between 17.85 and 112.75 mg·kg^{-1}. The average value is 36.00 mg·kg^{-1}, and 88.89% of the values are between 20 and 50 mg·kg^{-1}; this narrow gap may be considered as the natural geochemical background. A weak correlation can be noticed between the contents of Cu and Pb, As and Zn (0.37, 0.32, 0.30).

In soil, Fe is generally of natural origin; its anthropogenic sources may be the iron and steel industry, to which its use in preparing some of the herbicides and fertilizers may be added. The geochemical behavior of Fe has a high degree of complexity, determined by the ease with which it changes oxidizing states as a response to the variability of physical and chemical environmental conditions. It has a chemical behavior similar to that of Ni and Co. For 845 samples collected from surface soils during the conduct of the "Geochemical Atlas of Europe," the average content of Fe was of 3.51% (Salminen et al., 2005). In the soil investigated in Iasi, the distribution of Fe contents is set between relatively wide limits: 4,215 – 54,111 mg·kg^{-1} Fe (Iancu & Buzgar, 2008).

Fe is a chemical element that has a high areal variability, and in many cases the anomalies cannot be explained by certain sources of contaminations, as these are low scale anthropic contaminations. The concentrations recorded in the present study vary between 7,272.50 mg·kg^{-1} and 28,572.00 mg·kg^{-1}, with an average value of 17,599 mg·kg^{-1}. Fe is characterized by a very strong correlation with Co and Ni (0.93, 0.80), and a weak correlation with As and Mn (0.35, 0.34).

The content of Mn in the upper layer of different types of soils found in a quasi-natural state throughout the world is usually between 15 and 3,900 mg·kg^{-1}, with an average value of 510 mg·kg^{-1} (Lăcătuşu, 2008, fide Kabata Pendias & Pendias, 2000). For 837 samples collected from surface soils during the conduct of the "Geochemical Atlas of Europe," the average content of Mn was of 382 mg·kg^{-1} (Salminen et al., 2005). The content values for Mn recorded in soils throughout the area of Iasi are between 50 and 1,995.40 mg·kg^{-1} (Iancu & Buzgar, 2008).

In the investigated soils, the concentrations of Mn are between 453.50 mg·kg^{-1} and 1,174.50 mg·kg^{-1}, with an average value of 647 mg·kg^{-1}. As in the case of the above mentioned elements, the content of Mn is included in that determined for soils in the city of Iasi. This indicates a higher variability of the range of concentrations determined for heavy metals in the city of Iasi, both due to the wider research area and the higher industrialization in Iasi. Mn has a weak correlation with only two elements in the present study, namely Co and Fe (0.41, 0.34).

The content of Ni in soil varies from 0.2 to 450 mg·kg^{-1}; in Poland average contents of 8 mg·kg^{-1} in sandy soils, and of 18 mg·kg^{-1} in loamy soils were recorded (Kabata-Pendias & Pendias 1999). For 843 samples collected from surface soils during the conduct of the "Geochemical Atlas of Europe," the average content of Ni was of 18 mg·kg^{-1} (Salminen et al., 2005). High natural contents of Ni are noticed in soils formed on basic and volcanic rocks, especially in soils derived from serpentinite rocks, were Ni ranges from 700 to 7,375 mg·kg^{-1} (Kabata-Pendias & Pendias, 2001). The content of Ni in the soil of the city of Iasi and the neighboring areas ranges from 13.5 to 349.6 mg·kg^{-1} (Iancu & Buzgar, 2008).

For the investigated soils, the contents of Ni range from 16.5 mg·kg^{-1} to 76.5 mg·kg^{-1}, with an average of 36.0 mg·kg^{-1}. In 85.71 % of the samples, values range from 25 mg·kg^{-1} to 45 mg·kg^{-1}, which implies the geochemical background within the studied area. Regarding the correlation with the other analyzed elements, Ni has a strong correlation with Fe and Co (0.80, 0.69), and a weak correlation with As, Cd and Pb (0.45, 0.40, 0.35).

The average content of Pb in soil was calculated at 25 mg·kg^{-1} (Kabata-Pendias & Pendias, 2001). The contents measured in various soils throughout England and Wales range widely from 3.0 to 16,338 mg·kg^{-1} (McGrath & Loveland, 1992b). For 843 samples collected from surface soils during the conduct of the "Geochemical Atlas of Europe," the average content of Pb was of 22.6 mg·kg^{-1} (Salminen et al., 2005). The abundance of Pb in the A layer of Romanian soils, determined by a geometrical mean of 1,112 analyzed samples, is of 31 mg·kg^{-1} (Lăcătuşu et al., 1997). The contents of Pb determined in the soils of Iasi and the neighboring areas range from 4.5 mg·kg^{-1} to 1,995.4 mg·kg^{-1} (Iancu & Buzgar, 2008).

In the soils of Făalticeni, the content of Pb ranges from 14.75 to 102.40 mg·kg^{-1}, with an average value of 24.9 mg·kg^{-1}. 88.89 % of the samples reveal contents up to 30.00 mg·kg^{-1}, which proves that the high average value is not very representative for the Pb analyses. Contents that were recorded outside this range (14.75 to 30 mg·kg^{-1}) suggest a possible anthropogenic anomaly. There is a strong correlation of Pb with Zn and As (0.75, 0.70) and a weaker correlation with Cu, Ni and Cd (0.37, 0.35, 0.35).

The contents of Zn in the upper layer of different kinds of soils in the world range from 5 to 570 mg·kg^{-1}, with an average value of 66 mg·kg^{-1} (Lăcătuşu, 2008, fide Kabata Pendias & Pendias, 2000). For 845 samples collected from surface soil during the conduct of the "Geochemical Atlas of Europe," the average content of Zn was of 52 mg·kg^{-1} (Salminen et al., 2005). The contents of Zn in the soils of Iasi and the neighboring areas range widely from 10.1 to 5,624 mg·kg^{-1} (Iancu & Buzgar, 2008).

In the samples analyzed for the present study, there were revealed contents of Zn that range from 33.6 mg·kg^{-1} to 332.80 mg·kg^{-1}, with an average value of 95.8 mg·kg^{-1}. 84.13% of the analyzed samples range from 50 to 150 mg·kg^{-1}, which suggests a narrow variability of the results. Zn has a very good correlation with Pb (0.75) and As (0.52), and a weak correlation with Cd and Cu (0.48, 0.30).

A recent estimation of As in soils is of 5 mg·kg^{-1} (Köljonen, 1992). By conducting the "Geochemical Atlas of Europe," an average content of As of 7.03 mg·kg^{-1} was reported (Salminen et al., 2005). The analyses performed on surface soil samples from Sweden revealed As contents ranging between 0.4 and 10.5 mg·kg^{-1}, and an average value of 3.9 mg·kg^{-1} (Eriksson, 2001). In the US, average contents of 5.8 mg·kg^{-1} have been reported (Shacklette & Boerngen, 1984) . Following a study conducted on 2,600 soil samples collected at the border of Wales, an average content of 11 mg·kg^{-1} was revealed (McGrath & Loveland, 1992a).

The concentrations of As revealed in the present study range from 10.30 to 19.55 mg·kg^{-1}, with an average value of 13.5 mg·kg^{-1}. As has a strong correlation with Pb (0.70), a good one with Zn (0.52), and a weak correlation with Ni, Cd, Fe, Co, Cu, Cr (0.45, 0.45, 0.35, 0.33, 0.32, 0.31).

3.2. pH

For 818 samples collected from the upper layer of soil during the conduct of the "Geochemical Atlas of Europe," the average pH value was 5.51 (Salminen et al., 2005). In Romania, a thorough study of an urban area and its surroundings was conducted in Iasi, where average pH values of 7.41 for 1,027 analyzed samples were recorded (Iancu & Buzgar, 2008).

In the researched area, the pH values range from 3.90 to 8.10 (Fig. 3 & 4). This gap reveals that the lowest value leads to a highly acid environment, while the highest value leads to an alkaline one. 84% of the analyzed samples are lightly acid (5.9 pH) to lightly basic (7.8 pH). For 53% of the samples, the predominant reaction is neutral to strongly acid. The average value (6.61pH) is a good indicator for the analysis of data, it is set at mid-distance within the inter-quartile range and has values very close to the other parameters of the main tendency (geometrical mean, median).

Sample no. 28, with a pH value of 3.9 (the lowest value in the researched area), was collected from within a company which processes timber, especially resinous timber (Fig. 4). The low pH value is most probably the result of soil contamination with timber debris (it is a known fact that sawdust acidifies the soil).

3.3 Results of statistical analysis

Relevant results have been acquired for the distribution of statistical parameters; thus, for Cu, Pb, Zn, Cd, Cr, Co, Ni, Fe, Mn and As, the average contents (36.0; 24.9; 95.8; 0.52; 59.1; 10.5; 36.0; 17,599; 647 and 13.5 mg·kg^{-1}) can be found in the range of the 25% and 75% quartiles (Tab. 1). Most of the average values for these studied elements are similar to the other values that represent the central tendency, namely the median, the geometric mean and the module. In this case, the module has a low relevance because of the low number of samples taken into account, a fact which can be seen in the frequency values of the module. As regards Pb, the geometric mean and the median are more representative for a value of the central parameter than the arithmetic mean, the latter being outside the inter-quartile range. The low values of the variance and the standard deviation do not suggest high data variability. The skewness has low values, which suggests a close to normal distribution for most of the data, except for Cu, Pb, Zn, and in a lower degree for Ni, elements that show a slightly positive skew. The kurtosis coefficient shows a slight correlation with the skewness and has low amplitude for Cu, Pb, Ni and Mn.

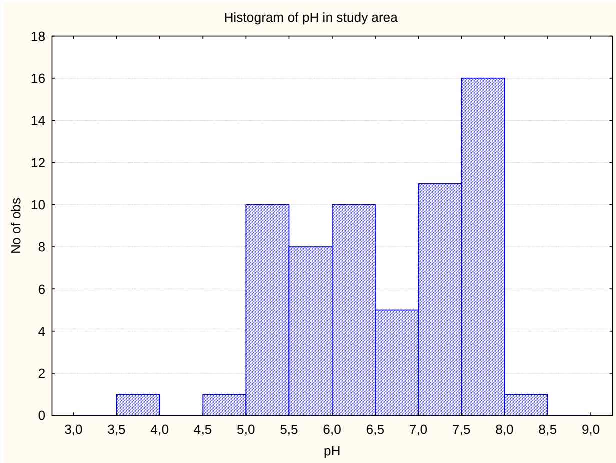

Figure 3. Histogram of the pH.

3.4. Spatial distribution of heavy metals and As

The spatial distributions for the analyzed elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were obtained using the GIS platform.

The geochemical maps (Fig. 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14) were devised so as to easily point out the areas with higher concentrations that might suggest an anthropogenic pollution source.

Copper generally has a uniform distribution. Only 2 small anomalous areas appear in the south-western and south-eastern parts (Fig. 5). In the south-western side, the high content of copper can be explained by the use of Cu (more exactly $CuSO_4$) in the process of sprinkling the fruit-trees grown in the orchard from that area. The only concentration that exceeds the alert threshold for sensitive terrains (113mg·kg^{-1}) was identified in the proximity of a $CuSO_4$ processing and loading station.

The geochemical map of Pb (Fig. 6) shows an area characterized by a slightly higher content. Thus, more in the urban area and less on the outskirts of the city, high contents of Pb can be observed. The causes are most likely the emissions from fossil fuel burning, as the town is crossed by the E85 highway, which has a dense traffic.

Table 1. Statistical parameters of metal content and pH in the soils of Fălticeni and the surrounding areas (metal and As contents are in $mg \cdot kg^{-1}$).

Parameter	Cu	Pb	Zn	Cd	Cr	Co	Ni	Fe	Mn	As	pH
Count	*63*	*63*	*63*	*63*	*63*	*63*	*63*	*63*	*63*	*63*	*63*
Arithmetic Mean	36.0	24.9	95.8	0.52	59.1	10.5	36.0	17,599	647	13.5	6.6
Geometric Mean	34.1	22.1	84.2	0.49	58.5	10.4	35.2	17,174	639	13.5	6.5
Median	32.9	18.8	73.6	0.50	60.6	10.4	35.2	17,008	641	13.5	6.7
Mode	30.1	18.5	-	0.63	53.7	10.8	37.5	-	594	13.5	7.7
Mode frequency	2.00	2.00	1.00	4.00	3.00	4.00	2.00	1.00	2.00	3.00	2.00
Minimum	17.8	14.7	33.6	0.20	35.8	7.1	16.5	7,272	453	10.3	3.9
Maximum	113	102	333	1.3	74.4	14.3	76.4	28,572	1,174	19.5	8.1
Low Quartile	28.9	17.0	60.8	0.39	53.7	9.6	32.2	15,749	593	12.2	5.8
Upper Quartile	38.2	24.4	113	0.63	64.5	11.2	38.0	19,457	698	14.3	7.5
Range	94.9	87.6	299	1.1	38.5	7.2	59.9	21,299	721	9.2	4.2
Quartile Range	9.3	7.4	52.0	0.24	10.7	1.5	5.8	3,708	105	2.1	1.8
Variance	209	277	3505	0.04	58.3	1.71	71.8	14,659,142	11,719	3.1	1.1
Standard Deviation	14.4	16.6	59.2	0.20	7.6	1.3	8.5	3,829	108	1.8	1.0
Variation Coefficient	0.40	0.67	0.62	0.38	0.13	0.12	0.23	0.21	0.17	0.13	0.16
Standard Error	1.82	2.10	7.46	0.03	0.96	0.16	1.07	482	13.64	0.22	0.13
Skew	3.18	3.15	2.25	1.26	-0.45	0.34	1.93	0.36	1.71	0.94	-0.40
Kurtosis	13.17	10.43	5.28	3.36	0.44	0.95	8.13	1.19	7.94	1.81	-0.86

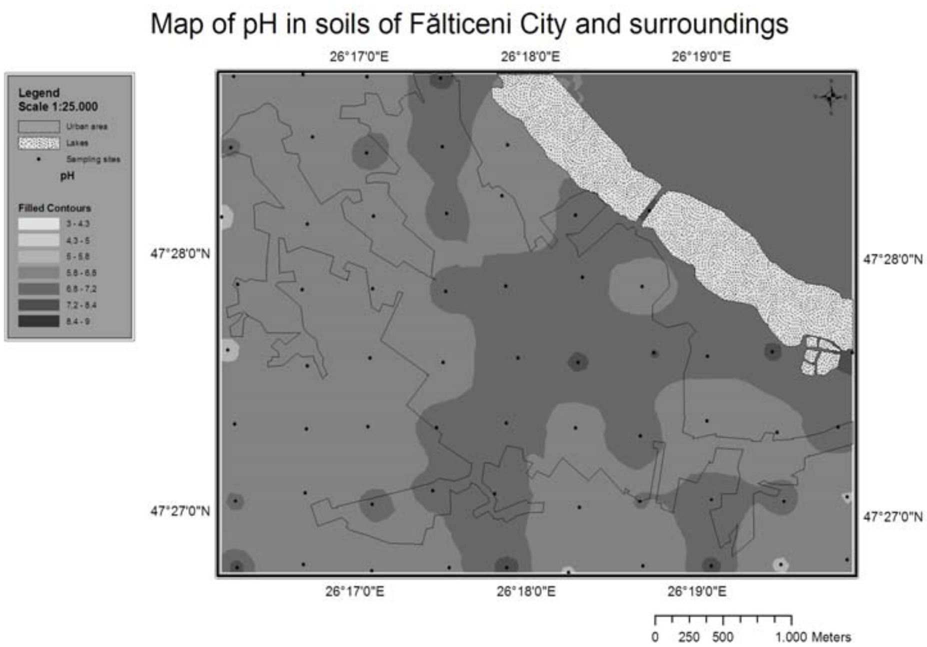

Figure 4. The map of pH in soils of Fălticeni City and surroundings.

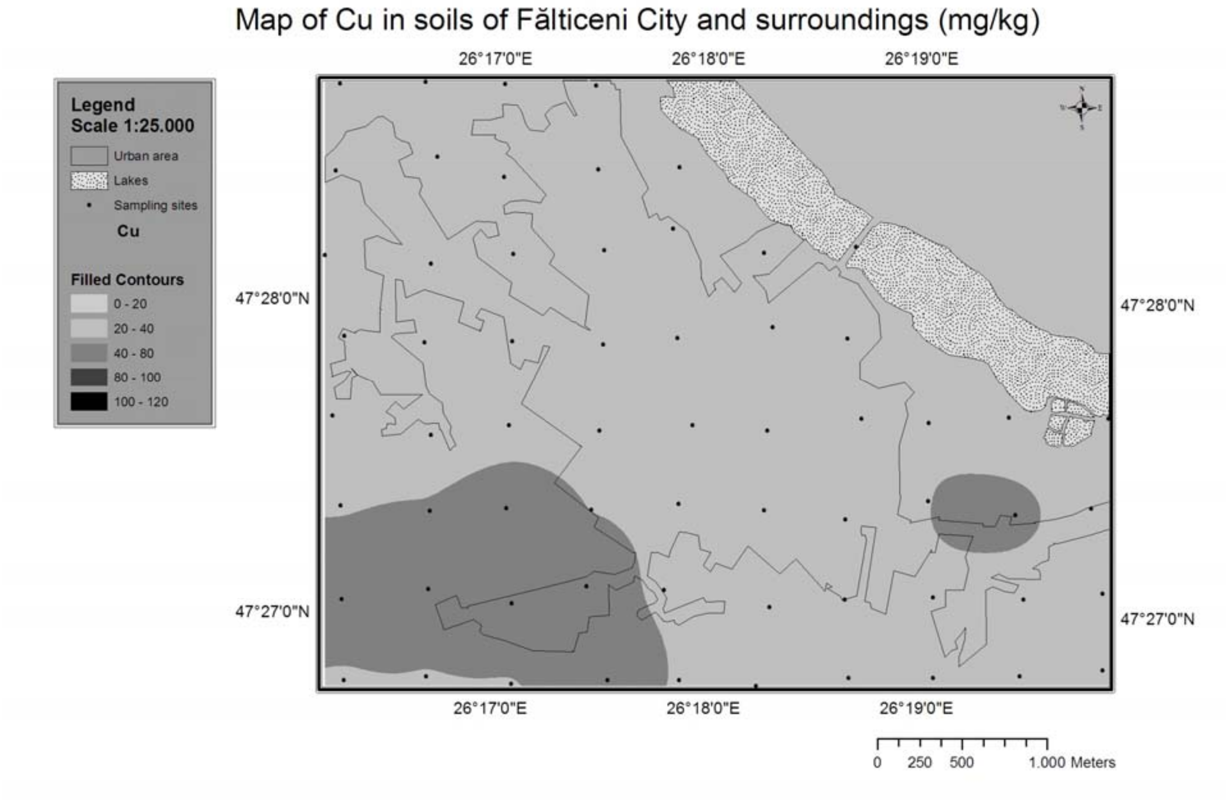

Figure 5. The distribution of Cu in soils of Fălticeni City and surroundings.

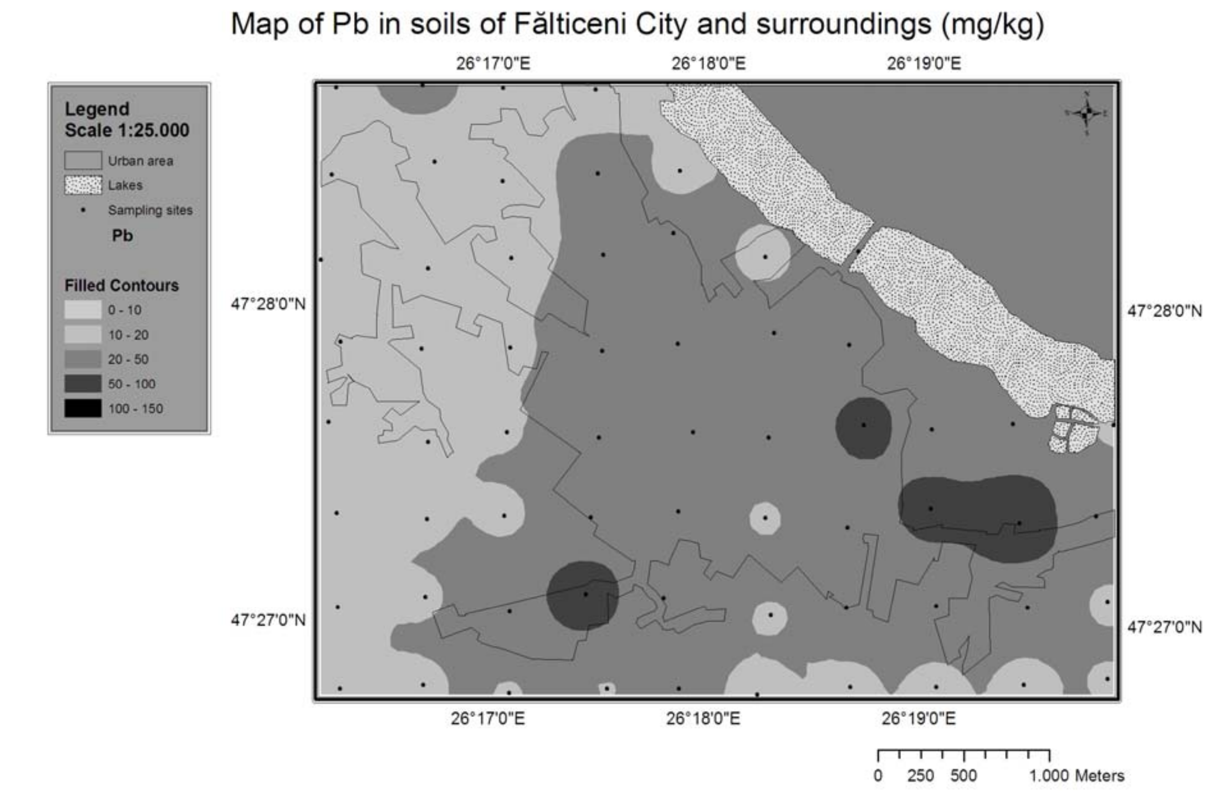

Figure 6. The distribution of Pb in soils of Fălticeni City and surroundings.

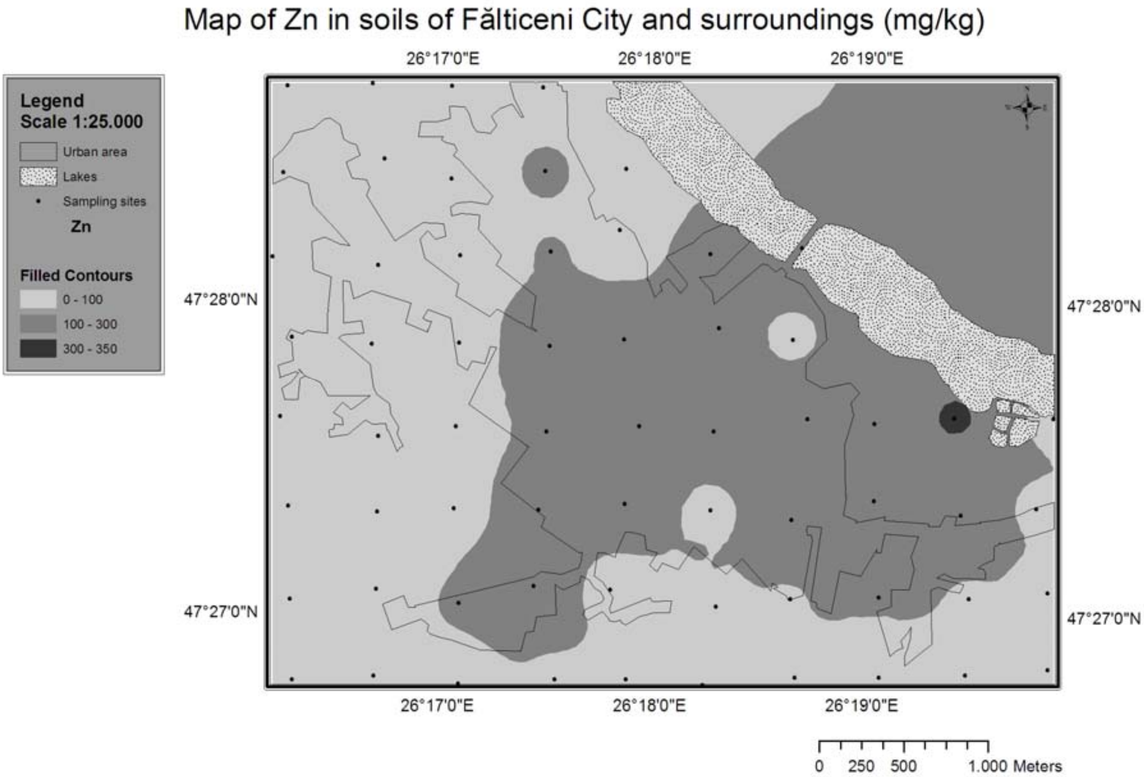

Figure 7. The distribution of Zn in soils of Fălticeni City and surroundings.

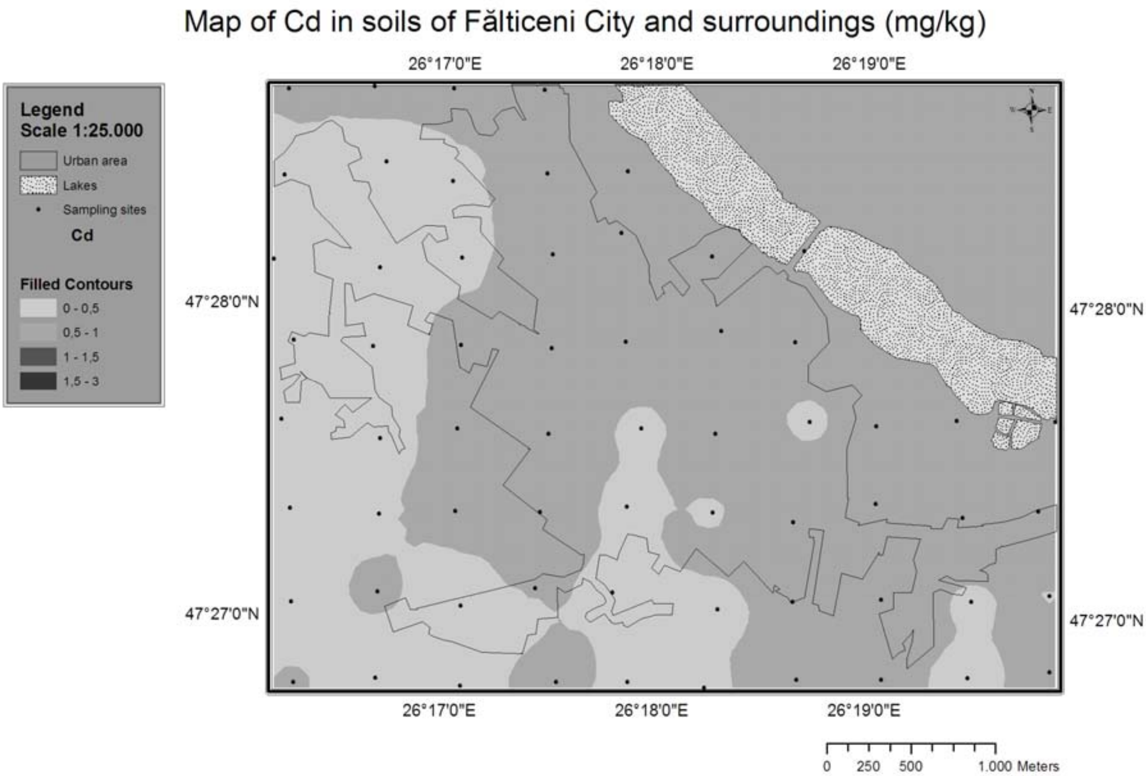

Figure 8. The distribution of Cd in soils of Fălticeni City and surroundings.

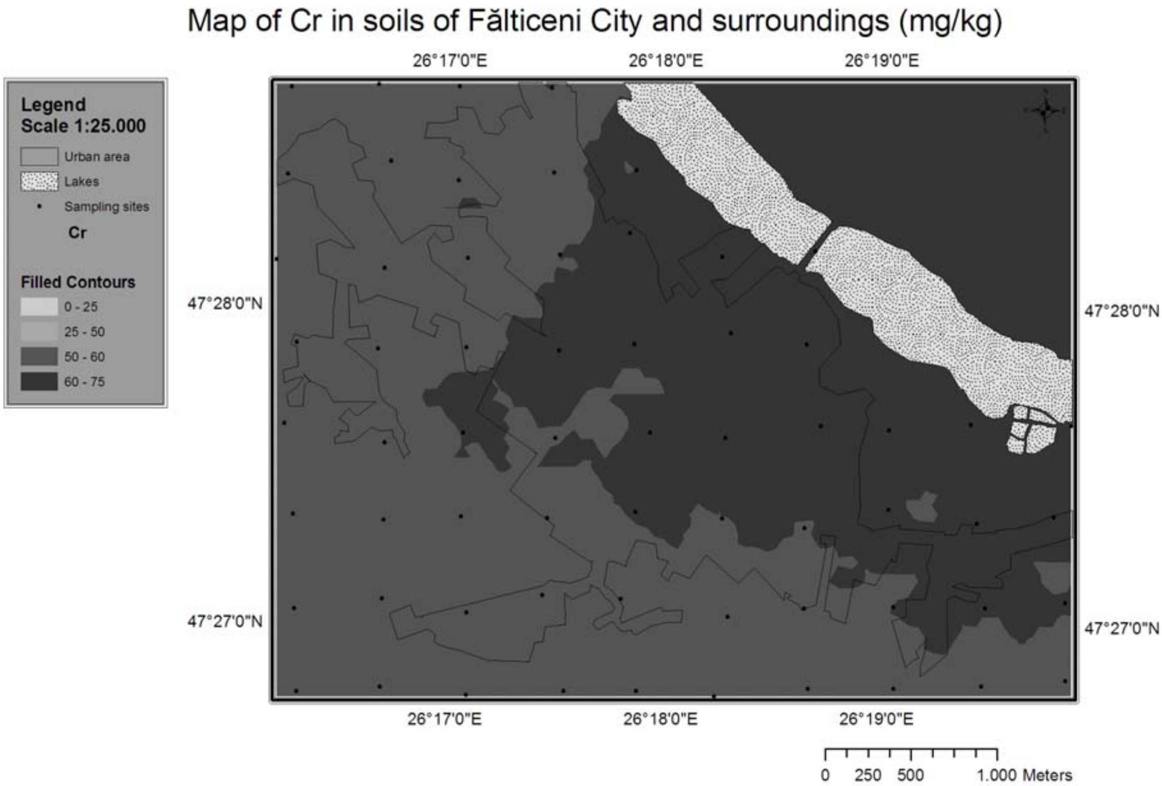

Figure 9. The distribution of Cr in soils of Fălticeni City and surroundings.

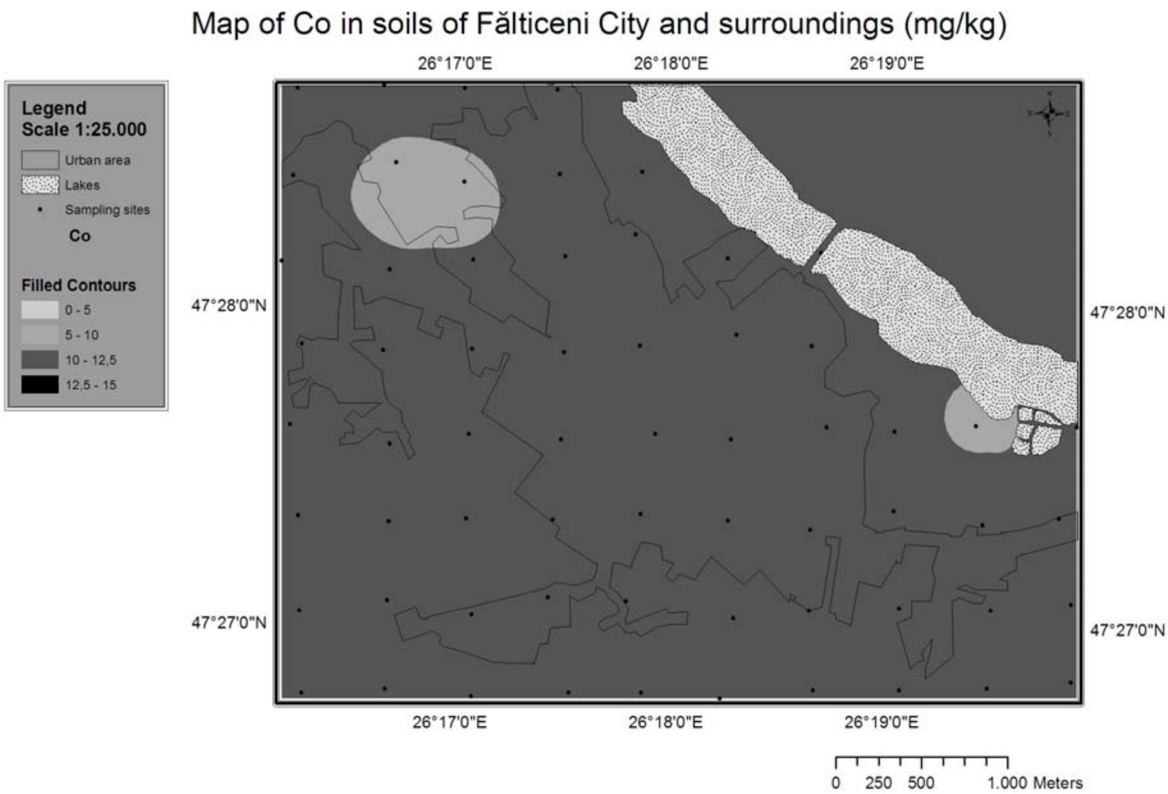

Figure 10. The distribution of Co in soils of Fălticeni City and surroundings.

The spatial distribution of Zn (Fig. 7), with higher contents in the industrial and urban areas, suggests an anthropogenic influence, most probably due to the fossil fuel burning, these areas corresponding to the ones on the geochemical map of Pb.

On the geochemical map of Cd, in the central-eastern zone, there is a well defined area, characterized by relatively high contents of Cd (Fig. 8) and Cr (Fig. 9). The extent of this zone is dominant in the urban area as compared to the surrounding area, which might suggest an anthropogenic pollution source (most probably the denser traffic in the urban area).

The spatial distribution of Co (Fig. 10) is characterized by a high homogeneity, which might be considered as a result of the lack of contamination from human activities in the studied area. The distribution of Ni obtained on the geochemical map (Fig. 11) suggests a natural diffusion, without significant anthropogenic influences. Small contents of Ni can be seen in the southern area, where the Fe contents are also high. Another higher punctual concentration can be seen in the industrial area of the town and it might be of a local origin, from the metallic wastes that were left in the old abandoned factories.

The graphical representation of Fe contents is characterized by local variations that cannot be fully explained by certain pollution sources, the causes of these anomalies being explained by the topography and the presence of coal in the formations on which the soils of Fălticeni have developed (Fig. 12). To support this hypothesis, there is a strong positive correlation of Fe, Ni and Co. Only the higher punctual concentrations are attributed to an anthropogenic factor.

The distribution of Mn on the geochemical map (Fig. 13) shows an almost uniform content, with slight variations and with a concentration of Mn in a small area situated in the southern part. This can be explained by the presence of coal intercalations in the bedrock layers existing in the Fălticeni area. Furthermore, in the same southern area, on the geochemical map of Fe, there is a stripe where the contents of Fe are also higher, suggesting a correlation with the presence of coal deposits.

On the geochemical map of As (Fig. 14) there are two concentration areas, correlated with the high content of Pb. High contents of Pb and As in soils are present because of the use of $PbHAsO_4$ (lead arsenate) as pesticide in the apple-tree orchards (Peryea & Creger, 1994).

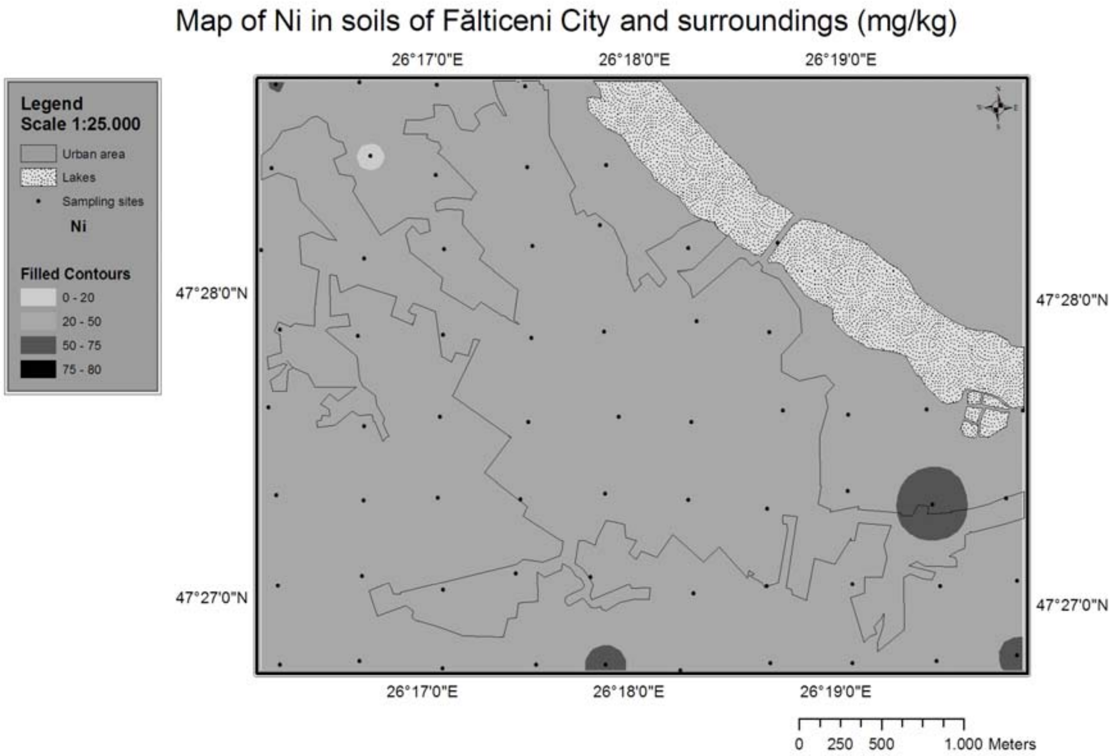

Figure 11. The distribution of Ni in soils of Fălticeni City and surroundings.

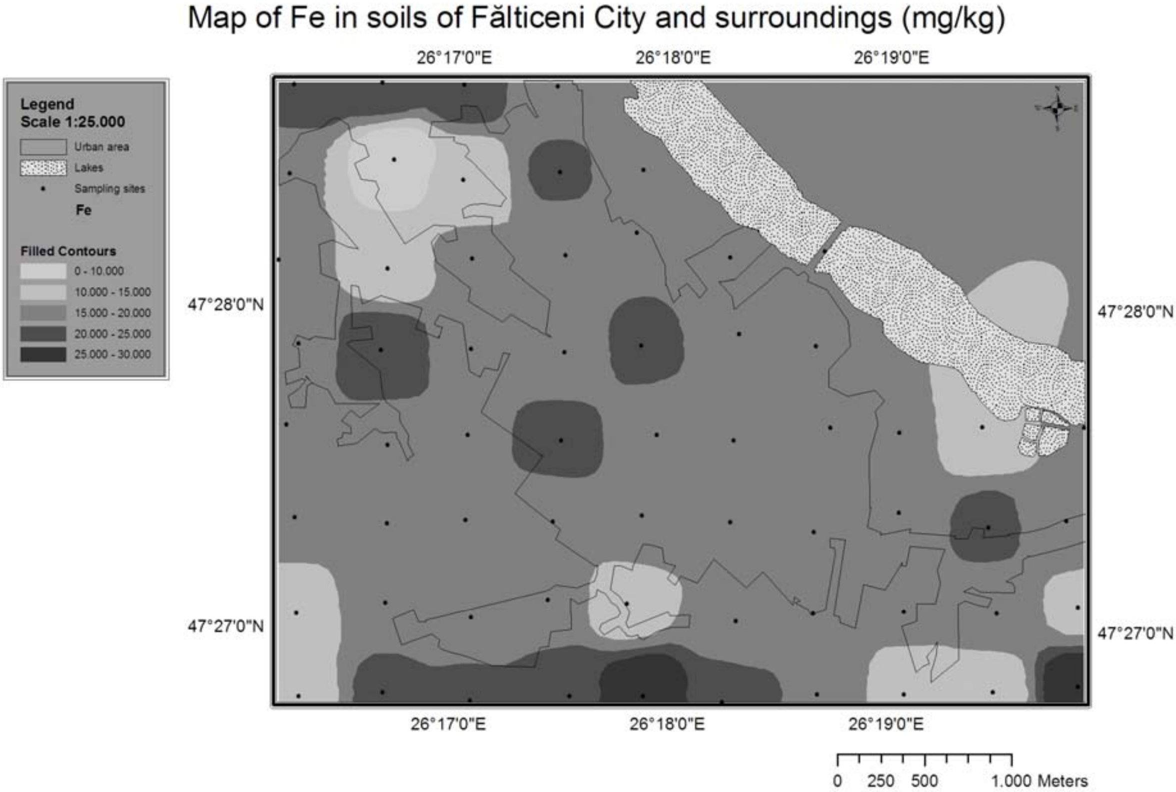

Figure 12. The distribution of Fe in soils of Fălticeni City and surroundings.

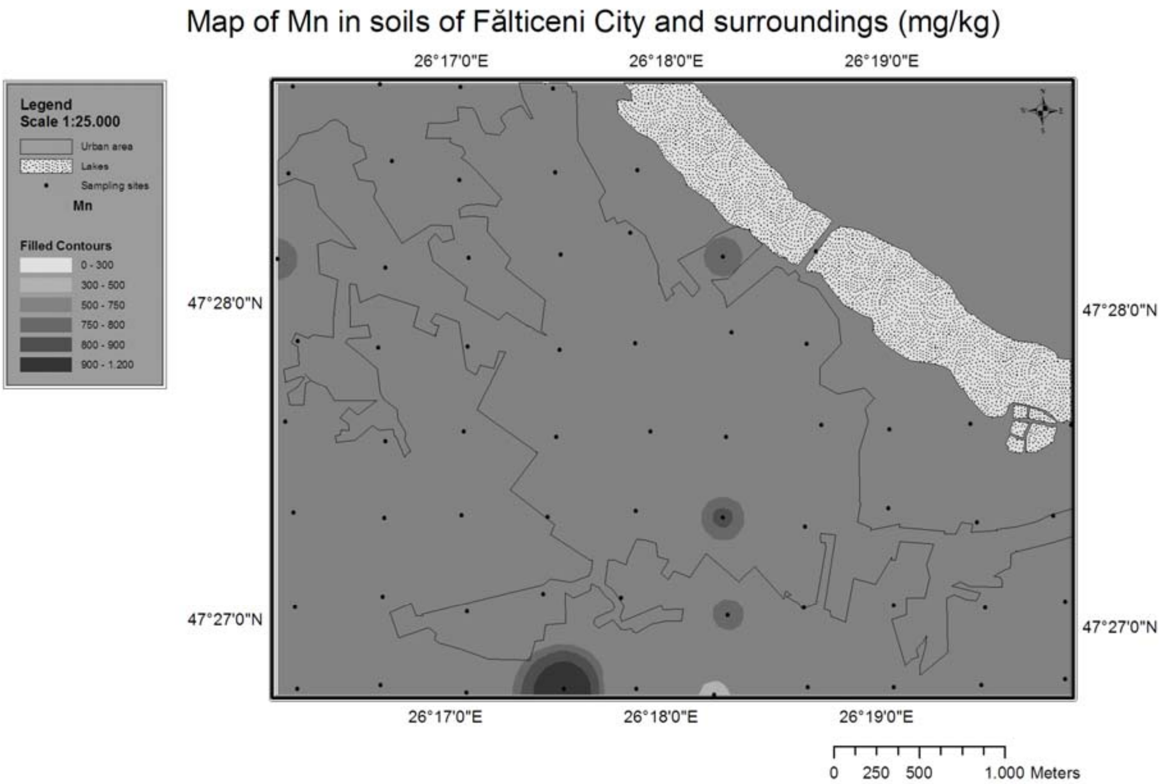

Figure 13. The distribution of Mn in soils of Fălticeni City and surroundings.

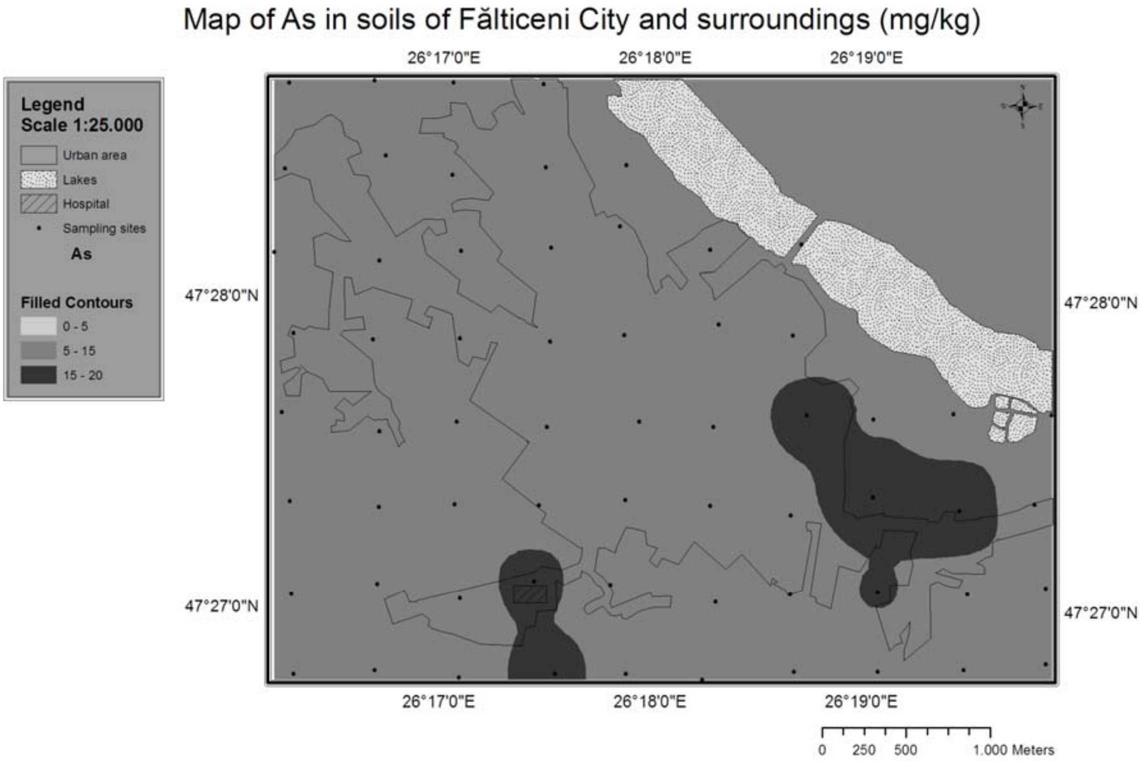

Figure 14. The distribution of As in soils of Fălticeni City and surroundings.

In the south-west, in the area contaminated with Pb and As, there is an orchard and an apple deposit, which are probably responsible for the contaminations with As and Pb on one hand, and with Cu (by using $CuSO_4$), on the other. In the south-eastern area, the concentration and contamination with As and Pb can be explained by the presence of industrial activities and some cereal, fruit and vegetable deposits that might have been contaminating the soil through their activities and the pesticides used.

CONCLUSIONS

The present study was conducted for the analysis of 10 chemical elements, potentially polluting heavy metals and metalloids in the soils throughout Fălticeni and in the surrounding area. The average values for Cu, Pb, Zn, Cd, Cr, Co, Ni, Fe, Mn and As, expressed in $mg \cdot kg^{-1}$, are the following: 36.0; 24.9; 95.8; 0.52; 59.1; 10.5; 36.0; 17,599; 647 and 13.5.

Although very high contents have not been revealed in the researched area, the strong correlations between Pb and Zn, on the one hand, and between Pb and As, on the other hand, are firstly due to vehicle exhaust gases, and secondly to the use of Pb- and As-based pesticides in orchards and food storehouses.

The presence of stronger correlations as regards Fe, Co and Ni is not the effect of a polluting anthropogenic factor, but of the existence of carboniferous strata within the parent rock (some crop out) on which soils in the Fălticeni area have formed.

Consequently, the contents revealed in the present study are, to a large extent, the result of natural evolution, even with some anthropogenic interference that should be kept under control in order to avoid soil contamination through agricultural, transportation or other human activities.

The database created throughout the present study may be used for future documentation on urban soils; its format is easily accessible even to users that are less experienced in working with particular data.

REFERENCES

Alloway, B. J., 1995. *Heavy Metals in Soils, 2nd edition.* Blackie Academic and Professional, London, UK., 179-180.

Bulgariu D. & Bulgariu L., 2007. *Distribution and mobility of Cadmiun and Lead in urban soils – case study: Municipality of Iasi - Industrial area.* International Symp. "Romanian Agriculture in EU opportunities and perspectives", 18-19 October

2007, Iasi, Romania, Book of Abstracts, p. 43 (In Romanian).
Damian Gheorghe, Damian Floarea, Năsui Daniel, Pop Corina & Pricop Cornel, (2010), *The soils quality from the southern – eastern part of Baia Mare zone Affected by metallurgical industry*, Carpathian Journal of Earth and Environmental Sciences, 5, 1, p. 139 – 147
Eriksson, J.E., 2001. *Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops*. Swedish EPA Rep 5159, Stockholm, 31-36.
Peryea F.J. & Creger T.L., 1994. *Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues*. Water, Air, and Soil Pollution, Volume 78, Springer Netherlands, 297 – 306.
Franco, C., Soares, A., & Delgado, J., 2006. *Geostatistical modelling of heavy metal contamination in the topsoil of Guadiamar river margins (S Spain) using a stochastic simulation technique*. Geoderma, 136, 852–864.
Iancu O. & Buzgar N. (eds), 2008. *The Geochemical Atlas of Heavy Metals in the Soils of the Municipality of Iasi and its Surroundings Areas*. Ed. Univ. „Al. I. Cuza" Iasi, 48 p. (A3), Bilingual Edition (ISBN 978-973-703-329-1).
Kabata-Pendias A., Pendias H., 1999. *Biogeochemistry of trace elements, 2nd edition*. Wyd Nauk PWN, Warszawa (in Polish).
Kabata-Pendias A. & Pendias H., 2001. *Trace elements in soils and plants, 3rd edition*. CRC Press, Boca Raton, FL, 121-325.
Köljonen T., 1992. *The geochemical atlas of Finland.* Geol Survey of Finland, Espoo, J. Environ. Qual., 32:2230–2237
Lăcătuşu R., Andăr P., Răuță C., Rîşnoveanu I., Lungu M., Dumitru M., Ciobanu C., Kovacsovics B. & Popa D., 1997. *Cadmium and Lead abundance in soil horizont A from Romania*. Scientific works of the XVth National Conference on Soil Science, Bucharest, August 26-30, 1997, Publ. SNRSS, 29B, 131-142 (In Romanian).
Lacătuşu, R. Lacatusu, A. R., Lungu, M &Breabăn I. G., 2008. *Macro- and microelements abundance in some urban soils from Romania*. Carpathian Journal of Earth and Environmental Sciences, 3, 1, 75 – 83.
Grath S.P. & Loveland P.J., 1992a. *The Soil Geochemical Atlas of England and Wales.* Kluwer Academic Publishers, London, UK., 101p.
McGrath S.P. & Loveland P.J., 1992b. *The geochemical survey of topsoils in England and Wales*. In: Beck BD (ed) Trace Subst Environ Health 25:39–51.
Răuță, C., Cârstea, S., Mihăilescu A., Rădulescu, V., Ionescu, A., Blănaru, V., Gameț, E., Lăcătuşu, R., Toti, M., Neață, G., Dumitru, M., Nastea, S. & Neonila, P., 1988. *Some aspects regarding the evolution of agricultural soil pollution in Romania*. Anal. ICPA, XLIX, 263-273, Bucharest, Ro (In Romanian).
Răuță C., Lăcătuşu R. & Cârstea S., 1992. *Heavy metal pollution in the soils of Romania*. Environmental, III, 4, 33-44, Iasi, Ro (In Romanian).
Salminen R. (Chief-editor), Batista M.J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P.J., Olsson S.Å., Ottesen R.- T., Petersell V., Plant J.A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A. & Tarvainen T., 2005. *Geochemical Atlas of Europe. Part 1– Background Information. Methodology and Maps,* EuroGeoSurveys, 525p.
Shacklette H.A.T. & Boerngen J.G., 1984. *Element concentrations in soils and other surficial materials of the conterminous United States.* U.S. Geol. Survey Prof. Papers, 1270:1–105.
Siegel F. R., 2002. *Environmental Geochemistry of Potentially Toxic Elements*. Springer-Verlag, Berlin, 80-93.

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