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GEOCHEMICAL DISTRIBUTION AND SOURCE OF HEAVY METALS IN URBAN SOILS FROM CHISINAU CITY (REPUBLIC OF MOLDOVA)

PhD THESIS

- SUMMARY -

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-IASI-
2013

ACKNOWLEDGEMENTS

First thoughts of gratitude go to the doctoral thesis coordinator prof. Dr. Ovidiu Gabriel IANCU who headed and guided my scientific work during this period with great competence and understanding. A thought of gratitude goes to conf. Dr. Gheorghe JIGAU from Moldova State University who assured me study condition and scientific support in Moldova. The contribution of mentioned Professors manifested through scientific guidance with great competence and professionalism resulted in the completion of this PhD thesis. I want sincerely express my gratitude to Prof. Official Reviewer Dr. Laurentiu Calin BACIU, Dr. Gheroghe JIGAU and Dr. Nicolae BUZGAR also to Dean of Faculty of Geography and Geology, prof. Dr. Corneliu IATU.

I would like to express my gratitude to entire teaching staff of Geology Department, Faculty of Geology and Geography, "Al. I. Cuza University" Iasi, Romania for education, knowledge acquired, professional and teaching activities provided during the years of study (Bacheler, Master and PhD studies). This thesis completed the Master's thesis under supervision of Professor Dr. Emanoil GANDRABURA whom we are profoundly grateful for decrypting the mysteries of geochemistry, as well as for interest and curiosity to study further the geochemical features and characteristics of particular environment.

I express my gratitude to all professors who have taken courses and conferences in the first year of doctoral study, for very useful advices and the constructive criticism. I would like to particularly thank prof. Dr. Radu LACATUSU and prof. Dr. Octavian GROZA. I would like to thank every one of my colleagues from Faculty, from Masters and Doctoral School for fellowship, kindness and time spent together.

In addition, I wish to thank my close relatives for understanding and patience which they have shown. The first thought of gratitude goes to Archimandrite Mina DOBZEU which I would like to thank him for moral support and words who have guided me during my stay in Romania. Thanks to my sisters (Gabriela and Adriana), brothers in law (Sergiu POGOREVICI and Vladimir MOCANU) and nephews (Particia, Andrei, Mihaela and Gabriel) whom I thank for the innocence that carries in the soul and motivation that have provided. I would like to thank my friends Ecaterina IANCU (Moldova), Andreea PINTILII, Alexandra IORDACHIOIU, Daniela and Alin MANOLE (Romania), Mariana and Sergiu STRATULAT (Moldova) for their patience and understanding.

I dedicate this doctoral thesis to my parents, Andrei and Iulia TOFAN I thank them for the unconditional support that they have given to me, for the love and understanding in the most difficult moments, not least for financial support assured.

ABSTRACT

Doctoral thesis examines the geochemical distribution of heavy metals in the urban soils in Chisinau, Moldova. The source or origin of heavy metals combined with physic-chemical parameters of urban soils was determined based on principal component analysis and factor analysis with practical application in the study area. Estimation of baseline helped to define the heavy metal spatial variations in the urban soils. Evaluation of soil pollution as summary pollution index Zc in the soils from Chisinau in 2012 highlighted the weak contaminated areas above background almost 76.5% of the city and about 19.3% moderate pollution. Unpolluted soils were identified on 4.2% of the city area.

Keywords: geochemical distribution, source, urban soils, pollution levels, anthropogenic contribution

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INTRODUCTION

At the present the state policies from Republic of Moldova tend to be aligned to European Union standards. From the perspective of the EU integration, Chisinau capital of Moldova could become a regional center of influence benefiting from new opportunities offered by cooperation with other urban centers in the European region. This PhD thesis is included in Geology/Geochemistry area but we hope to offer applicability in environmental protection and natural resources. The results and conclusions achieved in this study shall find application in basic research at national level in Republic of Moldova but as well it could become a source of information for environmental authorities operating in environmental protection institutions.

Geochemical mapping studies of urban environment provide recent information to environmental authorities with reference to the levels of heavy metals or potentially toxic elements which would allow an appropriate demarcation of areas subjected to risk for human health. Until this moment the maximum allowable limits or exposed values in soils in the Moldovan environmental legislation does not provide separate contents for urban areas with regard to functional use (residential and industrial).

Addressing this topic we established a geochemical background range for each analyzed metal and as well we established a baseline for each analyzed metal in soil sampling. The research study aimed to reflect a wide spectrum of theoretical and applied issues included in the field of environmental geochemistry, landscape geochemistry and soils science with reference to urban soils. Initial assumptions and hypothesis of study were:

- Presence of heavy metals in soils from urban area can be explained by their geochemical origin and may be due to anthropogenic contribution.
- The past land use and current functionality of urban land affect and influence the content of heavy metals in soils.
- Content and distributions of heavy metal are determined by the physic-chemical parameters of soil and anthropic activity.
- Mobility of heavy metals in urban soils is influenced by pH, soil texture and organic matter.
- Spatial distribution of heavy metal in urban soils is influenced by soil particle size composition and functionality of urban land use.

The purpose of the research study was to establish the source and origin of heavy metals and to provide an overall picture of geochemical distribution of heavy metals in Chisinau soils contained in geochemical investigation at the early date.

The main objectives are:

- Evaluation and completion of existing database with geochemical information and defining the level of knowledge
- Systematization of own analytical data and their interpretation
- Defining geochemical origin and anthropogenic source of heavy metals
- Identification and location of polluted areas with heavy metals
- Provide the geochemical information required to cover legal-normative framework in the urban environment

This study will contribute at defining and establishing a new baseline for Cr, Co, Ni, Pb, Zn and As. Through this PhD study we want to draw attention to the content of Cr and As which require additional geochemical studies in both urban and rural areas.

STRUCTURE OF THE THESIS

Chapter I – Principles and methods in the urban environmental geochemistry present the fundamental and theoretical aspects of the topic addressed in this PhD study. Geochemical researches in urban areas in recent decades in European and worldwide cities highlighted the importance of geochemical knowledge with reference to geochemical distribution and characteristic of heavy metals in urban soils. In Republic of Moldova (Former Soviet Socialist Moldova Republic) geochemical studies were started in the early 60s of the last century. Geochemical studies focused on agricultural and forestry landscapes and the main purpose was to highlight the geochemical particularities of the landscapes. With more detailed studies was noticed N. Mirlean which developed a series of research methods to study anthropogenic landscapes (technogenesis). In addition the mentioned author emphasized the role of geochemical landscape in studying the migration processes of elements in the biosphere. Is the first author of *Geochemical Atlas of Chisinau* (1992) under which emphasizes ecological-geochemical aspects of chemical elements in urban soils from Chisinau.

In the first chapter we presented the role of urban geochemistry, term proposed by Iain Thronton in 1990 highlighting the importance of this area of research. The current visions were presented in order to define the following terms used in urban geochemistry: geochemical mapping (Johnson and Ander, 2008), geochemical phenomena and geochemical attributes adapted to urban areas as tools detained by the geochemists (Lyons and Hamon, 2012; Filippeli et al., 2012).

In order to highlight fundamental side of the study we adapted the principle of successive approximations presented by Fortescue (1980). Applying the principle of successive approximations allowed a successive approach, stage by stage during which we have outlined an overall picture of geochemical urban environment. This approach assisted the definition of the particularities and origin of urban soils based on field studies and available cartographic materials, to identify sources of pollution in urban areas and then this information to relate to the geochemical data acquired in functional areas and sectors of Chisinau.

Sampling and sample preparation and analytical technique sections included the following information: the study area of Chisinau city has approximate size 12/12 square kilometer. Sampling was carried out on a network 1 km/1sq. km at a depth 0-20 cm. From the grid surface were collected 120 soils sampled with a sample weight 1.5-2 kg (Figure I.1).

Collecting of characteristic soils samples from urban area is very important in sampling stage. The soil samples were collected in October-November 2011 after being fixed in advance the location of sample points. Sampling points on Chisinau surface were identified using administrative map after having transported sampling points on Google Map (.kml). This technique helped to identify under laboratory conditions, street, functional area and sectors in which the sample was placed.

The soil samples for the analysis of heavy metals were sieved through a sieve with a fraction < 1 mm. It was weighted 20.0 grams of the soil over which was added 4.0 grams of powdered resin. The mixture was milled in the ball mill at 25/180 speeds and then was again weighed in a capsule 9 grams at analytical balance. This capsule was subsequently subjected to the press 20 tons for 30 seconds, resulting a pellet which was analyzed by fluorescence spectroscopy RX (EDXRF Epsylon 5). Samples were analyzed in the Geology Department laboratories of Faculty of Geography and Geology, „Alexandru Ioan Cuza" University.

In the Geology Department laboratories also was determined the pH of soil samples. Once the soil was weighted 10 grams of soils was added 25 ml distilled water in the solution by mixing one minute. The sample soil was in stand for one hour after which pH was measured with a pH/Ion meter Corning M-555 type.

Humus, CaCO3 and soil texture were determined in the laboratories of the Institute of Soil Science, Agrochemistry and Soil Protection „Nicolae Dimo" from Chisinau. Analysis of soil samples was coordinated by Mr. Doctor Habilitat Valerian Cerbari and laboratory analysis were performed by Emilia Gropa şi Liudmila Vrabie.

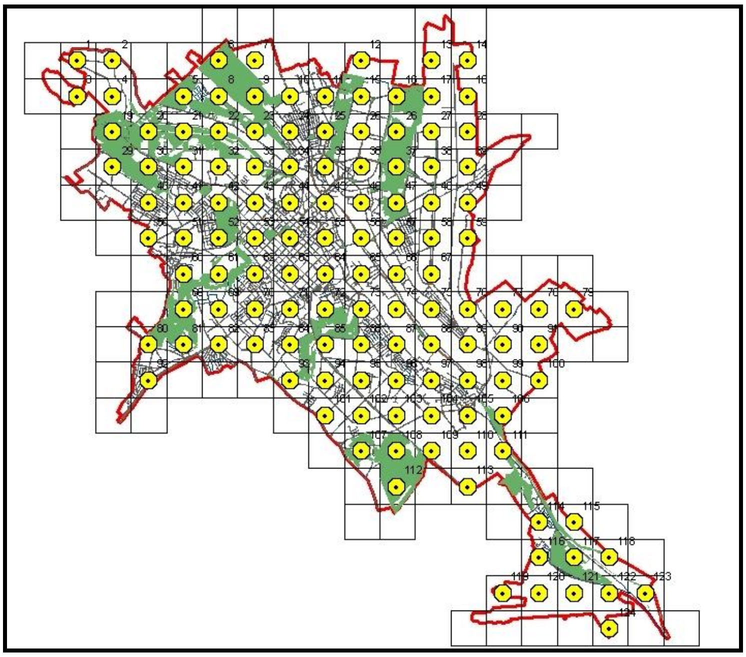


Figure I. 1 Point locations of 120 soil sampling (Chisinau, Moldova)

Chapter II – Geographical and geological framing of studied area present the location in the geographic space and geological structure of Chisinau city. Chisinau is located in south-east of the Forest Plateau (Podisul Codrilor). To the south of Chisinau is located South Moldavian Plain. The difference in altitude between relief from Forest Plateau and South Moldavian Plain causes different weather conditions and climate in this part of the Republic of Moldova (Putuntica, 2001). Putuntica (2001) explains that mezzo-climate and the built area overlapping this climate features gives distinct appearance of the municipal area. The author describes the following mezzo-climate sectors in the Chisinau area: rail-industrial, residential, old urban core and nonurban area.

In the Republic of Moldova *Law no. 431-XIII published in 19.04.1995* regulates the organization and functioning of public administration in Chisinau. According to mentioned law the capital of Moldova is Chisinau. Chisinau municipality is a territorial administrative unit divided into 5 sectors (districts): Botanica, Buiucani, Center, Ciocana and Rascani. Parts of the surface territory of Chisinau municipality comprise self-governing towns and villages (communes).

Geological structure is presented in section II.2 of the thesis where is presented geological structure. Studied area overlaps on the central part of Moldova located entirely on Moldovan Platform. Chisinau terrain as well as most of the Moldova is located entirely on Moldovan Platform, erosion acting on Sarmatian deposits. Deposits in which acting erosion, are accessible on direct observation, outcrops that knowledge on them are numerous and accurate (Ionesi, 1994; Ionesi et al., 2005). Geological structure is reflected on rocks occurring in outcrops or those found at a depth 20-30 m formed by alluvial-colluvial processes and wind erosion. According to the most recent publications (Moraru and Zincenco, 2005; Alcaz et al., 2005) in Chisinau first information about the geological structure was obtained in 1887 when the first wells were dug for water fountains up to 285 depth that demonstrated the presence of late Cretaceous deposits but a more detailed description has given to Cenozioc deposits. Quaternary deposits in the city Chisinau are of complex genetic origin: alluvial, eluvia and colluvium. Also are presented anthropogenic deposits (Figure II.1).

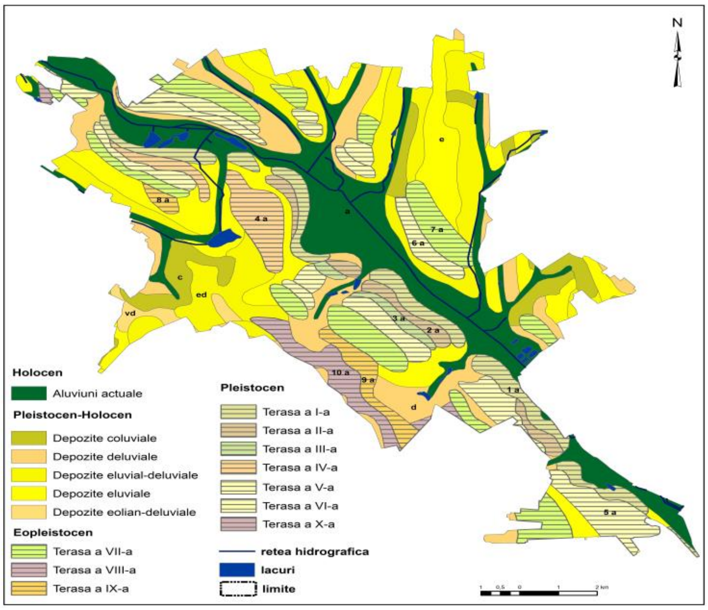


Figura II.1 Quaternary map of Chisinau

(Gh. Sirodoev, Tatiana Popusoi, Dinamic Geomorphology Laboratory, IEG, 2013)

Chapter III – General aspects concerning the urban soils provides an overview of the features of urban soils. The theoretical part shows how urban soils are formed and the factors determining pedogenesis and geochemical transformations of urban areas citing available scientific material in soil science with reference to urban areas (Lacatusu, 2005; Lacatusu et al., 2005 Hollis and Mullins, 1991). Soil science and ecological researches in urban areas demonstrated that urban soils belong to urban ecosystems being proposed their addition in the urban ecosystem investigation (Norra and Stuben, 2003). Pavao-Zuckerman (2008) found that environmental knowledge on urban soils is important because they can guide to achieve ecological restoration of urban ecosystems. Urban soils have suffered different historical pathways opposed to natural soils. Usually they are subject to disturbance with an anthropogenic origin with direct or indirect effects which are caused by environmental impact by urbanization. As a result urban soils are physically, chemical and biological modified. Under these circumstances it is necessary to know the characteristics of urban soils and urban ecosystems, which presents some problems and require ecological restoration or quality improvement of degraded urban soil.

In urban areas the soils are subject to change due to use of urban land. Into one functional area soil proprieties can be affected simultaneously by a number of factors, in soils are initiated transformational processes. In general, human activities in urban area imply complex actions and soils supports the highest impact in term of size, spatial extent, rate and duration (Lacatusu, 2005).

Studies conducted (Lacatusu et al., 2005) on soils from urban areas revealed that it is mandatory to include the description of pedogenesis processes underlying on the formation of soils and their functions in urban areas. In this regard were analyzed main physic-chemical characteristics of urban soils: grain size composition of urban soils, organic matter content, pH and carbonate content.

Textural classes of the investigated soils in the study area were determined based on the analysis of particle size classification after Kacinski and calculated using a ternary diagram. Textural species of urban soils in Chisinau was determined by particle size analysis of 37 soil samples. Samples were selected from the parks and green spaces (19 samples) and industrial and residential areas (18 samples). Interpretation of data from particle size analysis revealed that the predominant texture class is loamy-sand in the 70 % of analyzed soil samples and the textural class is sandy-loamy prevalent in 30 %.

Humus content (%) in urban soils from Chisinau was determined in 42 soil samples selected from urban functional areas while maintaining the same random sampling across the entire city. The average content of humus reported in 42 samples analyzed is 2.90 %. The maximum content noted is 4.59 % and the minimum is 1.08%.

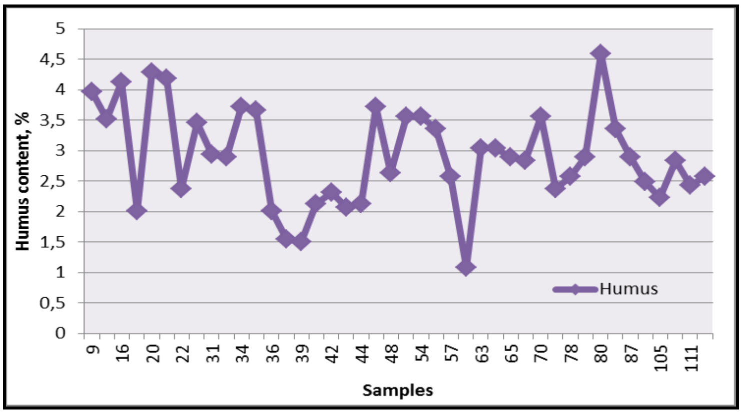


Figure III.1 Humus content in urban soils (42 soil samples)

Secu et al. (2008) highlighted the same values in chernozem soils in Iasi (Romania) so that the humus content varies from 3-5 % in clayey soil texture, respectively clay-loamy to clay. Lacatusu et al. (2008) based on comparative study between the cities Bucharest, Iasi and Baia Mare (Romania) showed that the C content varies significantly in the cities of Romania that is explained by their geographical location and the local environmental conditions. From the table III.1 can be seen that the mean organic content is slightly higher in Iasi towards Bucharest and in Baia Mare the content is significantly lower due to local environmental conditions.

In the second part of the table is calculated humus to compare results of the four cities: Chisinau (Moldova) and Iasi, Bucharest, Baia Mare (Romania). From the data analysis it is observed that average content of humus in urban soils from Iasi and Chisinau are slightly close. It may be concluded that there are some differences reported by soil particle size analysis in the urban soils from Iasi predominate fine clay-loam texture compared to Chisinau where the predominant texture is loam-sandy and sandy-loam.

Tabelul III.1

Organic matter contents in urban soils
(Lacatusu et al., 2008)

Parameter	Chisinau	Iasi	Bucharest	Baia Mare
C organic (%)				
Mean	-	1,80	1,74	0,88
Min	-	0,50	0,59	0,31
Max	-	2,80	2,22	1,27
Humus (%)				
Mean	2,90	3,1	2,99	1,52
Min	1,08	0,86	1,02	0,53
Max	4,59	4,83	3,83	2,19
Clay (%)				
Mean	22	26	24	30
Min	8	10	12	15
Max	32	34	31	40

In the investigated soils in Chisinau, carbonate content in the upper horizon of soils vary within a relatively wide range of values from 0.01 % to 22.3 %. High, very high and extremely high content are met in the 11 %, 12.5 % and 7 % of the soil samples analyzed (Figure III.2).

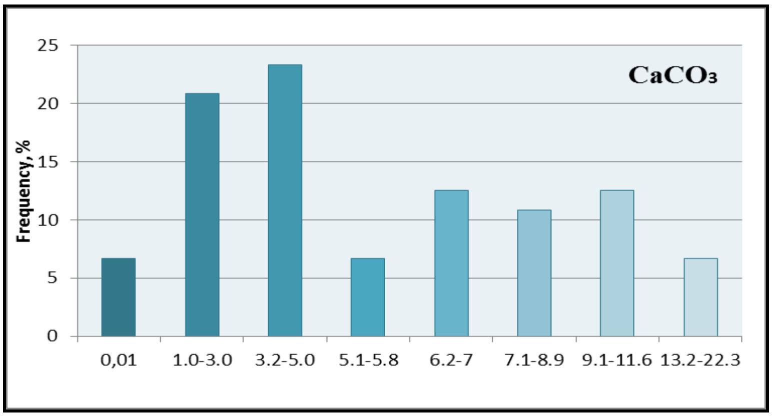


Figure III.2 Frequency distribution of $CaCO_3$ in urban soils (120 soils samples)

According to the values obtained for pH, predominant soil reaction in Chisinau was weakly alkaline. Soil reaction weakly-alkaline ranging from 7.82 to 8.44 was found in 87 % of analyzed soil sample from parks and some residential areas of the city and agricultural land. Alkaline-moderated was found in 8 % of the analyzed samples which reported pH values from 8.5 to 8.7 (Figure III.3). Samples were located in the industrial area of the city and a small number was found in parks (Parks Rascani and La Izvor).

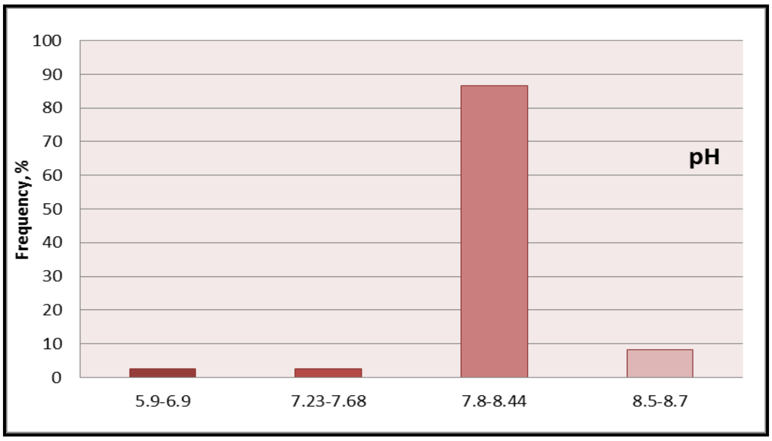


Figure III.3 Distribution frequency of pH in urban soils (120 soil samples)

Chapter IV – Source and distribution of heavy metals in urban area represent basic chapter of this PhD thesis. In this chapter are analyzed geochemical features of soils from Moldova and in the world. In the PhD thesis the term of heavy metal was used for the following reasons: to estimate the pollution level of soils in Chisinau city; to identify the toxicity degree of the studied elements and to assess the source of heavy metals. In the studied area were selected for analysis the following elements: Cr, Co, Ni, Pb, Zn, Cd and As.

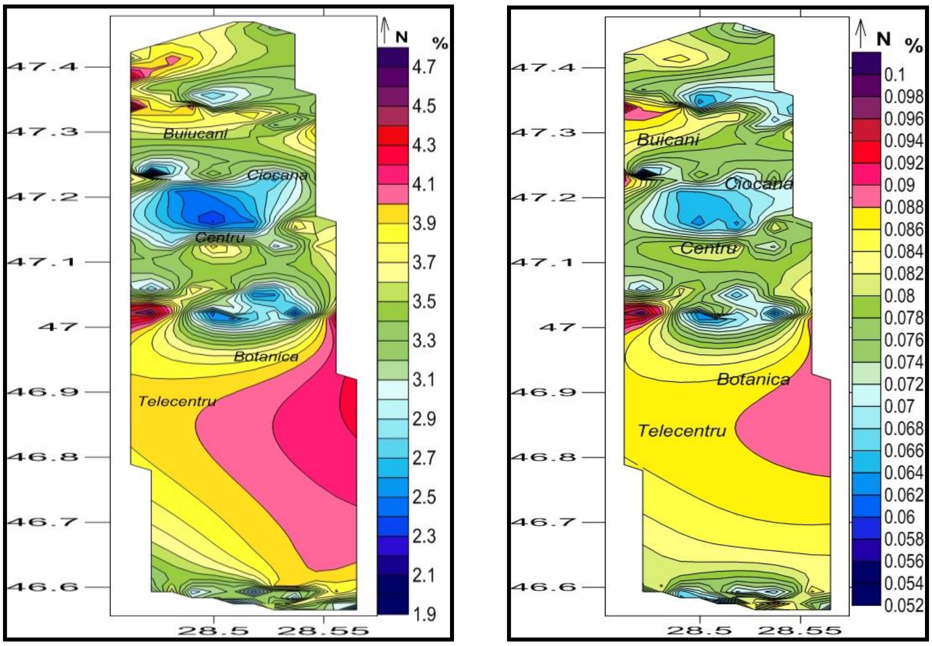
The research conducted in 2007-2009 in order to observe and analyze the distribution of heavy metals content in the upper horizon of soils from Moldova, under natural and relatively anthropic landscapes highlighted that in the pH range 6.37 to 7.9 the content of elements Zn, Cu, Pb, Co, Ni, Mn, Fe, As and Cd show a natural tendency distribution (Table IV.1). As a result, the behavior of the analyzed elements was directly influenced by pH, carbonates, organic matter and Fe and Mn oxides. Through studying the vertical distribution of heavy metals in two soil profiles in Moldova located in the forest and grassland was revealed the different values of heavy metal content in surface horizons compared to depth horizons.

Table IV.1

Mean content of heavy metals (mg/kg) and pH in the upper horizon of soils in Moldova

Statistic	pH	Zn	Cu	Pb	Co	Ni	Mn	Cd	As	Cr
Mean	7.16	56.23	21.45	11.46	6.91	23.53	653	0.54	1.89	32.38
Geometric mean	7.14	54.13	20.61	10.68	6.75	22.24	622.5	0.49	1.75	25.65
Max	7.9	86.3	31.8	25.9	9	34.1	1251	1	2.75	64.8
Min	6.37	30.3	11.1	6.9	4.4	10.1	345	0.15	0.75	1.4
Samples	21	21	21	21	21	21	21	21	21	21

Recent studies have demonstrated that Fe and Mn oxides are the most important in urban areas to follow and define the behavior of heavy metals in urban soils. In urban soils the first conclusions were drawn from analysis of Fe and Mn oxides. In the surface horizon of soils in Chisinau was reported average content 3.25 % for Fe_2O_3 which range from 1.79 to 4.86 % (Figure IV.1 a). Reported as percentage of the average content of MnO was 0.075 % and the content of Mn values were in the range of 0.047 and 0.102 % (Figure IV.2 b).



a. **Fe_2O_3 (%)** **b. MnO (%)**

Figure IV. 1 Distribution of Fe_2O_3 (%) and MnO (%) in urban soils (120 soil samples)

Principal component analysis and other derivate methods were widely used in geochemical applications to identify the sources of pollution and also to determine the contribution anthropogenic and/or geogenic origin of chemical elements (Faccinelli et al., 2000). Determination of source of heavy metals in urban soils was conducted while to establish pollutions sources near the sampling point which means that in the contaminated urban soils operate several factors which are difficult to identify and separate (Bityukova, et. al. 2000). Before using the statistical analysis through the principal component analysis and factor analysis for geochemical data obtained on 32 soil samples was first observed correlation relationship between physic-chemical parameters of all analyzed heavy metals in the PhD thesis.

Correlation matrix recalculated for principal component analysis and factor analysis of geochemical data revealed a positive correlation between clay and silt and also a negative correlation between sand-clay and sand-silt. Soil pH showed a significant correlation with $CaCO_3$ and a negative correlation with humus and Fe.

Table IV.2

Recalculated correlation matrix PC and FA after standardization and transformation of physic-chemical parameters with heavy metals (32 soil samples)

Parameters	Sand	Silt	Clay	pH	Humus	$CaCO_3$	Fe	Mn	Cr	Co	Ni	Cu	Pb	Zn	As
Sand	1,00														
Silt	**-0,85**	1,00													
Clay	**-0,73**	**0,57**	1,00												
pH	0,06	0,04	0,15	1,00											
Humus	-0,22	0,10	0,00	**-0,44**	1,00										
$CaCO_3$	0,13	-0,02	-0,23	**0,47**	-0,06	1,00									
Fe	**-0,75**	**0,68**	**0,70**	**-0,36**	**0,38**	-0,28	1,00								
Mn	**-0,67**	**0,55**	**0,62**	-0,24	0,34	**-0,51**	**0,78**	1,00							
Cr	-0,11	0,08	0,17	-0,10	0,03	0,18	**0,37**	-0,03	1,00						
Co	**-0,73**	**0,69**	**0,76**	-0,20	0,33	-0,29	**0,96**	**0,82**	0,30	1,00					
Ni	**-0,70**	**0,69**	**0,73**	-0,25	0,33	-0,28	**0,93**	**0,74**	0,23	**0,95**	1,00				
Cu	-0,20	0,13	0,24	0,05	0,28	0,02	0,30	0,29	0,26	0,35	0,34	1,00			
Pb	0,28	-0,33	**-0,38**	0,20	0,06	**0,60**	**-0,43**	**-0,50**	0,14	**-0,49**	**-0,52**	0,04	1,00		
Zn	-0,06	0,11	-0,20	0,18	0,25	**0,47**	-0,12	-0,23	0,22	-0,18	-0,13	0,21	**0,55**	1,00	
As	**-0,37**	**0,42**	0,15	0,23	0,34	**0,44**	0,29	0,18	0,12	0,30	0,25	**0,50**	**0,39**	**0,65**	1,00

** Marked correlation is significant at $p < 0.05$*

Interpretation of factor loadings obtained on the correlation between factors and variables revealed in the first factor important saturation with Fe, Mn, Co and Ni. The following factors showed a significant saturation the factor 2 for Pb, Zn and As and the factor 3 for pH and humus, the factors 4 and 5 showed an important saturation for Cr and Cu respectively (Figure IV.2).

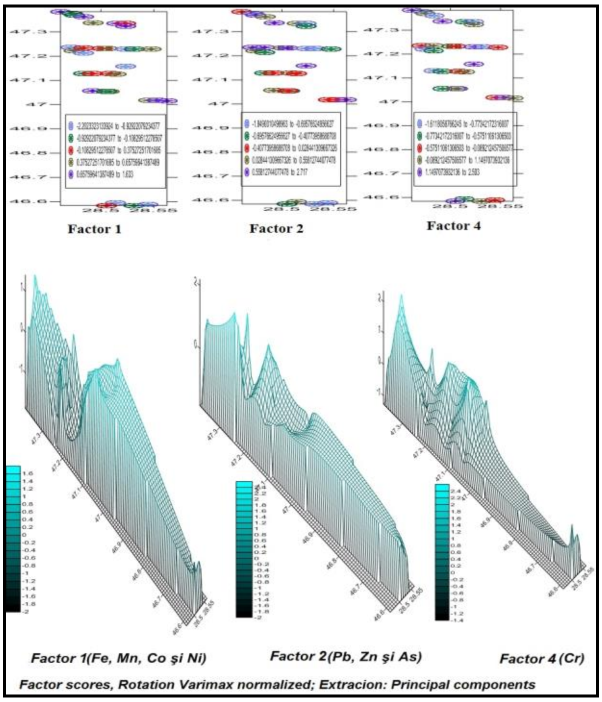


Figure IV.2 Distribution maps of first and second factors and fourth included in FA

Following a detailed analysis of the relevant literature to determine the range of geochemical background the most useful method with practical applicability in the study area was provide by Canadian researches Rencz, Garrett et al., 2011.

Estimation of geochemical background in Chisinau was conducted through following three stages. The first and second stages were based on direct observation on datasets trying to avoid subjective assumptions. The third stage comprises estimation of geochemical background range through calculation. Spatial visualization of each element on maps offered valuable information about their distribution in the study area. We concluded that distribution of heavy metal showed different values in sampling points and some elements outlined positive anomalies areas with a higher concentration. In the Chisinau city all analyzed heavy metals suggested anomalous content on distribution maps.

In this thesis the distribution of geochemical data were inspected on maps and then principal statistical parameters from the tables. In the next stage through inspection were analyzed graphical diagrams (box-plots) and were removed outliers and extreme values from datasets. Then we applied two methods to calculate range of background according to mean and median values of each element and their standard deviation (σ) and median standard deviation (MAD) from the datasets. Through the application of mean ± 2 σ and median ± 2MAD we defined the range of geochemical background. For Cr, Co and Ni the range of geochemical background was calculated by using both methods (mean ± 2 σ and median ± 2MAD). In the case of Cu, Zn, Pb and As were applied both methods after having been in advance removed the outliers and extreme values from box-plot diagrams. These elements showed a significant anthropogenic contribution and the median ± 2MAD method was more suitable (Table IV.3).

Table IV.3

Geochemical background range calculated by using methods Mean ± 2σ şi Median± 2MAD

Elements	Sample	Mean	σ	Median	MAD	Mean ± 2σ	Median± 2MAD	Outliers $^1/^2$
Cr	116	66,57	13,62	64,64	14,73	39,33– 93,81	35,19– 94,09	4/4
Log_{10}	119	1,82	0,094	1,82	0,093	1,631– 2,01	1,632– 2,01	6/6
Co	120	13,15	3,89	13,12	4,59	5,37 – 20,94	3,92 – 22,34	7/2
Log10	118	1,11	0,13	1,12	0,15	0,85 – 1,37	0,82 – 1,42	3/2
Ni	118	34,17	7,76	32,85	8,52	18,66 – 49,68	15,79 – 49,9	7/4
Log10	116	1,53	0,095	1,52	0,111	1,34 – 1,72	1,29 – 1,74	5/3
Cu	112	29,1	4,94	27,8	4,96	19,2 – 38,9	17,8 – 37,7	3/8
Log10	114	1,46	0,08	1,44	0,05	1,30 – 1,62	1,30 – 1,59	2/5
Zn	116	92,2	34,4	79,9	27,9	23,4 – 160,9	24,1 – 135,6	7/15
Log10	119	1,95	0,16	1,91	0,11	1,63 – 2,27	1,59 – 2,22	3/10
Pb	110	24,9	7,44	22,13	4,56	10,01 – 39,8	13,00 – 31,3	8/21
Log10	115	1,39	0,14	1,35	0,07	1,12 – 1,67	1,14 – 1,55	5/19
As	116	9,44	1,01	9,5	0,71	7,41 – 11,5	7,4 – 11,6	4/4
Log10	118	0,97	0,05	0,98	0,033	0,88 – 1,07	0,88 – 1,07	7/7
Cd	119	0,07	0,03	0,065	0,03	0,008 – 0,125	0,003 – 0,127	2/2

[1]Outliers excluded through the method Mean ± 2σ

[2] Outliers excluded through the method Median± 2MAD

Baseline estimation of heavy metals allowed us to define spatial variation in the urban soils. At the same time baseline contribute to distinguish the contribution of anthropogenic origin and pedogenic origin of heavy metals in environmental compartments (Zhan et al., 2007; Teng et al., 2009). Environmental impact assessment of heavy metals is very important tools because it makes a distinction between anthropogenic and geochemical anomalies of chemical elements because they occur simultaneously in environmental geochemical investigations.

Normalization procedure for calculating baseline is widely applied method for the calculation of regional baseline values. This method is mainly applied in sediment (Teng et al., 2009). This approach involved the normalization of the measured elements with a "conservative" element (Teng et al., 2009) or reference element (Zhang et al., 2007).

In the study are the Fe was selected as the reference element because presented a significant positive correlation with geogenic elements and negative correlations with elements those source is anthropogenic. Linear regression was applied to all the heavy metals. The marked correlations are significant at $p < 0.05$.

Normalization with Fe was performed for Cr, Co, Ni, Pb, Zn and As. The correlation coefficients showed no correlation between Fe and Cr, a weak negative correlation between Fe and Cu, and weak positive correlations between Fe and Pb and Fe and Zn also. A good correlation but not statistically significant presented Fe and Ni and also Fe and As. As a conclusion the data calculated based on the regression equation must be used with caution requiring further study. The following values are recommended for defining the baseline to be used with caution: Cr (67 mg/kg), Co (14 mg/kg), Ni (34 mg/kg), Cu (27 mg/kg), Pb (20 mg/kg), Zn (65 mg/kg) and As (9 mg/kg).

In the PhD thesis we compared the measured contents of analyzed heavy metals with values obtained in the soil analyzed during 2007-2009 from Republic of Moldova located in the natural conditions and landscapes affected partial by anthropogenesis. In the thesis we discussed the mean data obtained from soils in Moldova by Chiriliuc (2005). The soil contents were compared with the contents of the Moldova rock (Chiriliuc, 2010) and these contents were reported in the geochemical international literature (Salminen et al., 2005; Iancu and Buzgar, 2008).

Geochemical distribution of heavy metals in urban functional areas were described and presented in accordance with General Urbanistic Plan (2004). The content of Cu, Zn, Pb and As in the residential area showed a significant increase over background content in the soils from Republic of Moldova environmental legislation due to presence of multiple sources of pollution in the area.

In order to assess the degree of heavy metal pollution within the urban area in the Chisinau for each functional area we applied the Single-factor index analysis and Neremo index comprehensive evaluation method presented by Hong-Gui et al., 2012. Through the calculation we determined that heavy metal recorded multiple pollutions in each functional area of the city. Depending on the pollution index values for each functional area we found that Cu and Pb presented potential pollution in each functional area. Potential pollution of Cu and Pb noticed in the industrial, residential, parks, city center and to the sampling point close to road with more intense traffic. Zinc presented a potential pollution in several functional areas of the city and in the residential area because of maximum values recorded in the assigned functional area. Contents calculated for Co, Ni and Cr in the functional areas of Chisinau showed that there is punctual pollution with these metals.

Neremo index comprehensive evaluation method presented by Hong-Gui et al., 2012 refers not only to the extreme values measured but highlight the urban environment quality based on the weighted of several factors. In general the method reflects the level of pollution caused by various pollutants but in this thesis refers to the impact of heavy metals in functional areas. In the industrial area comprehensive pollution index (Pi) indicated moderate pollution. In the industrial area the moderated pollution level was due to recorded contents above the permissible limit or background content for Pb, As, Zn and Cu. Elements Cr, Co and Ni exceeded in several points the background content near pollution sources. In the residential area we found through calculation that comprehensive pollution index indicated a heavy pollution. As we observed in the residential area same pictures is presented in industrial area where calculated content values for Co, Cr and Ni was subunit.

Through application of the improved Neremo index method we established other results. We found that the maximum values calculated through the Neremo index comprehensive method influenced the final results. In the improved method we considered the weight factor of pollution and the final results showed significant differences compared to those presented previously. Pollution index (Pi) at the warning limit (≥ 0.7 Pi ≤ 1) was noted near schools or public space (0.956). Slight pollution was recorded in the industrial area, central part of the city and parks Pi included between 1 <Pi ≤ 2 is equal to 1.573; 1.176; 1.164 and 1.936. Moderated pollution included between 2 Pi <Pi ≤ 3 it was noted on agricultural lands where Pi is 2.281. Heavy pollution was recorded only in the residential area where Pi> 3 being 5.164.

Table IV.4

Neremo index calculated on the basis of pollution factors ω_j in each functional area

Functional area	Industrial area	Residential area	Center	Parks	Roads	Agricultural land	Public space
P_{ijmed}	1,215	1,325	1,127	1,108	1,109	1,121	1,029
P_{ijmax}	3,725	14,16	2,267	4,873	2,73	5,522	1,993
P'_{ijmax}	1,907	7,181	1,223	2,504	1,217	3,025	0,876
P_i	1,573	5,164	1,176	1,936	1,164	2,281	0,956
Pollution level	Slight pollution	Heavy pollution	Slight pollution	Slight pollution	Moderated pollution	Moderated pollution	Warning limit

In the section *IV.9 Evolution and dynamics of heavy metals from 1992-2012* we mentioned studies conducted in 1987-1990. Ecological geochemical studies in the Chisinau area at that time revealed a high degree of pollution with heavy metals, framing the city in heavily polluted category. Ecological geochemical methods applied in urban areas have taken into account the specificity of natural and anthropogenic factors, determined by the anthropogenic sources from residential and industrial areas. The degree of soil pollution with chemical pollutants was assessed according to the global (summary) index of pollution (Zc). Evaluation of soil pollution with heavy metals in Chisinau was based on studies conducted in the 1987-1990 years compared to soil sample collected in autumn 2011 and analyzed in 2012. Heavy metals pollutions in urban soils were determined through summarized pollution index according to known method (Revici, Saet et al. 1982). In the spectrum of Zc were include nickel, chromium, lead, molybdenum, vanadium, copper, zinc, silver, antimony and strontium. Determination of pollution degree has taken into accounts the methodological recommendations and legislation (Mirlean, 1992).

Local Environmental Action Plan (LEAP) of the Municipality of Chisinau published in 2010 presented the heavy metals contents from industrial platforms. Research results conducted in the Ecology of Human Settlements Laboratory from the Institute of Ecology and Geography were included in LEAP.

Chisinau from total area of municipality occupies 21.5 % with a density of populations 82.7% to the total municipality. We found that the 120 soil samples from the area of Chisinau presented significance only for 21.5 % from the municipality.

Reporting the 120 soil samples analyzed in the thesis to the urban functional areas of Chisinau we noticed that residential area comprised 28 % of soil samples, parks and green spaces occupied 23 % of the total number of samples and from the industrial area were analyzed 22 % of the soil samples. A lower percentage of samples returned to the samples located in the city center, near the road, public spaces and agricultural land. In terms of territorial administration we have concluded that the samples analyzed by sectors showed the greatest number of samples in Ciocana sector about 25 % of the total samples. Botanica sector occupies the second place after the number samples analyzed to 23 % and in Rascani sector has returned 17 % of all samples and in Buiucani were analyzed 15 %. The center of the city which included the sector Telecentru and Malina Mica corresponds to 18 % of the total number of samples.

Distribution of Zc index in urban soils from Chisinau city reveals weak polluted areas above background almost 76.5 % of the city and about 19.3 % of areas are moderated polluted. Unpolluted or clean soils were identifies to 4.2 % of the city area (Figure IV.3).

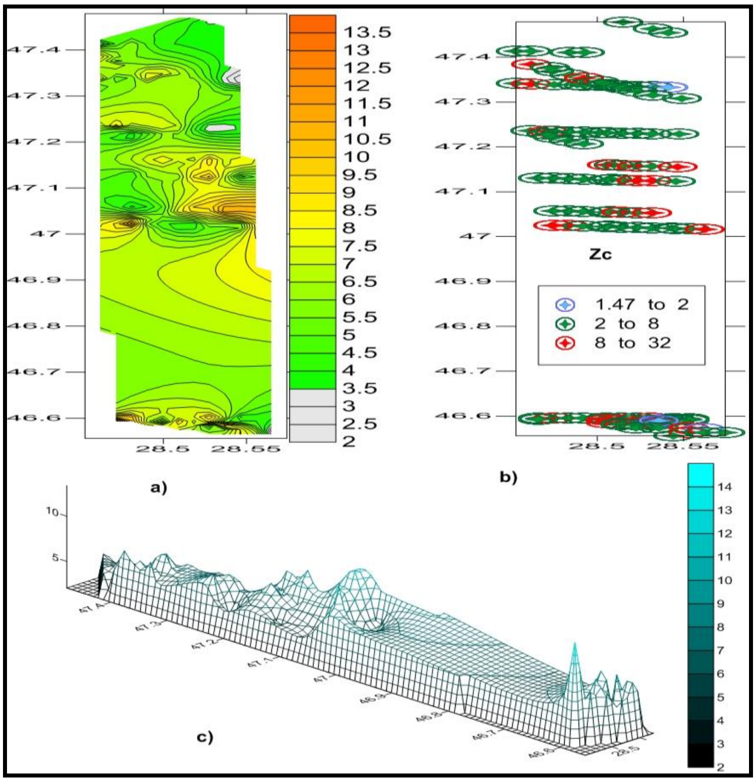


Figure IV.3 Zc distribution in urban soils from Chisinau city

Distribution and content of calculated Zc according to environmental legislation of the Republic of Moldova (Guidelines on the damage caused to soil resources, 2004) indicated in the Chisinau area three levels of pollution according to pollution degree calculating through summarized index: level unpolluted, slightly polluted and moderately polluted systematized in three classes studied in urban area. In the first class Zc index ranged from 1.47 to 2.00 contained about 4.2 % of sampling points or 5 soil samples. In the second class the summarized index Zc ranged within 2.00 to 8.00 representing 76.5 % of soil samples included in the category weak polluted this signifying low pollution degree in 91 sampling points. In a third class 8 to 32 the moderated degree of pollution included 19.3 % of soil samples that suggesting the higher content of heavy metals in the 24 sample points.

GENERAL CONCLUSIONS

The topic addressed in the PhD thesis has an interdisciplinary character. In this work we aimed to highlight the geochemical features of urban soils in terms of soil science and also to explain their geochemical characteristics as basic knowledge promoted in geochemistry complementary sciences (Landscape Geochemistry and Environmental Geochemistry and Urban Geochemistry). In the second part of the thesis we presented the interpretation of geochemical data for characterizations of soil physic-chemical parameters to describe properties of urban soils and description of heavy metals abundance in soils from Chisinau city. The thesis was divided into four chapters.

➢ Studies conducted (Lacatusu et al., 2005) on soils from urban areas revealed that it is mandatory to include the description of pedogenesis processes underlying on the formation of soils and their functions in urban areas. In this regard were analyzed main physic-chemical characteristics of urban soils: grain size composition of urban soils, organic matter content, pH and carbonate content.

- ✓ Interpretation of data from particle size analysis revealed that the predominant texture class is loamy-sand in the 70 % of analyzed samples and the textural class is sandy-loamy prevalent in 30 %.
- ✓ The average content of humus reported in 42 samples analyzed is 2.90 %. The maximum content noted is 4.59 % and the minimum is 1.08%.
- ✓ In the investigated soils in Chisinau carbonate content in the upper horizon of soils vary within a relatively wide range of values from 0.01 % to 22.3 %. High, very high and extremely high content are met in the 11 %, 12.5 % and 7 % of the soil samples analyzed.
- ✓ According to the values obtained for pH the predominant soil reaction in Chisinau area was weakly alkaline. Soil reaction weakly-alkaline ranging from 7.82 to 8.44 was found in 87 % of analyzed soil samples. Alkaline-moderated pH was found in 8 % of the analyzed samples that reported pH values from 8.5 to 8.7.

➢ Recent studies have demonstrated that Fe and Mn oxides are the most important in urban areas to follow and define the behavior of heavy metals in urban soils. In the surface horizon of soils in Chisinau was reported average content 3.25 % for Fe_2O_3 that ranged from 1.79 to 4.86 %. Reported as percentage of the average content of MnO was 0.075 % and the content of Mn values were in the range of 0.047 and 0.102 %.

- Principal component analysis and factor analysis revealed a positive correlation between clay and silt and also a negative correlation between sand-clay and sand-silt. Soil pH showed a significant correlation with $CaCO_3$ and a negative correlation with humus and Fe. Interpretation of factor loadings obtained on the correlation between factors and variables revealed in the first factor important saturation with Fe, Mn, Co and Ni. The following factors showed a significant saturation the factor 2 for Pb, Zn and As and the factor 3 for pH and humus, the factors 4 and 5 showed an important saturation for Cr and Cu respectively.
- Through the application of mean ± 2 σ and median ± 2MAD we defined the range of geochemical background. For Cr, Co and Ni the range of geochemical background was calculated by using both methods (mean ± 2 σ and median ± 2MAD). In the case of Cu, Zn, Pb and As were applied both methods after having been in advance removed the outliers and extreme values from box-plot diagrams. These elements showed a significant anthropogenic contribution and the median ± 2MAD method was more suitable.
- Baseline estimation of heavy metals allowed us to define spatial variation in the urban soils. As a conclusion the data calculated based on the regression equation must be used with caution requiring further study. The following values are recommended for defining the baseline but to be used with caution: Cr (67 mg/kg), Co (14 mg/kg), Ni (34 mg/kg), Cu (27 mg/kg), Pb (20 mg/kg), Zn (65 mg/kg) and As (9 mg/kg).
- The content of Cu, Zn, Pb and As in the residential area showed a significant increase over background content in the soils from Republic of Moldova environmental legislation due to presence of multiple sources of pollution in the area.
- In order to assess the degree of heavy metal pollution within the urban area in the Chisinau for each functional area we applied the Single-factor index analysis and Neremo index comprehensive evaluation method presented by Hong-Gui et al., 2012. Through the calculation we determined that heavy metal recorded multiple pollutions in each functional area of the city. Depending on the pollution index values for each functional area we found that Cu and Pb presented potential pollution in each functional area. Potential pollution of Cu and Pb we noticed in the industrial, residential, parks, city center and to the sampling point close to road with more intense traffic. Zinc presented a potential pollution in several functional areas of the city and in the residential area because of maximum values recorded in the assigned functional area recorded a slight pollution. Contents calculated for Co, Ni and Cr in the functional areas of Chisinau showed that there is punctual pollution with these metals.
- Through application of the improved Neremo index method presented by Hong-Gui et al., 2012 we established other results. In the improved method we considered the weight factor of pollution and the final results showed significant differences compared to those presented previously. Pollution index (Pi) at the limit warning (≥ 0.7 Pi ≤ 1) was noted near schools or public space (0.956). Slight pollution was recorded in the industrial area, central part of the city and parks Pi included between $1 < Pi \leq 2$ is equal to 1.573; 1.176; 1.164 and 1.936. Moderated pollution included between 2 $Pi < Pi \leq 3$ it was noted on agricultural lands where Pi is 2.281. Heavy pollution was recorded only in the residential area where $Pi > 3$ being 5.164.

- Chisinau from total area of municipality occupies 21.5 % with a density of populations 82.7% to the total municipality. We found that the 120 soil samples from the area of Chisinau presented significance only for 21.5 % from the municipality.
- Reporting the 120 soil samples analyzed in the thesis to the urban functional areas of Chisinau we noticed that residential area comprised 28 % of soil samples, parks and green spaces occupied 23 % of the total number of samples and from the industrial area were analyzed 22 % of the soil samples. A lower percentage of samples returned to the samples located in the city center, near the road, public spaces and agricultural land.
- In terms of territorial administration we have concluded that the samples analyzed by sectors showed the highest number of samples in Ciocana sector about 25 % of the total samples. Botanica sector occupies the second place after the number samples analyzed to 23 % and in Rascani sector has returned 17 % of all samples and in Buiucani were analyzed 15 %. The center of the city which included the districts Telecentru and Malina Mica corresponds to 18 % of the total number of samples.
- Distribution of Zc index in urban soils from Chisinau city reveals weak polluted areas above background almost 76.5 % of the city and about 19.3 % of areas are moderated polluted. Unpolluted or clean soils were identifies to 4.2 % of the city area.

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