CONTRIBUTIONS TO THE STUDY OF HEAVY METALS POLLUTING FROM THE ENVIRONMENT, BY ATOMIC SPECTROMETRY

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PhD Thesis Summary

Abstract. *In this scientific work are presented a part of the results included in the thesis entitled "Contributions to the study of heavy polluting elements from the environment by atomic spectrometry" which includes the innovative contributions to the study of the distribution of heavy metals in acacia leaves collected from Dâmbovița county and neighboring counties and the distribution of heavy metals from surface and deep soil collected from the main oil parks in Dâmbovița county. In the analysis of heavy metal concentrations in the studied samples, the spectrometric techniques were used: Atomic Absorption Spectrometry (AAS) and Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF), which were successfully optimized and provided valuable information used in following studies, to assess degree of heavy metal pollution of the environment. These methods were used in a complementary way with the biomonitoring technique in order to have as complete information as possible of the elemental composition of the analyzed samples.*

1. Introduction. Motivation of the study

Environmental pollution with heavy elements has become, in recent years, a pressing problem faced by the entire population of the Earth, due to increasing human activities [1 – 11]. Heavy metals have a potentially toxic effect on all living organisms, at concentrations above the maximum biologically acceptable limit. Toxic heavy metals are considered to be the invisible enemies that man faces in everyday life, especially through food, because they can accumulate in the tissues and vital organs of the body, triggering major health problems over

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time. Each heavy metal, due to its chemical properties, acts on specific target organs. Also, animals take toxic elements from the environment through food, habitat, and plants through accumulation from soil, air or water.

For heavy metals emitted into the environment, due to anthropogenic or natural factors, the soil acts as a storage system for them [1 - 11]. This behavior of the soil is also favored by the ability of polluting elements to accumulate over time. Obviously, the climatic factors, natural and anthropogenic, act on these deposits by mobilizing the metals, then passing them into the food chain, with serious consequences for life and the environment[13, 14].

In generally, the soil in urban areas, where industrial activity is developed, is much more polluted. In rural areas, the intense chemical of agriculture has intensified the acceleration of the migration of chemical elements in nature. Under this aspect, a particular danger is presented by heavy metals, whose concentration on the surface also increases due to the extraction of mineral and fuel deposits from the underground. The result is the uncontrolled increase in the flow of heavy metals into the biosphere [7, 8, 15, 16]. Over time, a natural selection of plant species was also achieved, some resisting and adapting to the conditions of high soil loading, thus becoming indicator plants for areas with abnormal concentrations of heavy metals. In any species, heavy metal concentrations can vary between different parts and organs of the plant as well as with the age of the plant. They are species that have the ability to concentrate high concentrations of heavy metals at the level of different vegetative organs [12, 13, 14].

This thesis contains the experimental results of the study of the distribution of heavy metals in acacia leaves collected from Dâmboviţa county and neighboring counties and the distribution of heavy metals in the surface and deep soil collected from the main oil parks in Dâmboviţa county [1].

Analysis methods by atomic spectrometry such as, Atomic Absorption Spectrometry (AAS) and Energy Dispersiv X-Ray Fluorescence Spectrometry (EDXRF) [6, 7, 9, 10, 25, 26] were successfully used and optimized and provided valuable information that will be used in future studies to assess the degree of the heavy metal pollution environment . These methods were used in a complementary way with the biomonitoring technique in order to have as complete information as possible of the elemental composition of the analyzed samples [10, 19, 20].

From the point of view of the study of the distribution of heavy metals in the soil, the analyzes carried out in the period 2010-2013 are insufficient to be able to conclude on the degree of heavy metal pollution of the soil in the studied areas. But considering that until now no such study has been carried out, in the specialized literature, no data were found to support the research carried out in this work, however, the data obtained represent a real information of the

population of the studied areas but also of competent persons in the field of environmental protection.

The objectives of the doctoral thesis facilitate the follow-up of the experimental approach and the interpretation of the results. The objectives of the investigations aim at:

1. Determination of the concentrations of elements and heavy metals Al, Ti, Mn, Fe, Co, Cu, Zn, As, Sr, Cd and Pb in biological and soil samples collected from Dâmbovița County and neighboring counties;

2. Reporting the results obtained to the national standards;

3. Identification of the best techniques and methods for the determination of toxic pollutant elements;

4. Completing the study on soil pollution using the biomonitoring technique as a complementary technique to spectrometric analytical methods;

5. Creation of maps for the polluting elements identified for each individual area and the risks to which the corresponding ecosystems are subject;

6. Identification of pollution sources for each area separately according to the statistical correlations made between the elements and the results obtained following the application of characteristic reports.

In order to monitor the quality of the surrounding environment from the point of view of pollution with heavy metals and toxic elements, the criteria derived from the proposed objectives were respected, namely:

- identification of sources of pollution with heavy metals and toxic elements;

- taking samples from established locations and documenting them;

- establishing the types of samples that will be analyzed, as well as the collection areas;

- establishing the analysis methods used for the study of environmental samples;

- elemental analyzes of samples and determination of their composition;

based on the obtained experimental results, establishing the degree of environmental pollution with heavy metals in the collection area.

In this context, a preliminary study was carried out on atomic analysis methods, Atomic Absorbtion Spectrometry (AAS) and Energy Dispersiv X-Ray Fluorescence (EDXRF), methods capable of determining, with high sensitivity, precision and accuracy, macro, micro and trace elements in biological and soil samples [6, 7, 9]. The comparative analysis of the methods addressed demonstrated that none of these techniques, used individually, is fully satisfactory for the wide variety of problems involved in the analysis of chemical elements (eg the heavy metals) at the trace element level. In order to cover the entire range of elements that must be analyzed in a sample, it proved necessary to use these methods in a complementary way with the biomonitoring technique, obtaining correlated results for a series of elements [1, 20, 21, 24].

The part of inovative Contributions of this doctoral thesis is characterized by:

- defining the field of investigation;

- careful indication of the physico-chemical investigation equipment, the methods and materials used;

- the rigorous interpretation of the results, with their tabular presentation;

- establishing the working conditions, through an important number of experimental determinations;

- comparing the results obtained with the national standards regarding the CMA of some toxic elements in biological and soil samples from the areas of interest.

It should be noted that all experiments of physico-chemical analyzes were carried out in the research laboratories of the Multidisciplinary Scientific and Technological Research Institute of Valahia University in Târgovişte (ICSTM-UVT).

2. Spectrometric analysis methods

The complex study carried out in the period 2010-2013, in order to evaluate soil pollution with heavy metals, aimed at the use of modern, sensitive analytical techniques, namely Atomic Absorption Spectrometry (AAS) and Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) [9, 10, 20, 11,26]. These methods were used in a complementary way, together with the biomonitoring technique, in order to have the most complete information about the elemental composition of the analyzed samples.

2a. Atomic Absorption Spectrometry (AAS). Principle of the AAS method [5, 7, 11, 26].

The method of chemical analysis by atomic absorption was introduced by Alan Walsh in 1952 and is based on a phenomenon of the inversion of spectral lines (discovered as early as 1859 by the German Gustav Robert Kirchhoff). namely, This phenomenon consists in the emission of radiation under the same conditions (temperature and pressure) in which it was absorbed by each individual element. The instrument with which the phenomenon can be studied determines the concentration of the chemical elements in the sample to be analyzed (quantitative analysis). This is done by determining the degree of absorption of monochromatic radiation by the sample. The monochromatic radiation emitted by the source is characteristic of each atom. This instrument is called an atomic absorption spectrometer.

The radiation emitted by the source characteristic of each type of element will be diminished in the flame in proportion to the concentration of the atoms of the

same chemical element, the atoms of the other chemical elements not participating in the absorption process. Therefore it is necessary to select the specific wavelength of an element and to know the elements present in the flame.

The elements in the samples to be analyzed are usually in the form of molecular compounds, and therefore a method must be found to release the atoms from the molecules, a process called atomization.

Atomic absorption spectrometry allows the quantitative and qualitative analysis of more than 60 metallic or semi-metallic elements.

Through this method, the presence of metals in materials, the environment or even organisms can be investigated.

The spectral lines fall in the range of 190-850 nm, allowing analyzes of the order of micrograms-ppm, and in certain cases even nanograms in a milliliter of solution -ppb.

The elements (Cu, Ni, Fe, Zn) were determined by flame atomic absorption spectrometry (FAAS) and the elements (Cr, Cd, Pb) by the graphite furnace electrothermal method (GAAS).

It is a method for monoelemental analysis. It is not a method of identifying a chemical element. The elemental composition of the analyzed sample must be known in advance and then quantitative analyzes can be performed.

The method cannot be used to determine elements whose resonance lines are located in the spectral range below the value of 2000 Å, as they are strongly absorbed when the radiation beam passes through the flame and through air. The use of the vacuum technique, which would eliminate the unwanted absorption, requires replacing the flame with other atomization systems, which would greatly complicate the entire installation.

In the flame with low temperatures, such as the one fed with methane gas - air (2100 K) and the one with propane - air (2000 K) some metals such as Mg, Fe, Co, are incompletely atomized and for this reason, upon their determination systematic errors appear, obtaining lower values of the concentration compared to the real one (formation of difficult volatile complexes)

2b. Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) [3,6,10,11,26].

The physical process of X - Ray Fluorescence takes place, successively, as follows:The inner electrons of the sample atoms are ejected due to collisions with X-photons of the primary X-ray source (excitation source). The electrons from the outer layers instantly occupy the vacant places on the lower layers (K, L, M). Following the transitions that take place, energy quanta are released from the field of characteristic X-rays (lines) that leave the sample in all directions. The characteristic X-ray spectrum specific to the sample atom species is detected and

recorded, the intensity of the X-ray lines being proportional to the number of sample atoms (concentration). The analysis of the X-ray spectra emitted by the sample is carried out according to the energy of the X-ray lines, a procedure that is the basis of Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF).

The advantages of Energy Dispersive X-Ray Fluorescence Spectrometers (EDXRF) are: simplicity of construction; lack of moving components; increased sensitivity and signal/noise ratio, etc.

However, this EDXRF analysis method cannot be used to determine the concentration in the sample of chemical elements that have a Z order number lower than 12.

The Energy Dispersive X-ray Fluorescence (EDXRF) Analysis Method is simple, fast, non-destructive, multi-elemental (elements with Z > 12), with an accuracy between 0.1 and 0.3%. Elements can be determined in concentrations between 0.2÷100 ppm in solid, liquid, aerosol or powder samples [6, 9, 26].

The EDXRF method is a universal investigation method in the sense that it can be used without restrictions to identify and determine the concentrations of all elements in the periodic table of elements whose order number is greater than 12.

The characteristic of this method of analysis, as well as of the other methods of atomic and nuclear analysis, is their independence from the nature of the chemical combinations in which the investigated elements enter, because the energies of the incident beams are several orders of magnitude higher than the energy of the chemical bonds.This analysis method is widely used for the qualitative and quantitative determination of the elemental chemical composition of a sample, especially for inorganic substances (minerals, ceramics, metals, soils, etc.) - especially in industry.

The experiments described in this thesis, regarding the determination of heavy metal concentrations in soil samples, were carried out in the Research Laboratories of the Multidisciplinarity Research Institute for Science and Technology of Valahia University in Târgovişte (ICSTM-UVT). Were used, the Avanta GBC Atomic Absorption Spectrometer, with flame and cavity cathode lamps, with the measurement precision of the order of *ppm* and respectively the X-Ray Fluorescence Spectrometer, ElvaX, with Dispersion in Energy, with a detection possibility of the elements with the order number from Z= 12, to Z= 92. The calibration curves were made for Fe, Mn, Ni, Zn, by the calibration curve method on the Avanta GBC atomic absorption spectrometer and the calibration curves of the X-ray fluorescence spectrometer, EDXRF, model ElvaX. For calibration were used the reference materials NIST-2711AMontana Soil. For the detection of characteristic X-rays, the ElvaX spectrometer uses a semiconductor detector, Si-PIN diode, with thermoelectric cooling and an energy resolution of 180 eV at the Kα line of 5.9 Ke of Fe. The method of regression coefficients was

used to process the X-ray spectra. The detection limit of the EDXRF method using the ElvaX spectrometer is in the (2 - 10) *ppm* range.

3. Environmental samples collected and analysed

For the research carried out in order to write this thesis, a number of 278 soil samples and biological samples (leaves, moss, bark) were taken, prepared and analyzed, of which 187 were samples of polluted soil from different areas of Dâmbovița county and neighboring counties. This extensive study on the distribution of heavy metals in polluted soil and implicitly in different biological samples (leaves, bark, moss) was not chosen by chance, knowing that in urban areas or in those where industrial or extractive activities are carried out there is a uncontrolled accumulation of toxic polluting elements, which can easily reach the food chain disrupting the quality of life and the environment. Thus, it was considered a necessity to study the distribution of heavy metal concentrations in the surface or deep soil of polluted urban environments, identifying and quantifying at the same time possible factors of influence on the increase in the concentration of heavy metals in the urban soil or in that in which carry out polluting anthropogenic activities [1].

3a. Distribution of heavy metals in acacia leaf [12, 21].

To the study of degree of heavy metal pollution of some areas in Dâmbovița county, as well as some areas in neighboring counties Argeş and Vâlcea, soil samples and acacia leaves were taken and prepared for spectrometric, AAS and EDXRF measurements. *Acacia is a species of shrubs and trees belonging to the Mimosoideae subfamily of the Fabaceae family. The genus Acacia contains about 1300 species, of which about 960 are native to Australia.* The samples were collected from 11 geographical points, (P1 - P11), from these counties, located with the help of a GPS device, as follows:

P1 Bogaţi (25°13'38.88"; 44°82'50.33"**),** P2 Bradu (24°89'60.86"; 44°75'39.46"**),** P3 Vedea (24°59'17.83"; 44°78'02.06"**),** P4 Vitomireşti (24°41'49.06"; 44°88'15.13"**),** P5 Dăeşti (24°89'45.56" ;45°18'32.66"**),** P6 Berislăveşti (24°41'80.50"; 45°30'59.05"**),** P7 Racoviţa (24°30'36.11"; 45°41'40.97"**),** P8 Câinenii Mici (24°29'60.16"; 45°50'42.19"**),** P9 Băjeşti (24°93'51.44"; 45°02'04.03"**),** P10 Priboieni (24°07'18.83" ;44°86'97.11"**)** and P11 Comişani (25°59'27.94"; 44°87'72.02"**).**

From the wide range of heavy metals, Fe, Mn, Ni and Zn were chosen for the study, because they are frequently used in the production of pesticides and foliar fertilizers. Collection points P1, P2, P4, P7, P10 and P11 are located in areas with agricultural activities (fruit growing, viticulture and cereal crops). Near the

collection point P8, there is a hydropower plant and a ballast. All other points (P3, P5, P6 and P9) are located in zones forestry. The concentrations of Fe, Mn, Ni and Zn in leaves and soil, which were collected between 14 - 28 August 2010, were determined by spectrometric, AAS and EDXRF methods. [13]. The concentration values (in mg/kg s.u.) determined by AAS and EDXRF analysis techniques were included in the following ranges: *in leaves*, Fe (200 - 292), Mn (58.01 - 223), Ni (2.47 - 3.03), Zn (18.89 - 52.35) and respectively in *soil*, Fe (5098 - 7624), Mn (231 - 854), Ni (65.13 - 161), Zn (368 - 1248). Relative standard deviation (RSD) was in the range (5 - 10)%. According to the legislation (Order 756/1997) the concentration values (mg/kg s.u.) in the soil must be: Fe (VN=3000, PM=4500, PI=7000), Mn(VN=900, PM=2000, PI=4000), Ni (VN=20, PM=200, PI=500), Zn (VN=100, PM=700,PI=1500), with the explanation VN-Normal Value, PM - Maximum Threshold and PI - Intervention Threshold) [1, 15, 16].

In the samples of acacia leaves, the highest concentration of Fe was obtained in the samples from the collection points P8 Câinenii Mici and P9 Băjești, the consequence of the activity of the ballast tanks, since the hydropower plants are apparently non-polluting units. Hydropower plants affect the environment by damaging the landscape and ecosystems, affecting the diversity and number of species, but also the water quality (concentration of salts). Due to the excessive atmospheric humidity in the area, climatic disturbances occur. The pollution resulting from the sand and gravel extraction activities from the riverbeds is represented by the dust released into the atmosphere, the noise and vibration emissions generated by the sorting and washing stations, by the transport and storage of the extracted materials.

The maximum concentration of Mn was obtained in sample 4 (collection point P4, Vitomirești), which can be explained due to the intense agricultural activities, the main activity of the local residents.

The maximum concentration of Ni and respectively Zn was determined in the sample 2 collection point P2, Bradu),which is also explained due to the agricultural activities in the area [1].

In the soil samples, the Fe concentration values exceed the maximum level (4500 mg / kg s.u.), and in 6 soil samples the Fe concentration exceeds the intervention level (7000 mg / kg s.u.). In points 3 and 5, the lowest value of Fe concentration in the soil can be observed. Also, 8 soil samples have Zn concentration that exceeds the maximum level (700 mg / kg s.u.), but none of the samples exceeds the intervention level (1500 mg / kg s.u.). In the cases of Mn and Ni, no exceeding of the maximum level is recorded (2000 mg / kg s.u. - Mn; 200 mg / kg s.u. - Ni). The concentration of Mn in the soil reaches the normal value only in points 2 and 4.

It turned out that in the soil, the concentration of Ni varies between normal values and the maximum allowed threshold, only in points P10 and P11 the values are closer to the maximum threshold. A concentration of Zn close to the intervention threshold is found in the soil sample from point P4 [1].

The collection points are located in areas with different types of activity and, thus, the degree of transfer of heavy metals from soil to leaves is different.The degree of transfer is defined by the **accumulation coefficient**. The accumulation coefficient was calculated as follows: $Ka = C_{leaf}/C_{sol}$,   where, C_{leaf} and C_{sol} are elemental concentrations in leaf and in sol, respectively.The values of K are in the range (0, 1) [1].

A plant is considered a bio accumulator of heavy metals if the accumulation coefficient (K_a) is at least equal to 1. The accumulation coefficients calculated from the experimental values of heavy metal concentrations (Fe,Mn,Ni,Zn) in the acacia leaf and in the soil have values in the following ranges: K_aFe (0.028 - 0.045), K_aMn (0.183 - 0.83), K_aNi (0.016 - 0.041), K_aZn (0.011 - 0.072), much lower than the value of 1, except for Mn, which shows that heavy metals are not accumulated from the soil in the leaves. The higher values of K_aMn are explained by the fact that manganese and iron represent the most important pair of catalysts for redox processes in plants; manganese is a component of chloroplasts and participates in the photolysis of water [1, 22].

In summary, research on the distribution of heavy metals in the acacia leaf and in the soil collected from Dâmboviţa, Vâlcea and Argeş counties (thesis, chapter 4) showed that:

- All leaf samples have Fe concentration higher than the maximum allowed concentration (CMA) by Romanian and European legislation. Thus, 6 samples contain Fe in a concentration higher than the intervention threshold. In the case of the soil samples, 8 of them have a Zn concentration higher than the maximum level, but none of the samples exceeds the intervention threshold, and the Mn and Ni concentrations are lower than the CMA, according to the order 756/1997.

3b. The distribution of heavy metals in the soil samples collected from the main oil parks in Dambovita county [1, 23, 27].

For this study, samples were collected from the main parks oil tankers of Dâmboviţa county: Park 800 Doicesti, Park 35 Şotânga, Park 7Gheboieni, Park 2 AR Moreni and Park 2 EPS Moreni. The realization of the distribution was followed quantitative of heavy metals such as: Cr, Cu, Zn, Cd and Pb, in soil collected from the surface and respectively from the depth. The indexing of the samples is given in the tables below, (tables 1 - 5), together with the determined

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pH values. The pH values are correlated with the concentration of heavy metals present in samples [24, 28].

Table 1.   The pH of soil samples collected from Park 800 Doiceşti

Proba	D_1A	D_1B	D_2A	D_2	D_3A	D_3B	D_4A	D_4B	D_M	D_MB
pH	7.64	7.43	7.73	7.21	7.63	7.39	7.69	7.23	7.29	7.11

Table 2. The pH of soil samples collected from Park 35 Şotânga.

Sample	S_1A	S_1B7	S_2A	S_2B	S_3A	S_3B	S_4A	S_4B	S_MA	S_MB
pH	7.98	7.61	7.83	7.61	7.96	7.50	7.82	7.64	7.26	7.21

Table 3. The pH of soil samples collected from Park 7 Gheboieni.

Sample	G_1A	G_1B	G_2A	G_2B	G_3A	G_3B	G_4A	G_4B	G_MA	G_MB
pH	7.99	7.67	7.73	7.51	7.67	7.49	7.88	7.62	7.25	7.29

Table 4. The pH of soil samples collected from Park 2 AR Moreni.

Samplee	M1_1A	M1_1B	M1_2A	M1_2B	M1_3A	M1_3B	M1_4A	M1_4B	M1_M	M1_M
pH	7.98	7.69	8.01	7.66	7.89	7.25	7.88	7.55	7.33	7.18

Table 5. The pH of soil samples collected from Park 2 EPS Moreni.

Sample	M2_1A	M2_1B	M2_2A	M2_2B	M2_3A	M2_3B	M2_4A	M2_4B	M2_M	M2_M
pH	7.97	7.62	7.89	7.63	8.09	7.61	8.04	7.63	7.29	7.11

From the tables above it follows that the collected soil has a moderate pH - basic in the surface samples, moderate - basic and in the deep samples, with the exception of the Parcul 800 Doicesti area, where at depth the pH of the soil is weak - basic [1].

Using the AAS and EDXRF techniques [7, 26], 50 soil samples were analyzed, of which, 25 soil samples collected from the surface (0-20 cm) and 25 soil samples collected from the depth (20-40 cm), respectively. Concentrations of the following heavy metals were determined ; Cr, Cu, Zn, Cd and Pb. The concentration values, minimum, average and maximum, together with the values regulated by Order no. 756 of November 3, 1997, for the approval of the Regulation on the assessment of environmental pollution (VN-normal value, PM-maximum threshold, PI-intervention threshold, ME-European average) [23, 27], are centralized in table 6 for surface soil samples and in table 7for soil samples collected from depth.

Table 6. Results, heavy metal concentrations [mg/kg s.u.], obtained on surface soil samples.

| Heavy metal	Cr*	Cu	Zn	Cd*	Pb
Minimum value	1.29	20.88	133	1.33	18.97
Maximum value	2.68	39.56	397	2.87	24.54
Medium value	2.12	30.19	264	2.38	22.18
VN**	30	20	100	1	20
PM**	100	250	700	5	250
PI**	300	500	1500	10	1000
ME**	60	13	52	0.145	22.6

Elements whose concentration was determined by the AAS technique.

** Order no. 756 of November 3, 1997, for the approval of the Regulation on evaluation environmental pollution [27].*** http://weppi.gtk.fi/publ/foregsatlas/articles/Statistics.pdf [23].

Table 7. Results, heavy metal concentrations [mg/kg s.u.], obtained on deep soil samples.

Heavy metal	Cr	Cu	Zn	Cd	Pb
Minimum value	1.02	20.03	117	1.11	18.12
Maximum value	2.28	30.23	279	2.43	23.98
Medium value	1.67	24.22	202	1.86	21.12
VN**	30	20	100	1	20
PM**	100	250	700	5	250
PI**	300	500	1500	10	1000
ME**	62	13.9	47	0.090	17.2

Elements whose concentration was determined by the AAS technique.

** Order no. 756 of November 3, 1997, for the approval of the Regulation on evaluation environmental pollution [27].*** http://weppi.gtk.fi/publ/foregsatlas/articles/Statistics.pdf [23].

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The distributions of Cr, Cu, Zn, Cd and Pb concentrations, determined by the AAS and EDXRF analysis techniques, in the surface soil samples and in the deep soil samples, are given in Figures 1, 2, 3, 4, 5, respectively, 6, 7, 8, 9 and 10, together with the normal value provided by the Romanian legislation in force, as follows [1]:
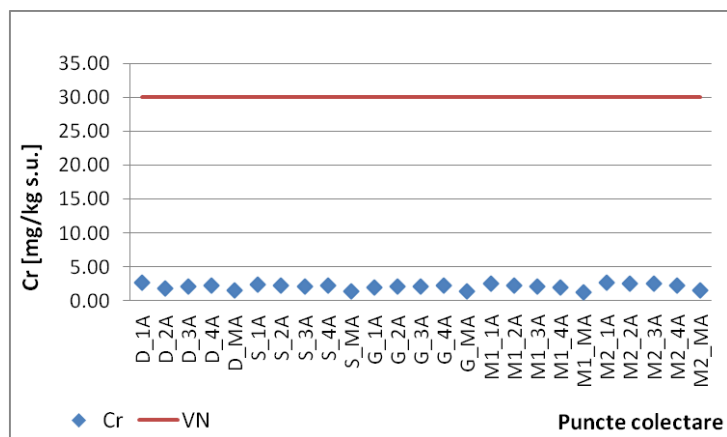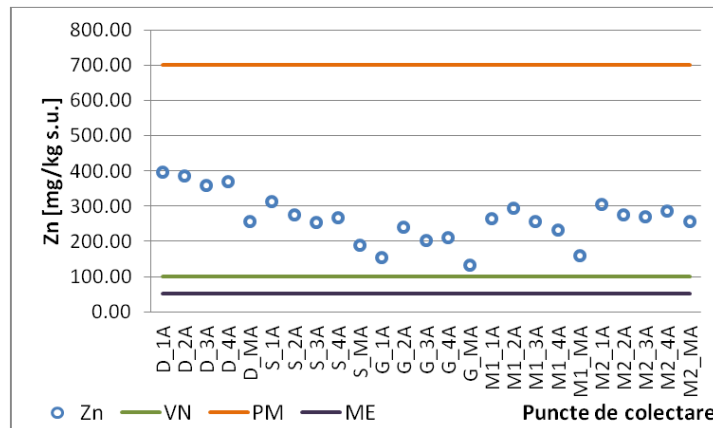

Figure 1. Quantitative distribution of Cr in surface soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

In the analyzed samples, from fig. 1, there is a concentration of Cr far below the normal value provided for in Romanian and European legislation.
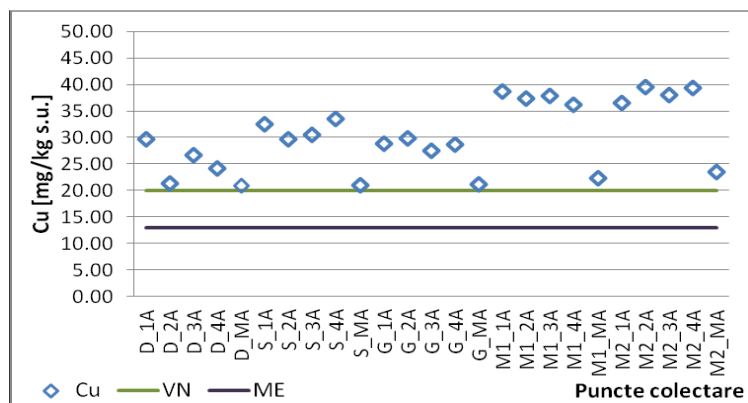
Figure 2. Quantitative distribution of Cu in surface soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

From fig. 2 results in an analyzed concentration of Cu, in the surface soil samples, with an insignificant exceeding of the normal value.
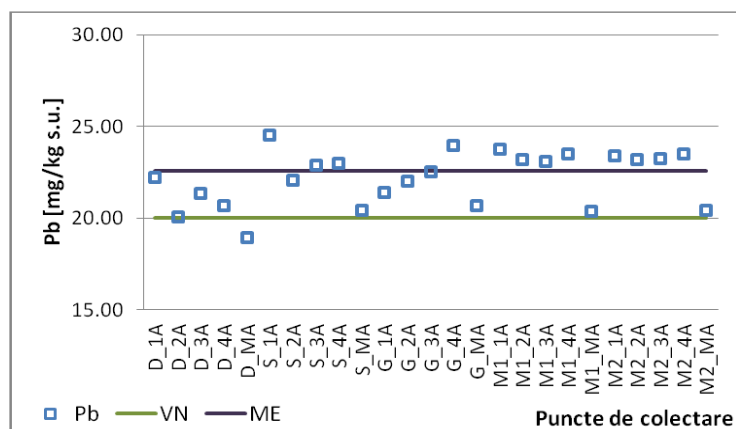

Figure 3. Quantitative distribution of Zn in surface soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

The concentration of Zn insignificantly exceeds the normal value and is located far below the maximum allowed threshold.
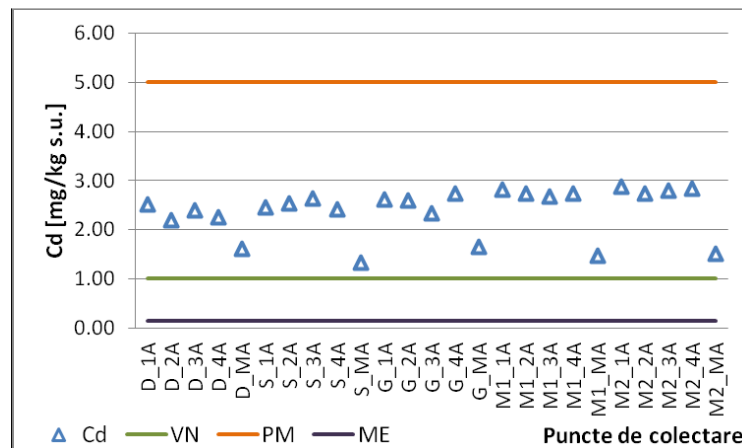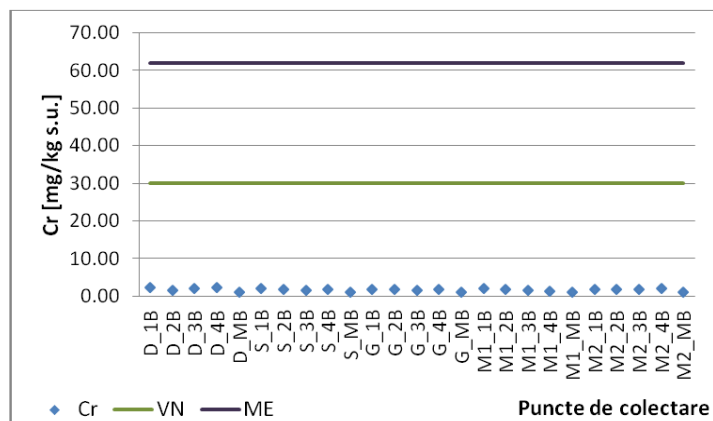

Figure 4. Quantitative distribution of Cd in surface soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

From fig. 4, shows that the value of the Cd concentration in the soil samples collected from the surface very slightly exceeds the normal value, but is far below the maximum allowed threshold.
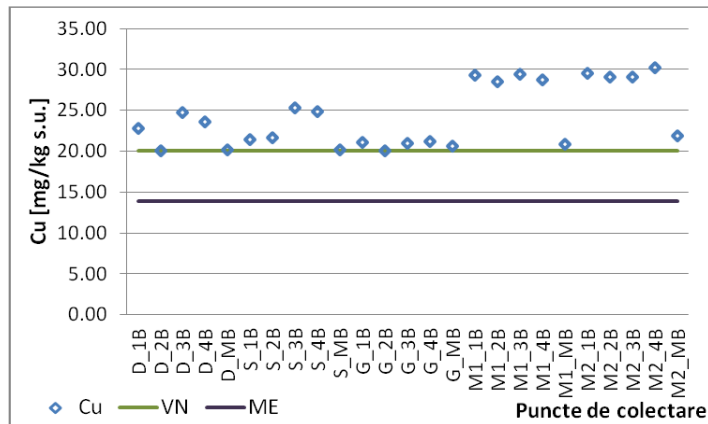
Figure 5. Quantitative distribution of Pb in surface soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

Figure 5 shows the quantitative distribution of Pb in surface soil samples from the studied areas, compared to the normal value provided by the Romanian legislation in force and the European average value.
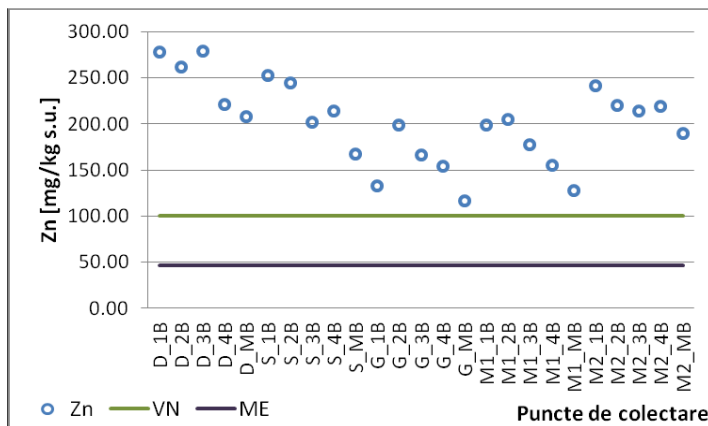

Figure 6. Quantitative distribution of Cr in deep soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

From (fig. 6) it follows that in the deep soil samples from the studied areas, the Cr concentrations are higher than the normal value provided by the Romanian legislation in force and the European average value.
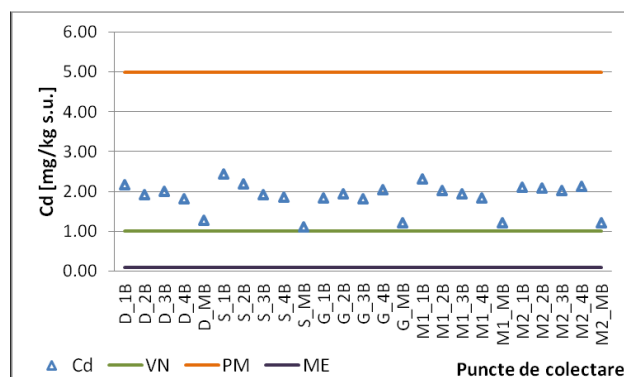
Figure 7. Quantitative distribution of Cu in deep soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value.

The quantitative distribution of Cu in the depth soil samples in the studied areas is given in fig. 7. The concentration values are statistically of the order of the normal value provided by the Romanian legislation and the average European value.
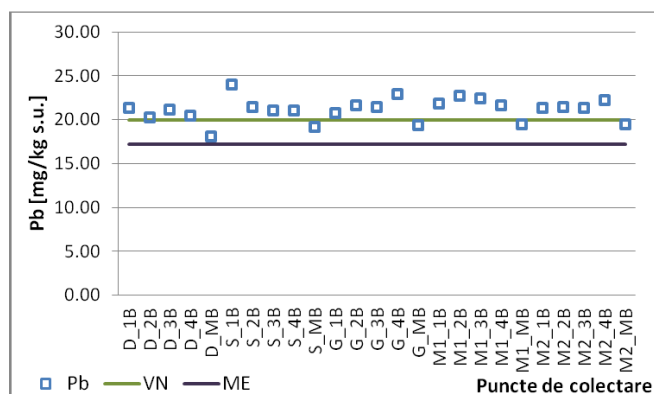

Figure 8. Quantitative distribution of Zn in   deep soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value..

The Zn concentration values (fig.8), from the deep soil samples collected from the studied areas, are, statistically slighltly higher than the normal value provided by the Romanian legislation in force and the European average value.

Figure 9. Quantitative distribution of Cd in deep soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value..

From figure 9 it can be seen that the Cd concentration values, in the deep soil samples from the studied areas, are approximately twice higher than the normal value and the maximum allowed threshold provided by the Romanian legislation in force and the European average value.

Figure 10. Quantitative distribution of Pb in deep soil samples from the studied areas, comparative with the normal value, according to the Romanian legislation in force and the average European value

The Pb concentration values (fig. 10), in the deep soil samples from the studied areas, are, statistically, of the same order of magnitude as the normal value provided by the Romanian legislation in force and the European average value.

In summary, it follows that,

a. from the analysis of soil samples taken from the surface:

The concentration of Cr in the soils taken from the surface has values between 1.29 mg/kg s.u. (minimum) and 2.68 mg/kg s.u. (maximum) with an

average value of 2.12 mg/kg s.u. It is found that the normal value regulated by Romanian legislation is twice lower than the average European value.

The concentration of Cu in the soils taken from the surface has values between 20.88 mg/kg s.u. (minimum) and 39.54 mg/kg s.u. (maximum) with an average value of 30.19 mg/kg s.u. does not registers a significant exceedance of the normal value.

The concentration of Zn in the soils taken from the surface has values between 256.70 mg/kg s.u. (minimum) and 397.10 mg/kg s.u. (maximum) with an average value of 264.26 mg/kg s.u. In the soil samples collected from the surface, the concentration of Zn insignificantly exceeds the normal value and is located far below the maximum allowed threshold. The highest concentrations were recorded in the Parcul 800 Doicesti area.

From the diagram, it can be seen that the value of the Cd concentration in the soil samples collected from the surface exceeds the normal value very slightly, but is located far below the maximum allowed threshold.The concentration of Cd in the soils sampled from the surface has values between 1.33 mg/kg s.u. (minimum and 2.87 mg/kg s.u. (maximum) with an average value of 2.38 mg/kg s.u.

The Pb concentration in the soils sampled from the surface has values between 18.97 mg/kg s.u. (minimum) and 24.54 mg/kg s.u. (maximum) with an average value of 22.18 mg/kg s.u. The Pb concentration is around the average European value but also the normal value in Romanian legislation.

b. from the analysis of the soil samples taken from the depth the following resulted:

The concentration of Cr in the soils taken from the depth has values between 1.02 mg/kg s.u. (minimum) and 2.28 mg/kg s.u. (maximum) with an average value of 1.67 mg/kg s.u. As in the case of the surface samples, the deep samples have a Cr concentration far below the normal value regulated by Romanian legislation but also compared to the European average.

The concentration of Cu in the soils taken from the depth has values between 20.03 mg/kg s.u. (minimum) and 30.23 mg/kg s.u. (maximum) with an average value of 24.22 mg/kg s.u.

 The concentration of Cu very slightly exceeds the normal value regulated by Romanian legislation. The highest value is recorded in the park area of Moreni, but it is far below the maximum allowed threshold.

 The concentration of Zn in the soils taken from the depth has values between 116.70 mg/kg s.u. (minimum) and 279.50 mg/kg s.u. (maximum) with an average value of 201.82 mg/kg s.u. It is found that, in the depth samples, the zinc concentration has a value slightly above the normal value regulated by the Romanian legislation, but it is far below the maximum allowed threshold. The highest values are recorded in the Parcul 800 Doicesti area.

The concentration of Cd in the soils taken from the depth has values between 1.11 mg/kg s.u. (minimum) and 2.43 mg/kg s.u. (maximum) with an average value of 1.86 mg/kg s.u. For the Cd concentration in the soil samples collected from the depth, a slight decrease of this value is observed. However, it remains slightly above the normal value regulated by Romanian legislation and compared to the European average, but well below the maximum threshold allowed.

The concentration of Pb in the soils taken from the depth has values between 18.12 mg/kg s.u. (minimum) and 23.98 mg/kg s.u. (maximum) with an average value of 21.12 mg/kg s.u. The concentration of Pb keeps approximately the same values in the case of depth samples as in the case of surface samples. This value is around the normal value regulated by Romanian legislation and very close to the European average.

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