Preliminary Data regarding the Content of Heavy Metals from the Soils of Târgu-Jiu Area

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This paper presents experimental studies regarding the determination of heavy metals content in soils from Târgu-Jiu. The soil samples were collected from four distinct points, and on two depth profiles: 0-10 cm, and 10-20 cm. Extraction using solution of H_2SO_4 98%, and H_2O_2 50% was performed with a Hach Digesdahl Mineralizer. Determination of Cd, Cu, Zn, Pb in soil extracts was performed by flame atomic absorption spectrophotometry, and a Perkin Elmer type atomic absorption spectrometer with graphite furnace was used for As determination. The experimental results indicate exceeding of the normal, heavy metals content, corresponding to the natural, and anthropogenic pollution.

Keywords: heavy metals, soil pollution, anthropogenic pollution

Soil is a vital component of the ecosphere together with the atmosphere and hydrosphere. Despite the vital importance of soil to ensure foods supply and raw materials for industry, nevertheless soil is subject to increased requests from all categories of activities, causing the closing of significant areas.

Natural and anthropogenic activities produce disruption of normal functioning of the soil as a biota in the various natural or artificial (anthropogenic) ecosystems that affect fertility and bio ability, both quantitatively and qualitatively [1].

Soils are generally subject to both a natural, and an anthropogenic deterioration.

Natural degradation occurs in many forms due to the internal factors related to the nature and evolution of Earth’s surface in different areas.

Anthropogenic degradation is due to external factors mainly related to human activities.

As many other areas from Romania, Târgu-Jiu area is facing with many problems in terms of soil pollution. Generally, soils in Târgu-Jiu area have low fertility, due to the presence of the secondary pedogenetic processes and the adverse physico - chemical characteristics (low humus content, presence of the mobile aluminium, high acidity, high colloidal clay content, and low edaphic volume). All these unfavorable characteristics, along with other factors, are reflected adversely on the crop development and thus in the yields obtained [2].

Even though, so far it was not made a mapping of soil polluted from anthropogenic sources, however, on Târgu-Jiu area this pollution is manifested in various forms.

In Târgu-Jiu area like in mostly urban areas the effect of heavy metals pollution over the environment is accentuated by the large number of stationary and mobile sources generating heavy metals in soil and the atmosphere [3-5]. Atmospheric deposition is an important source of heavy metals in soil and plants. Atmospheric transport of metals depends on the chemical properties of each metal. Some metals are transported as gases, or enriched particles (such as selenium, mercury, arsenic, antimony), others are transported as particles (cadmium, lead, zinc). Once they reached the soil, they can remain in its upper layers for a long time. Soil reaction to the heavy metal accumulation is different due to the time and soils quality [6]. Like in other urban areas, in Târgu-Jiu soil heavy metals come from various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion [7].

In case of Târgu-Jiu, soil pollution occurs primarily through uncontrolled waste disposal. The most affected area from this point of view is that from south of Târgu-Jiu located on the right side of Jiu river in the former town landfill area.

Another form of soil pollution in Târgu-Jiu area is that due to the particulate matter. Sources of particulate matter are residential heating, traffic, cement factories, power thermal plants. The content of particulate matter in soil depends on wind direction. Thus in case of Băresi cement factory high level of cement dust is achieved in the area surrounding the source of pollution with the highest level in the direction where wind has the highest frequency and intensity (south-west). Soil pollution with heavy metals has as effect decreasing of humification processes and organic matter decomposition, increasing of hidrolytical acidity and decreasing of base saturation level. In case of agricultural soils, the excessive accumulation of heavy metals leads to elevated heavy metal uptake by crops which may affect food quality and safety [8].

Deterioration of soil physical properties, decreasing of soil reaction, inhibiting activity of microorganisms, has as effect quantitative reduction of nutrients in the soil. Thus, soil becomes increasingly poor in nutrients, and unable to support large agricultural productions.

Concern about soil pollution with heavy metals is determined by the accumulation of them in large quantities in areas affected by air emissions. It is indisputable that heavy metal concentrations in urban soils are significant environmental issue, and a large number of researches have been conducted all over the world [9-13].

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In Târgu-Jiu area, an important source of soil pollution with heavy metals is Meteor area from Târgu-Jiu where are activities related to the metal smelting without comply with the most basic environmental standards. Pollutants resulted from metals smelting are: particles constituted from metal oxides that are smelted and that are resulted from oxidation and solidification in the air of metal vapor released; combustion gases containing sulfur and nitrogen oxides, particulate matter that are resulted from the burning fuel.

The assessment of pollution levels of heavy metals soil contamination is significant to human health and environmental management [14].

Cadmium is considered one of the most dangerous heavy metals being very toxic to humans and animals. Cadmium reaches the soil by using phosphorus fertilizers, and manure or by infiltration of waste. Depending on their origin, raw phosphates contain between 0.1 mg and 75 mg cadmium in 1 kg of phosphates. Around zinc smelters were recorded cadmium concentrations in soil and over 1700 ppm [2]. Soils with high adsorption capacity, for example, high clay and organic matter, may retain cadmium, and heavy metals in general, in the upper horizons.

Copper pollution affect physical and chemical properties of soil, in the sense of that soils polluted with copper have a lower percent of aggregates, a lower hydric stability of aggregates leading to the increase of susceptibility to erosion and compaction. Also, an increased copper concentration in the soil causes increasing of the mobile fraction of humus, changing of the composition of humus, hydrolytic acidification and reducing basic cations.

Zinc is an essential element for plants. It is absorbed by plants as zinc ions (Zn²⁺). Its solubility in soil is conditioned by several factors: the soil pH, other ions content, organic matter content. Its solubility is higher in acidic than in alkaline soils; it is set entirely in the soil at pH = 9. Zinc occurs in the soil generally in concentrations of 10-300 ppm, most commonly between 30-50 ppm [2]. For plants, zinc is toxic to higher levels of 400 ppm, probably due to the fact that it prevents the absorption of other essential elements.

Lead is commonly found in soil in amounts from 0.1 to 20 ppm [2]. Lead has adversely effects on the soil biological activity, inactivated yeast by reducing the intensity of carbon dioxide elimination and reduction of microorganisms number. Accumulation of lead in plants reduces oxidation processes, photosynthesis processes, and fats biochemistry.

Consequently the purpose of this research paper is to investigate the metal soil pollution from Târgu-Jiu area. Measurements performed in this area revealed high copper, zinc, lead and cadmium levels.

**Experimental part**

Samples were taken from four points in order to determine the content of heavy metals in soil. These points are: S1 - located in the southern city of Târgu - Jiu (Margaritarului Str); S2 - located in the west (the Meteor area); S3 - located in the east (the Drâgoieni area); S4 - located in the north - east (the ring area) (fig. 1). In each area, being collected samples at two depth profiles: 0 – 10 cm, and 10 – 20 cm.

The study was conducted during three consecutive years: 2009, 2010, and 2011.

Meteorological factors have a special importance due to the fact that air pollution with heavy metals influences heavy metal soil content. Thus climate data for Târgu-Jiu are:

- annual average temperature is 10.2°C;
- the average temperature of the hottest month is 21.6°C recorded in July, followed by August with 20.7°C;
- the average temperature of the coldest month is -2.5°C recorded in January, followed by February with 0.4°C;
- absolute maximum temperature is +40.6°C, and absolute minimum temperature is -31°C;
- the number of days with temperatures above 25°C is 102.7; from these 34.8 days are with temperatures above 30°C, and number of days with temperatures below 0°C is 107.5 – most of them being in December, January and February.

General climate factors, particular local ones are favourable due to the air circulation from lowland. Topoclimate is characteristic with predominant warm days, and with winters without blizzard. Winds are common in north-west – west and south-west. Annual precipitations are 753 mm, with an emphasized decreasing in recent years due to the climate changes characterized by lack of rainfall.

Soil nature is alluvial with low resistance unproper for large-scale buildings. Soil nature and climate factors influence heavy metals content in soils, especially air circulation and precipitations that influence deposition of particulate matter from air.
After sampling, soil samples were treated for analyzes performed according to standard ISO 11464/1998 - Soil quality. Pretreatment of samples for physico-chemical analysis [16]. Thus, soil samples were dried in an oven and crushed with an electric mill. The soil's pH was determined according to ISO 10390/1999 - Soil quality. The pH determination [17] using a JENWAY pH meter (Model 3051) calibrated with a buffer solution (pH 7).

Mineralization of soil samples for determination of heavy metals was performed according to the methodology described in the user manual of Hach Digesdahl Mineralizer using extraction with concentrated sulfuric acid and hydrogen peroxide 50%.

Soil samples weighing 0.5 g were placed into special mineralization flask, and 4 mL of concentrate sulfuric acid is added, and 15 mL of 50% H2O2 is added through the fractionation funnel after 5 min of boiling in Hach Digesdahl Mineralizer. Mineralization continues until the flask product no longer changes the colour. Soil samples obtained after mineralization were cooled, diluted with deionized water, and then filtered through filter paper. After filtration, volumetric flasks are brought to the mark with deionized water.

Cadmium, copper, zinc, lead, and arsenic content from soil extracts was determined using flame atomic absorption spectrophotometry [18].

For As, the result in mg kg⁻¹ dry substance is obtained directly from the analyzer.

Soil analyses performed during the three-year of study aimed to determine the level of loading of soil with heavy metals and comparing results obtained with standards.

Results obtained were analyzed according to the Order of the Ministry of Waters, Forests and Environmental Protection no.756/1997 for approving the Regulation on the Assessment of Environmental Pollution [15]. According to this order, each chemical element has three values: normal values, which correspond to background soil, alert threshold and action threshold.

Elements analyzed in each sampling point were: cadmium, copper, zinc, lead and arsenic content.

Soils analyzed from all four sampling points are the type of sensitive use. These are used for agriculture purpose. These are punctiform representing the state of soil pollution at the time of soil sampling.

In table 1 are presented results obtained for the soil samples from Târgu-Jiu area.

### Results and discussions

Analyzing the soil pH values from Tg - Jiu area, in all three years of study, it can be observed that in 2009, and 2010 these can be classified as weak acid because pH value ranging from 6.21 to 6.71 pH units. In 2011, it was observed an increasing trend of pH value towards neutral - slightly alkaline, most of value registered being above 7. The trend of the soil pH value in all three years of study is presented in figure 2.

![Fig. 2. pH variation in soil from Târgu-Jiu area](http://www.revistadechimie.ro)
The point S3 on the depth of 10-20 cm, and at the point S4 two depth profiles, and also was registered overtaking at normal limits. In 2010 remained overtaking for S2 on the direction (SW - southwest). In this area was registered sampling point (S2) is located on the predominant wind represented by non-ferrous metal smelters. The other where an important source of heavy metals pollution is attributed to the fact that S1 point is located in an area in S1, and S2 points on both depth profiles. This can be characteristic to normal copper content were overtaken limits and the threshold limits. Thus, in 2009 limits value three year study, it can be find that they are within normal intervention threshold of 200 mg/kg d.m.

Fig. 3. Cadmium content variation in soils from Târgu-Jiu area

Normal content of cadmium in soil is 1 mg/kg d.m. (dry matter) (1 ppm), and the alert threshold for sensitive uses is 3 mg kg d.m., and intervention threshold is 5 mg/kg d.m.

Values obtained for cadmium content in soils from Târgu-Jiu area indicate that they are mostly below normal content of 1 mg/kg d.m. (fig. 3).

As it can be seen in figure 3, it was registered only one overtaking of the normal value, which was registered for S2 sampling point (Meteor area) for the depth profile of 10 to 20 cm. Concentration determined was with 20% above the normal value. In 2009 year, cadmium content in soils for sampling points located to the east and northeast was zero. All remaining concentrations measured in the three years of study were between 10% and 80% of normal content. No exceeds, of the two thresholds: for intervention, and for sensitive uses, were registered.

Copper has a normal content in soils of up to 20 mg/kg d.m., an alert threshold of 100 mg/kg d.m. and an intervention threshold of 200 mg/kg d.m.

Evolution of copper concentrations in soils from different areas of Târgu - Jiu city is presented in figura 4.

Analyzing copper concentrations in the soil during the three year study, it can be find that they are within normal limits and the threshold limits. Thus, in 2009 limits value characteristic to normal copper content were overtaken in S1, and S2 points on both depth profiles. This can be attributed to the fact that S1 point is located in an area where an important source of heavy metals pollution is represented by non-ferrous metal smelters. The other sampling point (S2) is located on the predominant wind direction (SW - southwest). In this area was registered the highest copper concentration in 2009, this being 46% above the normal, but not exceeding the alert threshold. In the others areas, copper concentration in soil were in normal limits. In 2010 remained overtaking for S2 on the two depth profiles, and also was registered overtaking at the point S3 on the depth of 10-20 cm, and at the point S4 on both sampling depths. In S2 sampling point, (Meteor area) overtaking of limit value were between 1 and 10%. This time, the largest exceeds were recorded in S4, located on the ring from the north - east of the city of Târgu - Jiu. For profile 0-10 cm overcome was by 26% over the normal range and, for 10 to 20 cm profile, overcame was by 82% above this limit. In S1, copper concentrations in soil were within normal limits.

The highest concentrations of copper in soil were recorded during 2011. Overtaking was most significant for point S1, located in the south - east of the city. In this area, the values recorded for copper in soil were 263% above normal limit for the depth profile of 0-10 cm and 173% for 10 to 20 cm profile, without exceeding the alert threshold. It also remains overtaking for S2, and this time they were 8% and 32% above normal limits. In sampling point S3 copper concentrations were within normal limits, this being the only area where there have not been registered exceeding. In S4 sampling point, overtaking of the normal value was 69% for 0-10 cm soil profile, and 19% for 10 to 20 cm soil profile.

Zinc has a normal content, in the soil to 100 mg/kg d.m., a normal alert threshold of 300 mg/kg d.m., and an intervention threshold of 600 mg/kg d.m. for sensitive uses.

Zinc concentrations in the soil, recorded during the three years of study is situated in a very large range, which it shows in figure 5.

Thus, the highest concentrations of zinc in the soil were recorded in 2009, including exceeding the alert threshold. In all the four sampling points were exceeded the allowable normal value, and for two of them was exceeded the alert threshold. The highest concentrations of zinc were recorded in sampling point S2, located in the west of the city (the Meteor). In this area, the zinc concentrations in soil, for the two depth profiles exceeded the alert threshold for sensitive uses. Thus, in 0-10 cm depth profile value recorded was by 70% over the alert threshold and on the depth profile of 10 to 20 cm, approx. 6% above this threshold. In sampling point S3 zinc concentrations in soil were above normal value, but they were below the alert threshold. For 0-10 cm depth profile, exceeding of the normal value was approx. 93% and for the 10 to 20 cm depth profile by approx. 11%. At the sampling point, S4 was registered exceeding of both the normal and the alert threshold. Thus, for the soil depth profile (0-10 cm) the concentration of zinc exceeded the alert threshold of 12%, and for 10 to 20 cm depth profile zinc concentration was 124% above normal value.

The only sampling point where those not exceeding was that located in the south - east of the city (S1), where zinc concentrations in soil were below normal value, which is about 70%, 72% below it. In 2010 were the lowest values of zinc in the soil. Again, the highest concentrations were
still at the point S4, where the value for profile 0-10 cm was near the allowed limit, and for the profile, 10-20 cm was by 3.2% over the limit, which is only overcoming registered. The lowest concentrations were recorded at the point S3, for the two depth profiles being about 21% of the limit value. In other sampling points, concentrations recorded were about 30 and 60% below the limit value.

In 2011, concentrations of zinc in soil were lower than in 2009 but were above those of 2010. The highest concentrations were recorded throughout the sampling point S4, for the two depth profiles being above the allowable limit with 50%. The lowest concentrations were registered for the soil sample from Meteor area (S1), which are below the limit values allowed by approx. 60%.

Normal concentration of lead in soil is up to 20 mg/kg d.m., and alert threshold is 50 mg/kg d.m., and intervention threshold for sensitive uses is 100 mg/kg d.m.

Lead concentrations recorded during the three year study shows large variations and is presented in figure 6.

In 2009, all lead concentrations registered in the four sampling points were below the limit. Highest concentrations were found in the south – east sampling point (S1), and in the west sampling point (S2). In these areas, the values recorded on the two depth profiles were between 18 and 40% of the allowable limit. In other sampling points, lead concentrations were between 4.5 and about 12% of the limit. For 2010, recorded values are relatively higher than in 2009. Highest concentrations recorded were at point S2, and they represented 81% from the limit value for 0-10 cm depth profile, and 73% for 10-20 cm depth profile. In other areas of sampling concentrations ranged between 6.7 and 15% limit.

The highest concentrations of lead in soil were recorded in 2011 when on the three of the four areas analyzed concentrations were above the limit. Thus, the highest concentrations recorded during the three years of the study were at the sampling point S1, when on 0-10 cm depth profile, the threshold has been exceeded by 28%, and on the depth profile of 10-20 cm was exceeded limit value by 90%. Exceeding the normal value was observed at sampling points S2 and S3, these being with 2 and 106% above the normal limit. S4 sampling point was the only point where there were not exceeding for the two depth profiles. In this sampling point, lead concentrations were 73% and 86% below the normal limit.

Arsenic is found commonly in soil in amounts of from 0.1 to 20 ppm, reaching 8000 ppm in polluted soils. Arsenic, the tolerable limit in soil, according to some authors is 20 ppm, while others argue that at the 5 ppm mobile arsenic content in soil can be affected plant growth [2]. According to Order MAPPM no. 756/1997 normal value for arsenic in soil is 5 mg/kg d.s., and alert threshold for sensitive uses is 15 mg/kg d.m., and the intervention threshold is 25 mg/kg d.m.

Arsenic measurements were performed only during the years 2010 and 2011. Analyzing the values for the four sampling points and comparing them with existing regulations is found that there were no exceedance of the normal value of 5 mg/kg d.m. The variation of arsenic concentration in soil is presented in figure 7.

Relatively high concentrations were recorded in soil from sampling points S1 and S2. Thus, in 2010 on the 0-10 cm depth profile from the point S1, arsenic concentration in soil was 53.6% of normal value, and in 2011, it was 62.2%. At the sampling point, S2, on the same depth profile concentrations were in 2010 46% from normal value, and in 2011, 58.2% of normal value. The lowest concentrations of arsenic in soil were recorded at point S2 in 10-20 cm depth profile. For 2010, this represents 1.6% from normal value, and 2% from normal value in 2011.

Conclusions

The aim of this paper was to evaluate the soil pollution with heavy metals in the period 2009-2011. The main sources of soils from Târgu-Jiu pollution with heavy metals are: metal smelters, residential activities, atmospheric deposition, mining waste, industrial activities.

Results obtained from this research revealed that the pH of soils from Târgu-Jiu had a increasing tendency towards neutral, slightly alkaline in the period 2009-2011. This increasing was much higher during 2011.

The lowest concentrations of heavy metals in soil were recorded for cadmium and arsenic. During the three years of the study, was a single cadmium exceeding of the normal range for the sampling point S2 (the Meteor area), on the depth profile of 0-10 cm. This can be due to metals smelting.

Normal copper concentration in soil was exceeded on the points S1 and S2 for the year 2009. This can be attributed to the fact that S1 sampling point is situated near non-ferrous metal smelters, and the S2 sampling point is located on the predominant wind direction, and in an area with metals smelters. The highest concentrations of copper in soil were recorded during 2011 for the S2 and S4 (located in the north-east near ring area) sampling points.

Zinc has been exceeded both the normal value and the threshold values. Zinc content in soil is in a very wide concentration range. The highest concentrations of zinc were recorded in soil from the Meteor area (S2), in 2009, for the two depth profiles; they exceeded the alert threshold. Exceeding of the normal value was recorded in the eastern ring of Târgu - Jiu (S4), which is the only area where exceedance was maintained during the three years of study. In 2010 was determined the lowest values of zinc concentration in soil. For 2011 zinc concentration in soil was lower than 2009, but higher than 2010.
Lead presented variations of concentrations during the three years of study. For lead was registered exceeding of the normal value and the alert threshold. Any exceedance for lead was recorded in 2011, when for three (S1, S2, S3) areas analyzed, concentrations were above the normal, and S1 (0-10 cm) exceeded the alert threshold.

Arsenic is the only element of the analysis that has not been exceeded normal value in any of the areas analyzed. Relatively high concentrations were recorded in the South - East and West of Tg - Jiu (S1 and S2).

Thus, soil quality analysis performed in the four sampling points at two depth profiles (0-10 cm, and 10-20 cm) can be an important starting point for assessing heavy metals pollution in Târgu-Jiu area, and for establishing heavy metals impact to human health and environment.

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