

Arsenic and Antimony Content in Soil and Plants from Baia Mare Area, Romania

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Abstract: Problem statement: The objective of this research was to evaluate the degree of soil contamination with arsenic and antimony in Baia Mare, a nonferrous mining and metallurgical center located in the North West region of Romania. The soil in the area is affected by the emissions of powders containing metals from metallurgical factories. Previous studies indicated the soil contamination with copper, zinc, cadmium and lead, but there is few data about the actual level of soil pollution with arsenic and antimony. **Approach:** The soil samples were collected from 2 districts of Baia Mare: Ferneziu, which is located in the proximity of a lead smelter and Săsar district which is located along the Săsar River in the preferential direction of the wind over a metallurgical factory producing lead. As reference was considered Dura area located in a less polluted hilly area, in the west part of the town. Samples of soil and plants from the residential area of Ferneziu, Săsar and Dura districts were collected. The arsenic determination was carried out by inductively coupled plasma atomic emission spectrometry and the antimony determination by inductively coupled plasma mass spectrometry. **Results:** In Ferneziu area, the concentration of arsenic in soil ranged between 0.25 and 255 mg kg⁻¹. In Săsar district the arsenic concentration in the soil ranged between 5.5 and 295 mg kg⁻¹. Regarding antimony, in Ferneziu area the concentration ranged between 5.3 and 40.6 mg kg⁻¹; while in Săsar, antimony soils concentrations vary in the range: 0.9-18.4. Arsenic and antimony concentrations in plants were low for almost of the samples, both in Ferneziu and Săsar area indicating a low mobility of these elements in the studied soils. **Conclusion:** This study indicated the soil pollution with arsenic both in Ferneziu district and in Săsar district. The soil pollution with antimony was found especially in Ferneziu district.

Key words: Arsenic, antimony, soil, plant, polluted areas, statistic interpretation

INTRODUCTION

More and more studies have been lately published about the geochemical characterization of the soil and subsoil and about the differentiation of the additional contribution of metals and metalloids due to the ongoing human activities.

In this context, there is available data concerning the nonferrous metals content in soil and plants in the Baia Mare area which is significant for mining and metallurgical activities (Frentiu *et al.*, 2008; 2009;

Cordos *et al.*, 2007; Damian *et al.*, 2008), but only fewer works have investigated the Arsenic (As) presence and there is no paper referring to the content of antimony (Sb) in the soil in this area.

The researches conducted in Baia Mare area have highlighted multiple pollution by heavy metals (Pb, Cd, Zn, Cu) in the residential, agricultural and forestry soils felt at a distance over 25-30 km around the major pollution sources, as a consequence of the high emission levels and high frequency of exceeding the maximum admissible concentrations of Pb and Cd in

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the ambient air. Air pollution and dust deposition are favored by the local weather conditions resulting from the geographical position and topography of the area. The atmospheric calm and generally low wind speed ($<2.5 \text{ m sec}^{-1}$) characteristic for a period of approximately six months in the cold period of the year lead to a very poor ventilation of the area and to a very low capacity of dispersion of pollutants in the atmosphere.

The activities connected to the non-ferrous metallurgy are, due to their emissions in the air, important sources of soil pollution. Heavy metal pollution around metallurgical plants is often accompanied by pollution with As and Sb considering the fact that usually these elements accompany non-ferrous minerals (Nakamaru *et al.*, 2006; Tighe *et al.*, 2005). Generally, the pollution sources with As and Sb are represented by the metallurgical plants, ore preparation plants and the use of organic fertilizers.

The terrestrial abundance of arsenic is about 1.5-3 mg kg^{-1} and it is derived from natural and anthropogenic sources. Arsenic is a metalloid that occurs naturally, being the 20th in terms of abundance in the earth's crust. Arsenic and its compounds present environmental mobility. Natural oxidation of rocks transforms the arsenic sulfides in arsenic trioxide, which enters in the arsenic cycle in the form of powder or dissolved in rainwater, rivers or groundwater. Arsenic may enter in the food chain through plants or animals (Mandal and Suzuki, 2002).

Antimony is present in polluted soils mainly in immobile form. In contrast, in the areas with high mobile antimony a considerable accumulation in some plant is observed, especially in the leaves of spinach, but there are very few data on antimony accumulation in plants (De Gregori *et al.*, 2004). The abundance of antimony in the earth's crust is 0.2 mg kg^{-1} and the background concentrations in soils are in the range of $0.3\text{-}8.4 \text{ mg kg}^{-1}$ (He, 2007).

The biogeochemical behavior of antimony is less studied, but there is some evidence showing that it is similar to arsenic with which it is often associated in nonferrous ores. Both elements exist in either oxidation state +3 or +5, the latter being widespread in oxidizing conditions. The labile concentrations of Sb and As in soils are probably controlled by adsorption-precipitation reactions with the oxides from the clay surface and with the Fe, Al or Mn oxyhydroxides (Casado *et al.*, 2007).

The mineral assemblages from Baia Mare area include native elements (Au, Ag, Cu, As, S), sulphide minerals (pyrite, chalcopyrite, arsenopyrite, sphalerite, galena, stibnite) sulphosalts (tetrahedrite, jamesonite,

semseyite, pyrargyrite) and tungstates (wolframite, scheelite), together with quartz, clay minerals, adularia, carbonates, rhodonite and barite as gangue minerals (Grancea *et al.*, 2002).

Baia Mare was and still is a hot spot on the map of soil pollution with non-ferrous metals such as Pb, Cu, Cd, and Zn. The main sources of soil pollution have been and still are the particle emissions from metallurgical plants in the city, which besides the heavy metals listed above contain also As and Sb.

As regards the origin of arsenic species it is known that the non-Ferrous ores in the area contain Arsenic-Sulfides (FeAsS), which are processed by frying forming the volatile As_2O_3 that can be oxidized to FeAsO_4 and exhausted with ash particles. The particulate matter emitted is falling not only in the vicinity of plants but also in other areas in the city (Cordos *et al.*, 2006).

Currently, the metallurgical industry has considerably reduced its activity by closing or reducing its production capacity. However, Baia Mare has to face the historical soil pollution.

In the areas of industrial impact in Baia Mare, the soil contains between 10 and 1725 mg kg^{-1} As, of which over 90% is inorganic As (V) (Frentiu *et al.*, 2009). Similar results have been obtained by determining As in a network of 35 sampling points in the city of Baia Mare, on samples from 20 cm depth where the concentration of As ranged between 22.6 and 1910 mg kg^{-1} (Miclean *et al.*, 2008). Large amounts of non-ferrous metals in the soil, including the significant presence of As may indicate a severe situation that requires urgent actions in order to reduce the pollution and remediate the contaminated sites. These data should be connected with the possible presence of these metals in plants, which favors their uptake.

MATERIALS AND METHODS

Location of the studied area: The soil and plant samples had been collected from 2 zones of the Baia Mare municipality (Fernezium district and Săsar district), where, as shown in previous studies, higher concentrations of heavy metals have been found in the soil, as a consequence of the falling dust containing metals from direct, diffuse or fugitive emissions from the metallurgical plants from the area (Damian *et al.*, 2008). For the comparative analysis of the data, also a reference zone had been selected (Dura area). The zones of interest for the present study have been marked on the map in Fig. 1.



Fig. 1: Map of the studied areas

Soil and plant sampling: The soil samples had been taken during July-August 2009 from a depth of 0-10 cm and each soil sample was accompanied by a sample of the plants growing on it. The soil samples were collected from several locations representing garden soils, residential area soils and industrial area soils. The plant samples from the garden soils were vegetables used in human alimentation as onion (*Allium cepa*) and dill (*Anethum graveolens*); while for the other locations the plant samples had been collected from the spontaneous flora (*Agrostis*, *Agropirum*, *Trifolium repens*, *Urtica dioica*). The samples were conditioned and prepared in laboratory for the determination of pH in the aqueous extract of the soil and of the As and Sb content. The locations for sampling have been chosen in each studied zone by drawing an imaginary area of 1 m² on whose diagonal 3 samples of approximately 0.5 kg have been extracted from a depth between 0-10 cm, out of which through mixing and homogenization the representative sample had been obtained. In the same time, there had been collected aerial parts of the plants growing in the locations from where the soil samples had been drawn, with the exception of the onion whose bulb had been also collected.

Samples preparation: The soil samples were crushed and dried at room temperature for 48 h, then passed through a 2 mm sieve. Thus from the processed sample a sub-sample of 100 g was obtained through the method of quarters, which was at its turn milled and passed through a sieve of 100 microns. From this sub-sample 2 g of soil were taken and subjected to mineralization with aqua regia according to ISO 11466: 1999. The plant samples were intensely rinsed with tap water and deionized water and were dried in oven at a temperature of max. 40°C, broken up, homogenized, passed through

a 0.1 mm sieve. All the soil and plant samples had been kept in sealed and carefully labeled plastic bags. The plant samples were digested in aqua regia following the method from ISO 11466: 1999. A quantity of 1 g soil sample was subjected to extraction with aqua regia and hydrogen peroxide. The content of As and Sb in the obtained extracts was determined by spectrometric methods.

Samples analysis: The pH measurement of the aqueous suspension 1:5 (w/v) of the <2 mm fraction of the soil samples was performed. The pH was measured with Consort 2000 pH-meter equipped with a combined pH electrode. The distilled water used for the preparation of the suspension had been previously boiled and cooled. The determination of As was made using the inductively coupled plasma atomic emission spectrometer, ICP-AES, with simultaneous detection Optima 5300 DV (Perkin Elmer), with axial and radial dual vision, while for the determination of Sb the ELAN DRC II (Perkin Elmer) inductively coupled plasma atomic emission spectrometer, ICP-AES was used.

The reagents used during the process were of analytical grade: Concentrated nitric acid, concentrated hydrochloric acid and 30% hydrogen peroxide from Merck (Germany). For the dilution ultra pure water obtained through a Direct Q3 Millipore system was used. The calibration was made using monoelement As and Sb standards of 1000 µg mL⁻¹ (Merck, Germany). The calibration solutions were prepared by dilutions with 2% HNO₃ (v/v).

RESULTS

The As and Sb average contents and their variation range in the soil and plant samples are presented in Table 1. The average content of As in the soil of Ferneziu district, in the close vicinity of the metallurgical plant that produces primary lead was 53 mg kg⁻¹. In the residential area from the central and north-west part of the city (Săsar district) the average content of As in the soil samples was almost double, respectively 102 mg kg⁻¹. As compared to the values admitted by the current legislation of Romania, in Ferneziu district 50% of the samples had a higher content than the alert threshold (15 mg kg⁻¹) and 25% of the samples had a content that exceeded the intervention threshold (25 mg kg⁻¹) and in Săsar district the content of 70% of the samples exceeded the alert threshold and the content of 60% of samples was above the intervention threshold. In both studied areas the assessed contents of As were scattered over a relatively larger area than the average.

Table 1: As and Sb contents in soil and plant samples

Parameter	Ferneziu area (n ^a = 8)	Săsar district area (n ^a = 10)	Dura area (n ^a = 5)
As in soil (mg kg ⁻¹)	53/2.4-255 ^b	102/5.5-295	0.73/0.25-1.25
As in plants (mg kg ⁻¹)	0.99/0.22-5.33	0.63/0.11-1.45	0.36/0.29-0.43
Sb in soil (mg kg ⁻¹)	21/5.3-40.6	6.0/0.9-18.4	under DL ^c (0.5)
Sb in plants (mg kg ⁻¹)	0.05/0.02-0.14	0.03/0.02-0.08	under DL ^c (0.015)
pH in soil (units of pH)	6.9/5.7-7.5	6.0/4.5-7.2	5.8/5.6-6.0

^a: Number of samples; ^b: Average/min-max value; ^c: DL detection limit

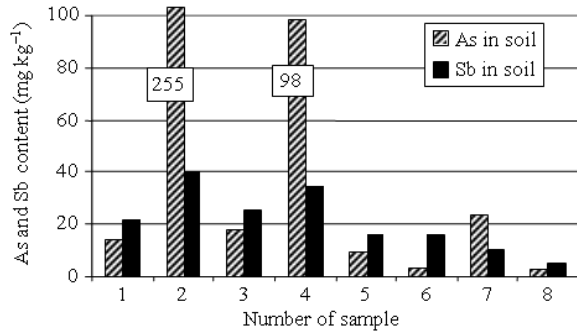


Fig. 2: As and Sb content in the soil samples from Ferneziu district

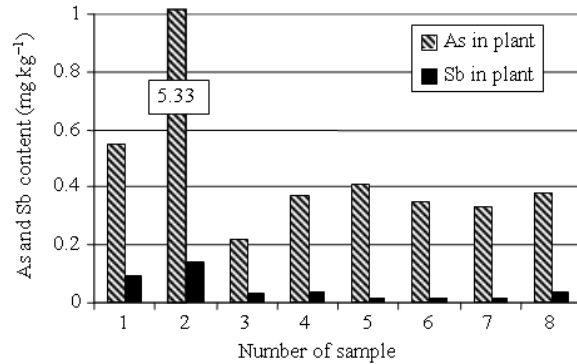


Fig. 3: As and Sb content in the plant samples from Ferneziu district

The As and Sb content in the soil and plants samples from the studied areas are represented in the graphs from Fig. 2 and 3 (Ferneziu district) and Fig. 4 and 5 (Săsar district).

As concerns Sb the situation was different, higher concentrations had been found in the Ferneziu district, near the metallurgical plant. The average content of Sb in Ferneziu district was 21 mg kg⁻¹, while in the central and north-west residential area of the city (Săsar district) the average content of Sb was 5.5 mg kg⁻¹; in comparison with the values admitted by the current legislation, in the Ferneziu district 88% of the samples had a content of Sb exceeding the alert threshold (12.5 mg kg⁻¹) and 50% of the samples had a Sb content that was above the intervention alert (20 mg kg⁻¹),

Table 2: Pearson's correlation coefficients (r) of As and Sb in soil and plants and pH of soil

	As-S ^a	As-P ^b	Sb-S ^c	Sb-P ^d	pH
As-S ^a	1	0.523*	0.453*	0.368	-0.158
As-P ^b		1.000	0.509*	0.800*,**	-0.297
Sb-S ^c			1.000	0.538*,**	0.429
Sb-P ^d				1.000	-0.093
pH					1.000

^a: As in soil; ^b: As in plant; ^c: Sb in soil; ^d: Sb in plant; *: Significant on the level of probability 0.05; **: Significant on the level of probability 0.01

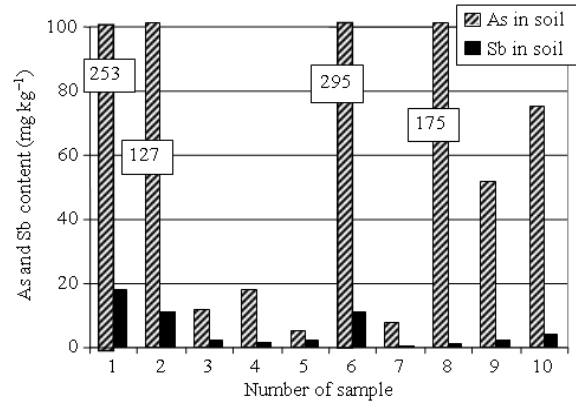


Fig. 4: As and Sb content in the soil from Săsar district

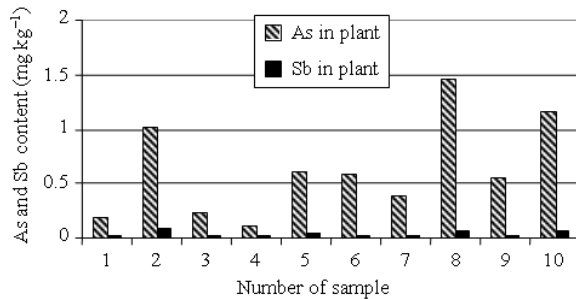


Fig. 5: As and Sb content in the plants from Săsar district

as to the Săsar district, 10% of the samples were above the alert threshold and the content of none of the samples exceeded the intervention threshold.

The domain of variation of the Sb contents was more limited in both studied areas in comparison with

the variation domain of As. Generally, the Sb contents were 3-15 times lower than those of As, in the way in the earth crust the As:Sb ratio is 10:1.

The highest As content in plants were found in the samples from Ferneziu district, the average content being 0.99 mg kg^{-1} , while 25% of the samples had a higher content than 0.5 mg kg^{-1} , which is the limit admitted by the Romanian legislation for the content of As in the plants used as food products. In Săsar district, the average As content in plants was 0.63 mg kg^{-1} and 60% of the samples had a higher content than the admitted limit, while in the Dura reference zone, the average content of As in plants was 0.36 mg kg^{-1} and all the contents in plants were less than the admitted limit of 0.5 mg kg^{-1} . The highest As concentration in plants recorded in Ferneziu district was 10.7 times higher and in the center of the city the content of As in plants was maximum 3 times higher than the admitted limit.

The highest content of Sb in plants had been found also in the samples from Ferneziu district, the average concentration being 0.05 mg kg^{-1} . In Săsar district, the average content of Sb in plants was 0.03 mg kg^{-1} and in the Dura reference zone, the Sb content in the plant samples was below the quantification limit of the analysis method (i.e., less than 0.03 mg kg^{-1}).

Table 1 presents also the pH values of the studied soil samples. The majority of the soil samples have an average of slightly acid pH. The highest acidity is found in the samples from the reference zone and it diminishes as one comes closer to the polluting source. Around the metallurgical plant, the average pH of the soil samples was 6.9 (the variation domain between 5.7 and 7.5).

The low contents of As and Sb in plants in comparison with the much higher contents from the soil may suggest a potential inhibition of their transfer due to the other metals abundant in the soil in the zone (Pb, Cu, Zn, Cd). It has been demonstrated that the plants' absorption of Zn from the soil inhibits that of cadmium, but has no effect on the Mn and Cu absorption (Wu *et al.*, 2003).

DISCUSSION

Taking into consideration the limited number of samples and locations under study, for the interpretation of the data we have used the boxplot type of diagram that offers information concerning the central tendency and form of the studied distribution. The boxplot diagram reflects graphically the summary through 5 values of the studied distribution: the minimum value,

the first quartile Q1 (25%), the median, the third quartile Q3 (75%) and the maximum value. The graphic represents also the values situated outside the distribution (outliers). The values higher than $Q3+1,5IQR$ and lower than $Q1-1,5IQR$ are considered aberrant values/outliers. The IQR interval is the one between Q3 and Q1 and is graphically represented by a rectangle (box). Inside it is the median graphically represented by a horizontal line. The intervals (Xmin, Q1) and (Q3, Xmax) are represented each by a line („moustache”) as an extension of the rectangle. The aberrant values are represented by void circles.

Figure 6 and 7 represent the boxplot diagrams for As and respectively Sb in Soil (S) and Plant (P) samples from the studied areas. The representation of boxplot diagrams in Fig. 6 and 7 shows a homogeneity of the As and Sb contents in plants in all the studied areas, while the soil contents vary in a wide range of limits, except the Dura reference area.

The Pearson's correlation analysis as shown in Table 2 (Pearson r coefficient) between As and Sb content in soil and plants as well as pH of the soil had been also made, using the statistical instruments offered by Windows Excel. A strong positive correlation between As and Sb contents in plants was noticed. A significant correlation both for the probability levels $p < 0.05$ and $p < 0.01$ was observed between the Sb content in the soil and in the plants.

In the same way, for a level of probability $p < 0.05$, we can notice a positive correlation between As contents in soil and in plants, as well as for the As and Sb contents in the soil. No correlation has been obtained for the As and Sb content in the soil and respectively in the plants with the pH of the soil.

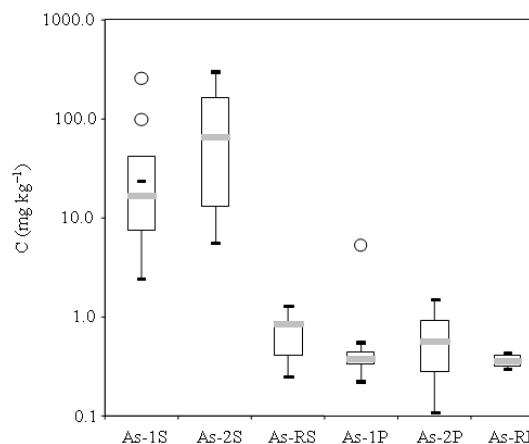


Fig. 6: Boxplot diagram for As in Soil (S) and Plant (P) samples in the studied zones; (1) Ferneziu district; (2) Săsar district; ® Dura reference area

Table 3: Comparison of As and Sb content in soil and plants found in Baia Mare area with other studies

Location of the studied area	As (mg kg ⁻¹)		Sb (mg kg ⁻¹)	
	In soil	In plants	In soil	In plants
Germany (mining site) (Hammel <i>et al.</i> , 2000)			Max 500	0.09-2.2
Poland (metallurgical site) (Gal <i>et al.</i> , 2006)	3.13-9.16			
Spain (mining site) (Casado <i>et al.</i> , 2007)	42-4530	0.02-2.77	60-230	0.002-4.25
Scotland (mining site) (Gal <i>et al.</i> , 2006)	17.4-50		1.19-10	
Italy (mining site) (Gal <i>et al.</i> , 2006)	16-691		1.63-11.44	
Bulgaria (reference soil) (Kabata-Pendias and Pendias, 2001)			1.25-2.32	
England (reference soil) (Kabata-Pendias and Pendias, 2001)			0.29-1.3	
Norway (reference soil) (Kabata-Pendias and Pendias, 2001)			0.17-2.2	
China (metallurgical site) (He, 2007)			100.6-5045	
Australia (mining site) (Sultan, 2007)	7.44-395.8			
New Jersey (chemical pesticides with As) (Cheng <i>et al.</i> , 2007)	3.8-387			
New Jersey (reference soil) (Cheng <i>et al.</i> , 2007)	1.6-4.6			
Canada (reference soil) (Kabata-Pendias and Pendias, 2001)			0.05-2.0	
Brasilia (in park) (Figueiredo <i>et al.</i> , 2007)	11.5-21.5		1.4-2.5	
Mexico (mining site) (Rosas <i>et al.</i> , 1999)	Max 30	0.24-3.06		
Romania, Present study (mining and metallurgical site)	2.4-295	0.11-5.33	0.85-40.6	<0.03-0.14
Romania, Present study (reference soil)	0.25-1.25	0.29-0.43	<0.5	<0.03

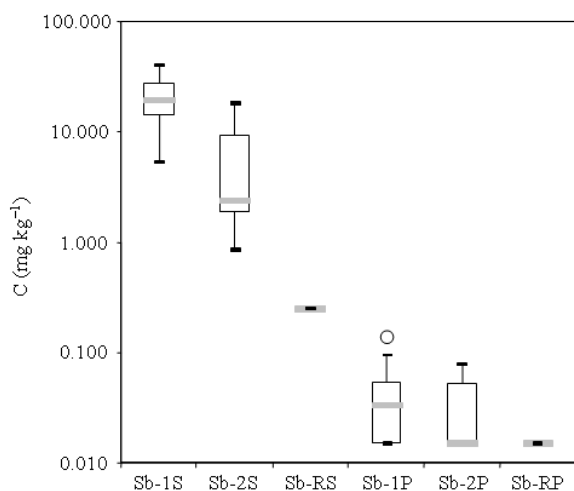


Fig. 7: Boxplot diagram for Sb in the Soil (S) and Plant (P) samples from the studied areas; (1) Ferneziu district; (2) Săsar district; (R) Dura Reference area

The results show the existence of a correlation between the As and Sb contents in the soil and respectively in the plants, taking us to the presumption that these elements follow a common cycle between the polluting source, soil and plant. It is generally accepted that in the process of the absorption of metals from the soil by plants the dominant factor is the metal content from the soil, but in the same time it can be affected by other factors as well including the pH of the soil (Jung and Thorntorn, 1996).

In this context it is of interest that there is no correlation between the studied content of microelements from the soil and plants and the pH of the soil, although recent studies have concluded that the pH can be the most important factor that determines the metal absorption by the plants from the soil (Kirkham, 2006; Jung, 2008). But the soluble forms of Sb, especially Sb (V) are absorbed from the surface of minerals and the process of adsorption is favored by the acidic pH and the oxidizing conditions (Casado *et al.*, 2007).

Through the regression analysis a significant statistical correlation has been obtained ($p < 0.05$) only between the As and Sb contents in plants (the construction of the regression line, $y = 0.0465x + 0.0052$ cu $R^2 = 0.5942$), according to the graphic representation from Fig. 8. Other research studies have shown also poor correlations between the total content of elements from the soil and their content in the plants, the absorption from the soil being more plausibly controlled by the soil solution composition (Chojnacka *et al.*, 2005).

Comparing the results obtained in this study for the As and Sb content in the soil and in the plants, in the areas with anthropogenic impact and the reference areas, one can notice that these follow the same tendencies as in other countries in Europe or the rest of the world, taking into consideration for each area the specificity of the impact of the predominant anthropogenic activities. The comparative data is represented in Table 3.

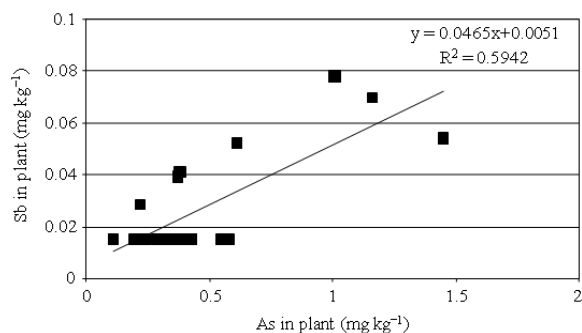


Fig. 8: The relation between As and Sb in the plant samples from the studied areas

CONCLUSION

The study presents original results on the soil pollution in Baia Mare area as regard to the As and Sb contents in soil and plants. It should be highlighted that no results concerning the content of Sb in soil and plants in Baia Mare area have been previously reported in scientific papers.

Hence, the following conclusions can be drawn up:

The average content of As in the soil of Baia Mare area (Ferneziiu and Săsar districts) exceeded the intervention threshold (25 mg kg^{-1}), while the average content of Sb in the soil exceeded the intervention threshold (20 mg kg^{-1}) only in the Ferneziiu district. Generally, the Sb contents were 3-15 times lower than those of As.

Most of the soil samples have slightly acidic pH. The highest acidity is found in the samples from the reference zone and it diminishes as one comes closer to the polluting source.

The highest As concentration in plants recorded in the Ferneziiu district was 10.7 times higher than the admitted limit and in the center of the city (Săsar district) the content of As in plants was maximum 3 times higher.

The Boxplot diagrams show the homogeneity of the As and Sb contents in plants in all the studied areas, while the soil contents vary in a wide range of limits, except the Dura reference area.

The Pearson's correlation analysis shows the correlation between the As and Sb contents in the soil and respectively in the plants. Hence we can presume that these elements follow a common cycle between the polluting source, soil and plant.

A significant statistical correlation has been obtained ($p < 0.05$) only for the As and Sb contents in plants through the analysis of regression.

Comparing the results obtained in this study for the As and Sb content in soil and plants in the areas with

anthropogenic impact and the reference areas, one can observe that these follow the same trends as in other countries in Europe or worldwide.

The results of the present study reveal the low bioavailability of Sb and As in the soil within the studied areas and the importance of establishing the transfer coefficients from soil to plant for these elements as a real indicator for the soil pollution level.

ACKNOWLEDGEMENT

The present researches were supported by the Romanian Ministry of Education and Research, within the PNCDI II Program (Project CISPPA no. 52157/2008).

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