# XRF-AAS ANALYSIS OF HEAVY METALS IN SOILS AROUND OF A FERROUS METALLURGICAL PLANT IN EASTERN PART OF ROMANIA

Ene A.[1], Stihi C.[2,3], Popescu I.V. [2,3,4], Bosneaga A.[1], Radulescu C.[2,3] , Gheboianu A.[3]

[1] Physics Department, Faculty of Sciences, „Dunărea de Jos” University of Galati, 111 Domneasca St., 800201 Galati, Romania
[2] “Valahia” University of Targoviste, Faculty of Sciences and Arts, Sciences Department, 2 Carol I street, 130022, Targoviste, Romania
[3] “Valahia” University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 130024, Targoviste, Romania
[4]Academy of Romanian Scientists, Bucharest, Romania

**Abstract**

The main objective of this paper is to determine the level of soil pollution with some heavy metals (HM) and lithogenic elements in the vicinity of Iron and Steel Integrated Works at Galati, Romania which is one of the most important metallurgical complexes in the South-East of Europe and represents a great potential of environmental contamination.

The concentrations of HM in the soil samples were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) technique and Atomic Absorption Spectrometry (AAS) at “Valahia” University of Targoviste. For Zn and Pb the results obtained in this work were compared with those previously reported using a portable XRF spectrometer NITON XLj at Dunarea de Jos” University of Galati. The concentrations of heavy elements decrease with the distance from the metallurgical works and they are greater than the ones detected in the control soil sample collected from a zone situated far from traffic and industrial activity. For the majority of metals, pronounced maximum concentrations for all depths were detected in the locations near the South gate of the integrated works, in the prevailing wind direction. The soils located in influence zones of industrial objectives with ferrous processing activities recorded heavy metals loading (contamination) or pollution. The soil heavy metal concentrations were compared with the maximum values admitted by the Romanian guideline (O.M. 756/03.11.1997).

## 1. INTRODUCTION

The most important sources of heavy metals in the environment are the anthropogenic activities such as mining, smelting procedures, steel and iron industry, chemical industry, traffic, agriculture as well as domestic activities. Chemical and metallurgical industries are the most important sources of heavy metals in soils. The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity, plant growth, etc [1-3].

The main objective of this paper is to determine the level of soil pollution with some heavy metals, in the vicinity of Iron and Steel Integrated Works (ISIW) at Galati, Romania, whose activity has lasted since 1965, being one of the most important metallurgical complexes in the South-East of Europe and representing a great potential of environmental contamination. Galati is a city in Eastern part of Romania (Moldavia region) with a total population of 291,354 (in 2009), on the banks of the Danube, very close to Braila county.

The attractiveness of non-destructive methods and the ability to perform simultaneous multi-elemental determinations has led to an extensive application in industrial and research laboratories of accurate, precise and sensitive atomic and nuclear analytical techniques for the investigation of different types of materials (industrial, geological, archaeological, biological, environmental, etc), such as neutron activation analysis (NAA), X-ray fluorescence (XRF) and particle-induced X-ray emission (PIXE). For the analysis of environmental samples, XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation [4-8]. XRF technique is a promising analytical technique for simultaneous determination of chemical composition in different vegetation species as an alternative to the classical destructive analytical methods, such as Atomic Absorption Spectrometry (AAS) [8].

The main goal of the present research was to use XRF and AAS techniques in order to assess the heavy metals distribution in some areas near the industrial complex of Galati, Romania, and to compare the soil heavy metal concentrations with the maximum values admitted by the Romanian guideline. The soils investigated in this work were sampled from the vicinity of the contaminated area from the Iron and Steel Integrated Works (ISIW) at Galati, from a district of Galati town (site 4) and three communes: Vadeni – sites 1a, 1b and 1c; Sendreni (localities: Sendreni – sites 2a and 2b; Movileni village – site 2c) and Smardan (localities: Smardan – site 3a; Mihail Kogalniceanu village – sites 3b). Also, a control soil sample was collected from a zone situated far from traffic and industrial activity, in the North of the Galati county, in Adam village, Draguseni commune (control sample No. 5).

This study is part of a partnership project funded by National Plan of Research, Developing and Innovation, of implementation of high precision and sensibility methods for the bio-monitoring of the environmental pollution in South, South-East and Central regions of Romania (Project 72-172/2008). It will be continued with moss biomonitoring of air pollution in some regions of Romania, in the frame of a 2010 bilateral project JINR-Romania, “Nuclear and related analytical techniques for Environmental and Life Sciences”, Theme no. 03-4-1036-2001/2010, the Romanian consortium being formed by four Universities - Targoviste, Galati, Iasi and Baia Mare.

## 2. EXPERIMENTAL RESEARCH

The collected soil samples were dried and all the roots and rocks were removed from the samples. A quantity of soil was grinded and sieved using a sieve of 250 μm. The concentrations of Cd and Se in the samples were determined by AAS using the AVANTA GBC spectrometer from Valahia University of Targoviste, with flame and hollow cathode lamps (HCL). The dried samples were digested in an acid solution using a Berghof MWS-2 microwave digestion system. The soil samples (2g) were introduced into the digestion vessels together with 3 mL nitric acid and 9 mL hydrochloric acid (aqua regia). After a digestion time of 30 min the vessels have been cooled to room temperature and the clear solution volume was made up to 50 mL for each sample using deionised water. Determination of elemental concentrations in soil samples was performed using the method of calibration curve according to the absorber concentration. Several standard solutions of different known concentrations have been prepared and the elemental concentration in unknown sample was determined by extrapolation from the calibration curve. The concentrations of Zn and Pb in the soil samples were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) technique, using the ELVAX spectrometer from Valahia University of Targoviste, having a X-ray tube with Rh anode, operated at 50 kV and 100 μA. Samples were excited for 300 s and the characteristic

X-rays were detected by a multichannel spectrometer based on a solid state Si-pin-diode X-ray detector with a 140 μm Be window and a energy resolution of 200 eV at 5.9 keV. ElvaX software was used to interpret the EDXRF spectra. The accuracy and precision of the results as evaluated by measuring a certified reference sample.

Table 1. Some characteristics of the investigated soils and sampling sites

| Soil No. | Distance from ISIW (km) | Other characteristics |
|---|---|---|
| 1a | 6.32 | Margin of Vadeni commune, Braila county |
| 1b | 7.81 | Center, Vadeni commune, 150 m from railroad |
| 1c | 9.8 | Vadeni commune, near European road E87 (National road 2B) |
| 2a | 4.37 | Sendreni commune, Galati county, near cultivated zone |
| 2b | 4.14 | Sendreni commune, near slag dump of ISIW |
| 2c | 3.59 | Movileni village, Sendreni commune, near ISIW South gate |
| 3a | 5.43 | Mihail Kogalniceanu village, Smardan commune, Galati county |
| 3b | 1.72 | Smardan commune, near ISIW North gate |
| 4 | 5.04 | Galati town, urban background, far from traffic, 300 m from Danube |
| 5* | 155.19 | Adam village, Draguseni commune, Galati county, unpolluted site |

* Control sample

## 3. RESULTS AND DISCUSSION

Table 2. Cd, Se, Pb and Zn in the investigated soils analyzed in this work by AAS and XRF and compared results for Zn and Pb (from reference [7]), in mg/kg dry matter

| Soil No. | Depth (cm) | Cd | Se | Zn | Pb | Zn [7] | Pb [7] |
|---|---|---|---|---|---|---|---|
| 1a | 0 | Nd | Nd | 100.45 | 27.94 | 100.20 | 27.74 |
| | 5 | Nd | Nd | 92.75 | 23.18 | 92.80 | 23.87 |
| 1b | 0 | Nd | Nd | 79.4 | 19.03 | 79.46 | 18.71 |
| | 5 | Nd | 0.40 | 70.8 | 18.15 | 70.63 | 17.84 |
| 1c | 0 | Nd | Nd | 63.23 | 15.02 | 63.11 | 15.48 |
| | 5 | Nd | Nd | 102.86 | 16.47 | 102.57 | 17.11 |
| 2a | 0 | 0.40 | Nd | 52.37 | 20.02 | 52.60 | 21.59 |
| | 5 | 0.48 | Nd | 51.84 | 18.72 | 51.40 | 18.90 |
| 2b | 0 | 0.51 | Nd | 60.32 | 20.07 | 60.88 | 23.31 |
| | 5 | 0.49 | 0.54 | 62.31 | 18.36 | 62.03 | 20.82 |
| 2c | 0 | 0.57 | Nd | 120.78 | 50.75 | 121.00 | 52.24 |
| | 5 | 0.63 | 0.86 | 71.65 | 28.60 | 71.48 | 30.37 |
| 3a | 0 | Nd | Nd | 58.43 | 20.34 | 58.81 | 19.97 |
| | 5 | Nd | Nd | 54.92 | 16.72 | 54.59 | 15.46 |
| 3b | 0 | 0.84 | Nd | 72.24 | 31.40 | 72.69 | 29.07 |
| | 5 | 0.81 | Nd | 61.40 | 25.12 | 61.62 | 25.63 |
| 4 | 0 | Nd | Nd | 85.76 | 38.20 | 86.19 | 40.07 |
| | 5 | Nd | Nd | 72.69 | 35.72 | 72.45 | 36.51 |
| 5 | 0 | Nd | Nd | 34.74 | 12.04 | 35.10 | 11.63 |
| | 5 | Nd | Nd | 33.62 | 11.61 | 34.07 | 11.02 |

Nd – non detectable

Cd, Se, Pb and Zn content in the investigated soils is given in Table 2. All the concentrations in soil samples were reported as mg/kg dry weight of material. From the experimental results presented in Table 2 it can be seen that the concentrations of heavy elements decrease with the distance from the metallurgical works and they are greater than the ones detected in the control soil sample collected from a zone situated far from traffic and industrial activity, in the North of Galati county (control sample No. 5). For the majority of metals, pronounced maximum concentrations for all depths were detected in the locations near the South gate of ISIW, in the prevailing wind direction. The soil heavy metal concentrations are generally greater than those obtained for the control sample for all depths. The concentrations of Zn and Pb in the soil samples obtained in this work were compared with those previously determined by XRF technique using portable spectrometer NITON XLj at Dunarea de Jos" University of Galati, which were reported in another paper [7].

Table 3. Concentrations of As, Cr, Cu, Fe, Mn, Ni, Rb, Sr and V in the investigated soils analyzed in previous works [5-7] by portable XRF spectrometer, in mg/kg dry matter

| Soil No. | Depth (cm) | Sr | Rb | As | Cu | Fe* | Mn | Cr | Ni | V |
|---|---|---|---|---|---|---|---|---|---|---|
| 1a | 0 | 81.34 | 88.26 | 8.51 | 32.79 | 2.95 | 801.42 | 86.86 | 60.51 | 93.80 |
| | 5 | 99.47 | 97.05 | 9.09 | 32.02 | 3.11 | 796.31 | 85.35 | 61.41 | 110.74 |
| 1b | 0 | 76.18 | 74.56 | 10.07 | 25.06 | 2.19 | 648.72 | 74.13 | 48.32 | 82.912 |
| | 5 | 76.05 | 79.34 | 8.81 | 30.54 | 2.32 | 630.83 | 82.05 | 53.3 | 84.38 |
| 1c | 0 | 97.18 | 74.21 | 10.10 | 30.03 | 2.23 | 672.35 | 71.57 | 57.36 | 81.36 |
| | 5 | 102.85 | 74.38 | 8.54 | 52.78 | 2.18 | 656.92 | 74.04 | 61.5 | 84.06 |
| 2a | 0 | Nd | 63.96 | 9.05 | 21.74 | 1.89 | 563.28 | 88.91 | 42.13 | 68.45 |
| | 5 | 20.42 | 68.91 | 9.50 | 23.68 | 2.06 | 593.97 | 83.73 | 51.64 | 84.77 |
| 2b | 0 | 20.7 | 66.87 | 9.44 | 21.02 | 2.32 | 818.21 | 100.60 | 52.39 | 78.87 |
| | 5 | Nd | 71.98 | 9.19 | 21.85 | 2.34 | 706.39 | 90.15 | 58.7 | 76.14 |
| 2c | 0 | 40.79 | 60.71 | 9.89 | 31.38 | 4.28 | 1041.27 | 53.00 | 50.65 | 98.19 |
| | 5 | 44.71 | 71.10 | 10.3 | 29.89 | 3.44 | 784.75 | 52.91 | 65.55 | 85.28 |
| 3a | 0 | Nd | 70.56 | 9.81 | 24.70 | 2.08 | 606.74 | 77.42 | 47.38 | 101.15 |
| | 5 | Nd | 74.85 | 10.03 | 23.64 | 2.14 | 583.26 | 95.16 | 60.33 | 98.35 |
| 3b | 0 | Nd | 81.34 | 8.76 | 21.78 | 2.59 | 786.46 | 101.26 | 60.88 | 76.64 |
| | 5 | Nd | 85.32 | 9.81 | 25.13 | 2.58 | 744.03 | 99.19 | 62.67 | 106.08 |
| 4 | 0 | 17.65 | 74.69 | 12.06 | 24.24 | 2.28 | 655.64 | 79.78 | 54.18 | 88.75 |
| | 5 | Nd | 76.27 | 10.99 | 24.61 | 2.27 | 626.59 | 95.08 | 56.46 | 106.08 |
| 5 | 0 | Nd | 44.67 | 5.94 | $< 15$ | 1.26 | 412.5 | 84.90 | 41.93 | 59.50 |
| | 5 | Nd | 47.49 | 7.19 | 18.38 | 1.38 | 437.5 | 69.32 | 44.71 | 62.67 |

* expressed in %.

Using the data for Pb and Zn in this work (Table 2) and those previously reported in [5-7] for As, Cu, Fe, Mn, Cr, Ni and V, and the lithogenic elements Sr and Rb (Table 3), we have calculated the correlation matrices for the two depths – 0 cm and 5 cm, which are presented in Fig.1. Because concentrations for Cd and Se in several soil samples were not detectable by AAS, these elements were nor included in the correlation matrices.

From the correlation matrices presented in Fig.1, it can be seen that the Pearson coefficient *r* has values greater than 0.70 for the following pairs of elements: a) at 0 cm depth: Fe-Mn; Fe-Pb; Fe-Zn; Mn-Zn; Mn-Pb; Ni-Rb and Cu-Zn; b) at 5 cm depth: Fe-Mn; As-Pb; Ni-Mn; V-Pb and Cu-Zn.

Correlation matrix for soils collected from 0 cm depth

| | *Rb* | *Pb* | *As* | *Zn* | *Cu* | *Fe* | *Mn* | *Cr* | *Ni* | *V* |
|---|---|---|---|---|---|---|---|---|---|---|
| Rb | 1 | | | | | | | | | |
| Pb | -0.245 | 1 | | | | | | | | |
| As | -0.223 | 0.293 | 1 | | | | | | | |
| Zn | 0.095 | 0.811 | 0.107 | 1 | | | | | | |
| Cu | 0.246 | 0.292 | -0.054 | 0.691 | 1 | | | | | |
| Fe | -0.158 | 0.810 | -0.109 | 0.891 | 0.620 | 1 | | | | |
| Mn | -0.131 | 0.714 | -0.193 | 0.764 | 0.447 | 0.930 | 1 | | | |
| Cr | 0.384 | -0.425 | -0.407 | -0.567 | -0.656 | -0.543 | -0.290 | 1 | | |
| Ni | 0.755 | 0.117 | -0.137 | 0.316 | 0.364 | 0.251 | 0.374 | 0.241 | 1 | |
| V | 0.068 | 0.422 | 0.227 | 0.580 | 0.597 | 0.509 | 0.364 | -0.582 | 0.115 | 1 |

Correlation matrix for soils collected from 5 cm depth

| | *Rb* | *Pb* | *As* | *Zn* | *Cu* | *Fe* | *Mn* | *Cr* | *Ni* | *V* |
|---|---|---|---|---|---|---|---|---|---|---|
| Rb | 1 | | | | | | | | | |
| Pb | 0.103 | 1 | | | | | | | | |
| As | -0.196 | 0.752 | 1 | | | | | | | |
| Zn | 0.431 | 0.061 | -0.430 | 1 | | | | | | |
| Cu | 0.084 | -0.248 | -0.561 | 0.858 | 1 | | | | | |
| Fe | 0.394 | 0.463 | 0.159 | 0.289 | 0.026 | 1 | | | | |
| Mn | 0.534 | 0.388 | -0.054 | 0.388 | 0.097 | 0.891 | 1 | | | |
| Cr | 0.301 | -0.084 | 0.121 | -0.345 | -0.443 | -0.582 | -0.362 | 1 | | |
| Ni | 0.253 | 0.244 | 0.138 | 0.365 | 0.276 | 0.675 | 0.706 | -0.337 | 1 | |
| V | 0.737 | 0.428 | 0.421 | 0.133 | -0.159 | 0.215 | 0.220 | 0.477 | 0.236 | 1 |

Fig.1. Correlation matrices for As, Cr, Cu, Fe, Mn, Ni, Pb, Rb, V and Zn in soils collected in the vicinity of the ferrous metallurgical plant of Galati, Eastern part of Romania

The quantitative results revealed that the values obtained in this work for Cd and Se are within the normal legal values (1 mg/kg) according to the Romanian norms (Table 4) admitted for the trace elements content in soils (O.M. 756/03.11.1997) [9]. Also, for information, we present in Table 4 the median elemental concentrations reported in literature for European [10] and world [11] soils. Zn and Pb concentrations exceed the Romanian normal value (100 mg/kg for Zn and 20 mg/kg for Pb) in several sites in the vicinity of the metallurgical unit. The highest concentration of Pb was found at site no. 2c, near ISIW South gate, where in topsoil the alert level in the sensitive area (50 mg/kg) is exceeded, and at site no. 4, located in Galati town.

Table 4. Elemental concentrations reported in literature for European and world soils and Romanian norms

| Element | Literature values | | Romanian norms [9] | | | | |
|---|---|---|---|---|---|---|---|
| | European median in topsoil [10] | World median [11] | NV* | ALS* | ALLS* | ITS* | ITLS* |
| As (mg/kg) | 7.03 | 6 | 5 | 15 | 25 | 25 | 50 |
| Cd (mg/kg) | 0.145 | 0.35 | 1 | 3 | 5 | 5 | 10 |
| Cr (mg/kg) | 60 | 70 | 30 | 100 | 300 | 300 | 600 |
| Cu (mg/kg) | 13 | 30 | 20 | 100 | 250 | 200 | 500 |
| Fe (g/kg) | 35.1 | 40 | - | - | - | - | - |
| Mn (mg/kg) | 650 | 1000 | 900 | 1500 | 2000 | 2500 | 4000 |
| Ni (mg/kg) | 18 | 50 | 20 | 75 | 200 | 150 | 500 |
| Pb (mg/kg) | 22.6 | 35 | 20 | 50 | 250 | 100 | 1000 |
| Rb (mg/kg) | 80 | 150 | - | - | - | - | - |
| Se (mg/kg) | - | - | 1 | 3 | 10 | 5 | 20 |
| Sr (mg/kg) | 89 | 250 | - | - | - | - | - |
| V (mg/kg) | 60.4 | 90 | 50 | 100 | 200 | 200 | 400 |
| Zn (mg/kg) | 52 | 90 | 100 | 300 | 700 | 600 | 1500 |

* : NV = Normal Value; ALS and ITS = Alert level and Intervention threshold in the sensitive area; ALLS and ITLS = Alert level and Intervention threshold in the less sensitive area;

## 4. CONCLUSIONS

AAS and EDXRF techniques have been employed in order to evaluate the pollution of soil with heavy metals in the vicinity of Iron and Steel Integrated Works (ISIW) at Galati, Romania, which is one of the most important metallurgical complexes in the South-East of Europe. From the experimental results presented in this work it can be seen that the concentrations of heavy elements decrease with the distance from the metallurgical works and they are greater than the ones detected in the control soil collected from a zone situated far from traffic and industrial activity. For the majority of metals, pronounced maximum concentrations for all depths were detected in the locations near the South gate of ISIW, in the prevailing wind direction. The comparison of the soil heavy metal concentrations with the maximum values admitted by the Romanian guideline has also been made. The soils located in influence zones of industrial objectives with ferrous processing activities recorded heavy metals loading (contamination) or pollution.

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