

## INTER-ELEMENT RELATIONSHIPS FOR SOILS AROUND A FERROUS METALLURGICAL PLANT

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**Abstract.** *The main objective of this paper is to establish inter-element relationships for soils around the Iron and Steel Integrated Works (ISIW) at Galati, Romania, using Energy Dispersive X-Ray Fluorescence (EDXRF) atomic technique. In this work the correlation matrices are presented for some major and minor elements (As, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Sr, V and Zn) in the soil samples collected in the vicinity of the ferrous metallurgical plant in Galati county, which have been quantified in previous researches using a NITON EDXRF spectrometer from “Dunarea de Jos” University of Galati. Also, the concentrations for some elements are compared with those obtained using XRF technique at Environment Protection Unit of ISIW, the results for Fe, Mn and Rb using the two methods being strongly correlated.*

**Keywords:** *soil pollution, EDXRF technique, heavy metals, ferrous metallurgical plant*

### 1. INTRODUCTION

Soil pollution is one of the most serious problems in the world, with long term consequences on human life. In recent years, with the rapid development of industry, various dangerous pollutants such as heavy metals have been released due to production, smelting and tailings, and got deposited in soils around industrial areas causing serious pollution and soil quality degradation [1-8]. Several analytical techniques have been employed for environmental pollution monitoring, including soil monitoring, such as: Instrumental Neutron Activation Analysis (INAA) [1, 4-7], X-Ray Fluorescence (XRF) [2, 3, 6, 8], Particle-Induced X-ray Emission (PIXE) [9], Atomic Absorption Spectrometry (AAS) [1, 7] and Inductively Coupled Plasma Spectrometry (ICP) [1]. The main objective of this paper is to establish inter-element relationships for soils around the Iron and Steel Integrated Works (ISIW) at Galati, Romania - which is one of the most important metallurgical complexes in the South-East of Europe, representing a great potential of environmental contamination [10] - using Energy Dispersive X-Ray Fluorescence (EDXRF) atomic technique.

### 2. METHOD AND RESULTS

The soils investigated in this experiment were sampled from three depths (0, 5 and 30 cm) from the vicinity of the Iron and Steel Integrated Works (ISIW) at Galati, Romania, 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 – site 2c) and Smardan (localities: Smardan – site 3a; Mihail Kogalniceanu – sites 3b). Fig.1 presents the concentrations chart for some major and minor elements (As, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Sr, V and Zn). In Tables 1-3 are presented the correlation matrices for the investigated elements, using the previously data obtained in another stages of research using a NITON XRF spectrometer from “Dunarea de Jos” University of Galati [2, 3, 11].

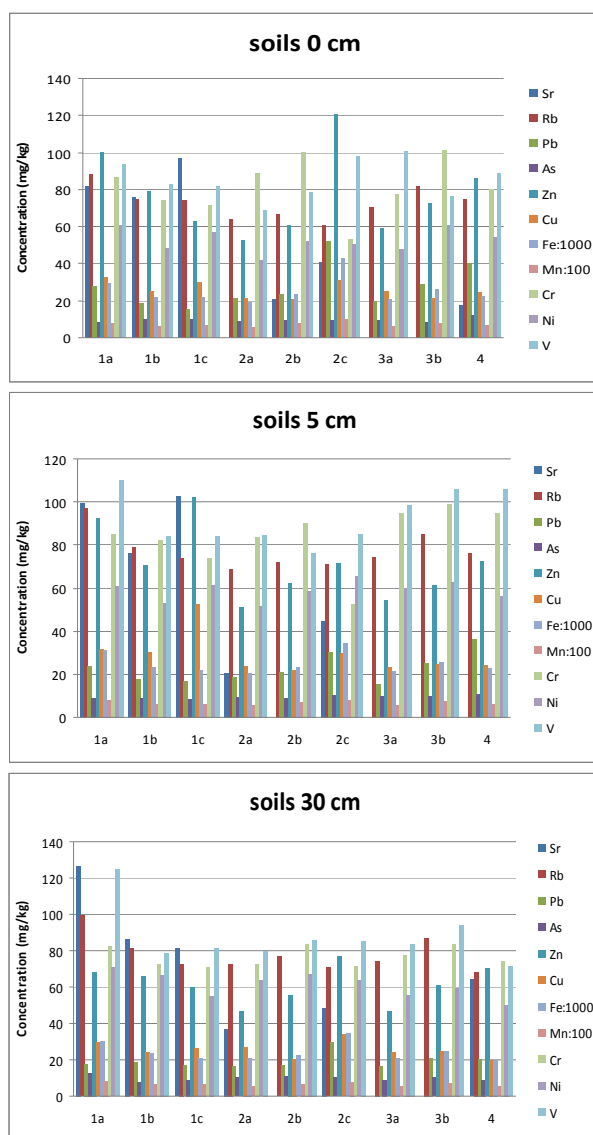


Fig. 1. Elemental chart in soils around the ferrous metallurgical plant of Galati.

Table 1. Correlation matrix for soils collected from 0 cm depth

	<i>Sr</i>	<i>Rb</i>	<i>Pb</i>	<i>As</i>	<i>Zn</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Cr</i>	<i>Ni</i>	<i>V</i>
<i>Sr</i>	1										
<i>Rb</i>	0.359	1									
<i>Pb</i>	-0.193	-0.245	1								
<i>As</i>	-0.0002	-0.223	0.293	1							
<i>Zn</i>	0.332	0.095	0.811	0.107	1						
<i>Cu</i>	0.734	0.246	0.292	-0.054	0.691	1					
<i>Fe</i>	0.180	-0.158	0.810	-0.109	0.891	0.620	1				
<i>Mn</i>	0.140	-0.131	0.714	-0.193	0.764	0.447	0.930	1			
<i>Cr</i>	-0.406	0.384	-0.425	-0.407	-0.567	-0.656	-0.543	-0.290	1		
<i>Ni</i>	0.366	0.755	0.117	-0.137	0.316	0.364	0.251	0.374	0.241	1	
<i>V</i>	0.148	0.068	0.422	0.227	0.580	0.597	0.509	0.364	-0.582	0.115	1

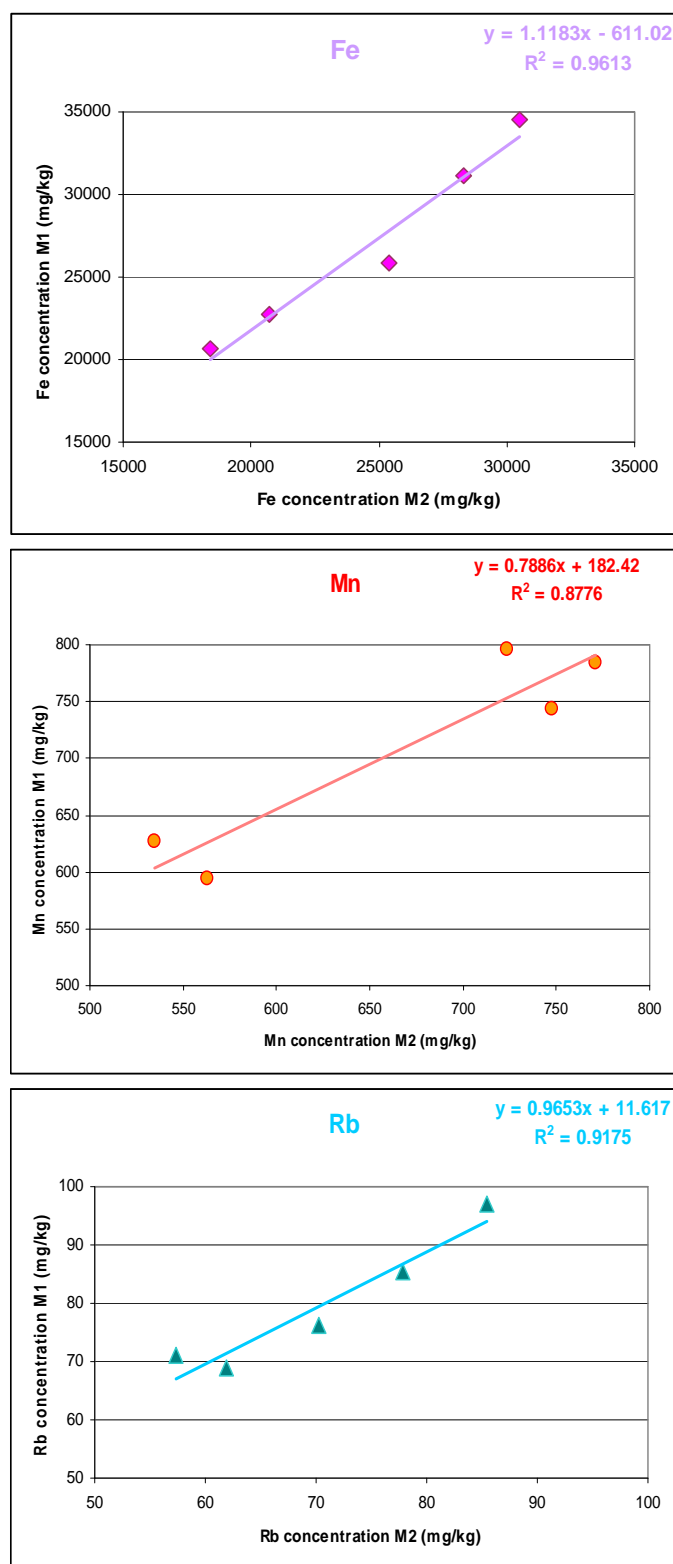
**Table 2. Correlation matrix for soils collected from 5 cm depth**

	<i>Sr</i>	<i>Rb</i>	<i>Pb</i>	<i>As</i>	<i>Zn</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Cr</i>	<i>Ni</i>	<i>V</i>
Sr	1										
Rb	0.402	1									
Pb	-0.265	0.103	1								
As	-0.676	-0.196	0.752	1							
Zn	0.834	0.431	0.061	-0.430	1						
Cu	0.799	0.084	-0.248	-0.561	0.858	1					
Fe	0.295	0.394	0.463	0.159	0.289	0.026	1				
Mn	0.291	0.534	0.388	-0.054	0.388	0.097	0.891	1			
Cr	-0.502	0.301	-0.084	0.121	-0.345	-0.443	-0.582	-0.362	1		
Ni	0.116	0.253	0.244	0.138	0.365	0.276	0.675	0.706	-0.337	1	
V	-0.064	0.737	0.428	0.421	0.133	-0.159	0.215	0.220	0.477	0.236	1

**Table 3. Correlation matrix for soils collected from 30 cm depth**

	<i>Sr</i>	<i>Rb</i>	<i>Pb</i>	<i>As</i>	<i>Zn</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Cr</i>	<i>Ni</i>	<i>V</i>
Sr	1										
Rb	0.367	1									
Pb	-0.031	-0.209	1								
As	0.101	0.611	-0.0005	1							
Zn	0.534	0.136	0.723	0.092	1						
Cu	0.340	0.156	0.549	0.316	0.347	1					
Fe	0.298	0.376	0.726	0.485	0.654	0.815	1				
Mn	0.426	0.666	0.442	0.651	0.600	0.674	0.888	1			
Cr	-0.312	0.667	-0.259	0.646	-0.157	-0.322	0.054	0.293	1		
Ni	0.255	0.601	-0.003	0.557	0.092	0.374	0.530	0.638	0.334	1	
V	0.392	0.903	-0.079	0.809	0.191	0.395	0.570	0.792	0.606	0.603	1

The results for some elements have been compared with those obtained using EDXRF technique at Environment Protection Agency of ISIW (Table 1). From Fig. 2 it can be observed that the results for Fe, Mn and Rb using the two methods (M1- Environmental Protection Unit of ISIW Galati and M2 – Dunarea de Jos University of Galati) are strongly correlated.



**Fig. 2. Correlation between the ED-XRF techniques for Fe, Mn and Rb in soils from 5 cm depth (Table 4): M1- Environmental Protection Unit of ISIW Galati; M2 – Dunarea de Jos University of Galati.**

**Table 4. Concentrations of Fe, Mn and Rb in soil samples collected from 5 cm depth**

Soil No. (5 cm depth)	Rb, mg/kg		Fe, mg/kg		Mn, mg/kg	
	M1	M2	M1	M2	M1	M2
1a	85.5	97.05	28300	31150	723.5	796.3
2a	61.9	68.9	18400	20631	562.8	594.0
2c	57.3	71.1	30500	34489	771.0	784.7
3b	77.8	85.3	25400	25868.5	747.5	744.0
4	70.3	76.3	20700	22693	534.7	626.6

From the correlation matrices presented in Tables 1-3, it can be seen that the Pearson coefficient  $r$  [3] 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; Cu-Sr and Cu-Zn; b) at 5 cm depth: Fe-Mn; Zn-Sr; As-Pb; Cu-Sr; Ni-Mn; V-Pb and Cu-Zn; c) at 30 cm depth: V-Rb; Fe-Mn; V-As; Fe-Cu; Zn-Pb; Fe-Pb and V-Mn.

Also, a control sample from North region of Galati county, far from traffic and industrial activities was collected and the concentrations for the three depths are given in Table 5. The soil heavy metal concentrations (Fig. 1) are generally greater than those obtained for the control sample (Table 5) for all depths.

**Table 5. Concentrations of As, Cr, Cu, Fe, Mn, Ni, Pb, Rb, V and Zn in control sample**

Depth (cm)	As (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (g/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Rb (mg/kg)	V (mg/kg)	Zn (mg/kg)
0	5.94	84.90	< 15	12.61	412.5	41.93	11.63	44.67	59.50	35.1
5	7.19	69.32	18.38	13.76	437.5	44.71	11.02	47.49	62.67	34.07
30	6.24	96.15	<15	11.77	400.4	36.0	11.15	40.77	60.1	19.51

### 3. CONCLUSIONS

The soils located in influence zones of industrial objective with ferrous processing activities at Galati (SE of Romania) recorded heavy metals loading (contamination) or pollution. There is a good correlation in the investigated soils between Fe and Mn, Pb, Cu or Zn and between V and Rb or Mn.

The results for Fe, Mn and Rb have been compared with those obtained using EDXRF technique with NITON spectrometer at Environment Protection Agency of ISIW, the experimental data showing a good correlation between the two techniques.

**Acknowledgement:** 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 biomonitoring of the environmental pollution in South, South-East and Central regions of Romania (Project PN2 No. 72-172/1.10.2008). The work of Bosneaga Alina was supported by Project SOP HRD - SIMBAD 6853, 1.5/S/15 - 01.10.2008.

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Manuscript received: 30.04.2010

Accepted paper: 15.08.2010

Published online: 04.10.2010