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## Characterization of soils around a former chemical plant in Braila, SE Romania, using high performance atomic techniques (EDXRF, AAS, ICP-MS)

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### Abstract

This paper presents the problem of soil pollution in the vicinity of a former chemical plant, given that production activity was stopped for more than thirty years ago. The old chemical plant was located in the southern part of Braila town, SE Romania, just a few kilometers from the left bank of the Danube River. Prior to 1990, there was a significant production of industrial chemical goods, such as sulfuric acid, carbon dioxide for synthetic fibers, chlorine gas and hydrochloric acid obtained by electrolysis processes with mercury electrodes and heavy metal catalysts (Cd, Ni, Zn), sodium sulfide and sulphate, etc. For the good development of the experimental program, a number of 10 soil samples were collected from the north, northwest, west, southwest and south of the former chemical plant. The multi-element analysis method used to determine the trace elements in the soil samples was energy-dispersive X-ray fluorescence spectrometry (EDXRF), using a Genius XRF portable spectrometer manufactured by Skyray Instruments Inc., equipped with a large surface Si with a Be window and a 40 kV/100  $\mu$ A miniature X-ray tube excitation source with Ag target. The spectrometric system has an energy resolution up to 139 eV, and the detection limits of the order of ppm. A total of 21 chemical elements were identified in the target soil samples, such as: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Hg, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Pb. The compositional analyses of contaminated industrial soils were completed by using the AAS and ICP-MS high performance and selectivity techniques.

**Keywords:** high performance atomic methods, former chemical plant, toxic elements.

## 1. INTRODUCTION

The effect of pollution is a major problem worldwide, being manifested in many areas due to anthropic activities such as mining, metallurgy, petrochemical refining, chemical synthesis of various materials, etc. Numerous studies have established the negative effects and ecotoxicological character of heavy metals and other trace elements on the quality of the environment and human health [1]. However, many governments around the world and Eastern Europe have regulated the limits of toxic elements in soils, sediments and waters, both in industrial and populated areas, in order to protect the health of their citizens [2].

Some studies in Eastern Europe have reported the presence of heavy metals in industrial soils, using primary analytical methods. Detection of heavy metals in environmental and geological materials can be performed by several high-performance analytical techniques, such as atomic or nuclear spectroscopic techniques [3]. Atomic absorption spectrophotometry (AAS) analysis is a well-known analytical method for detecting heavy metals in liquid samples. For solid samples the extraction procedures for heavy metals must be applied, and these procedures lead to a long process that requires the use of specific substances and auxiliary equipment. For example, the extraction method using royal water involves the digestion of solid samples by the use of HCl and HNO<sub>3</sub>, and finally a pseudo-total extraction of trace metals is obtained [4]. Also, the inductive plasma coupled mass spectrometry (ICP-MS) analytical technique is a very advanced method, allowing the detection of chemical elements in very small concentration ranges (ppb) [5].

Through portable X-ray fluorescence spectrometry with energy dispersion (EDXRF) instruments, direct in situ analysis of solid samples can be performed without the need for digestion [6-8]. These spectrometers are capable of performing a rapid and non-destructive analysis of environmental samples including soils, sediments and rocks. Up to 25 elements can be determined simultaneously, significantly reducing the time required for sample analysis [8]. The use of portable X-ray fluorescence (PXRF) spectrometers is constantly increasing due to the minimal preparation time of samples and the non-destructive character of this technique in environmental investigations, material engineering and other applications in various fields [3,6,8]. PXRF spectrometers provided useful information successfully obtained in the detection of heavy metals such as: Pb, As, Cd, Hg, Ag, Ni, Fe, Al, Cu, Co, etc.. The PXRF technique can quickly detect elements that have very low concentrations (ppm), being a complementary tool to expensive and time-consuming destructive techniques AAS and ICP-MS.

Near the city of Brăila, Romania, at coordinates: 45°10'48 "N and 27°54'58" E, a chemical plant (Celhart Donaris) was built to produce artificial fibers, as well as cellulose derivatives (paper, cardboard, etc.). The technological processes for the production of artificial fibers were based on chemical and electrochemical methods to obtain the finite material. From these processes we can list: obtaining carbon sulphide (CS<sub>2</sub>), sodium sulfide (Na<sub>2</sub>S), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), obtaining chlorine gas (Cl<sub>2</sub>) and sodium hydroxide (NaOH) by electrochemical methods of alkalizing chlorine using a cathode of mercury (Hg) and catalysts formed of heavy metals (Cd, Ni, Zn), cellofibres, etc. [9].

The aim of this work is the quantification of trace elements and heavy metals and assessment of their ecological risk in industrial soils collected around the former chemical enterprise of Braila, SE Romania, using a combination of accurate and high performance analytical techniques.

## 2. METHODOLOGY

Ten soil samples were collected around the former chemical plant, Braila, Romania [10]. The detailed sampling map is shown in Figure 1 and indicates that the samples were collected from the north (samples 1, 2, 3), west (samples 4, 5, 6, 7) and south (samples 8, 9, 10) parts of the industrial unit.

The soil samples were taken with the help of plastic tools from a depth of 10 cm, stored in a polyethylene bag and brought to the laboratory of INPOLDE international research network, at Dunarea de Jos University of Galati, Romania. In the laboratory, soil samples were labeled and dried at ambient temperature for 7 days. The soil was separated from foreign bodies (stones, roots, leaves, stems, etc.), grounded, passed through a sieve with 0.125 mm mesh and dried in the oven at 50 °C for 48 hours. Finally, the samples were stored in polyethylene bags free of humidity and light and divided in subsamples for further investigations in INPOLDE partner laboratories.



Fig. 1. Soil sampling locations around a former chemical plant, Braila, Romania [15].

### 2.1. AAS analytical technique

The soil samples were digested based on ISO 11466 (digestion method with aqua regia). Weighed to the analytical balance 3 g of soil, they were quantitatively transferred to a 100 ml graduated flask, where 21 ml concentrated HCl (35%) and 7 ml concentrated HNO<sub>3</sub> (65%) were added by pipetting. The solutions in the listed flasks were heated on an electric hob at 200 °C for two hours.

During boiling on the electric hob, 25 ml of distilled water was added. After cooling, the obtained solutions were filtered on filter paper, the filtered residue being washed 3 times with 5 ml HNO<sub>3</sub> solution (3%).

The filtered solutions were transferred quantitatively into 100 ml graduated flasks and HNO<sub>3</sub> solution (3%) was added to the filling mark. Heavy metal concentrations in the digested samples were determined using the ZEE nit 700 Analytikjena AAS equipment at Institute of Geology and Seismology, Chisinau, Republic of Moldova. The calibration curves were obtained using standard calibration solutions.

### 2.2. EDXRF analytical technique

For the irradiation of the samples with the portable EDXRF spectrometer, approximately 10 g of each soil sample initially prepared at Dunarea de Jos University of Galati were weighed and transferred into capsules covered with Mylar foil. The EDXRF instrument used in this analysis campaign was a portable Genius XRF spectrometer manufactured by Skyray Instruments Inc., at SETCAR SA Braila, using an agreement protocol for collaboration with INPOLDE network. The spectrometer was equipped with a large area Si detector with Be window and an excitation source of 40 kV / 100 μA miniature X-ray tube with a silver target. Each soil sample was irradiated for 120 seconds [7] in SOIL mode. The spectrometric system has an energy resolution up to 139 eV, and the detection limits up to ppm for most of the elements. The calibration was made automatically, using an internal Ag standard [11].

### 2.3. ICP-MS analytical technique

In principle, inductive coupled plasma mass spectrometry (ICP-MS) analyzes liquid samples. Before analysis, the solid samples were weighed at the analytical balance ( $\approx 3$  g), add 30 ml of strong HCl and HNO<sub>3</sub> mixture in a ratio of 1:3 (aqua regia), put in a microwave oven (Berghof MWS- 2, P = 2000 W) and the following parameters were set: T = 200 °C, P = 90%, t = 25 minutes.

After digestion, the obtained solutions are filtered, transferred quantitatively into graduated flasks (100 ml) and diluted with 5% HNO<sub>3</sub> solution to the filling mark. The sample analysis was performed by an Agilent 7900 ICP-MS equipment at International Hellenic University at Kavala, Greece. The calibrations were performed using multi-element certified standards and verified by an independent certified standard.

## 2.4. Risk assessment methods

The geoaccumulation index ( $I_{geo}$ ) is used to measure the degree of anthropogenic influence on the individual concentration of heavy metals in soils [12-15]. It is calculated with the formula:

$$I_{geo} = \log_2 \left[ \frac{C}{1.5 \cdot B} \right] \quad (1)$$

where: C – concentration of heavy metal content in soil,

B – content of heavy metal in geochemical background.

The geoaccumulation classification using this index is the following: class 0:  $I_{geo} \leq 0$  - uncontaminated; class 1:  $0 < I_{geo} \leq 1$  - uncontaminated to moderately contaminated; class 2:  $1 < I_{geo} \leq 2$  - moderately contaminated; class 3:  $2 < I_{geo} \leq 3$  - moderately to strongly contaminated; class 4:  $3 < I_{geo} \leq 4$  - strongly contaminated; class 5:  $4 < I_{geo} \leq 5$  - strongly to extremely contaminated; class 6:  $I_{geo} > 5$  - extremely contaminated.

The pollution index (PI) is used to evaluate the degree of individual contamination with heavy metals in soils and sediments [12-15]. It is calculated using the formula:

$$PI = \frac{C}{B} \quad (2)$$

where: C – concentration of heavy metal content in soil,

B – content of heavy metal in geochemical background.

The pollution classification using this index is: class 1:  $PI < 1$  - absent; class 2:  $1 \leq PI < 2$  - low polluted; class 3:  $2 \leq PI < 3$  - moderate polluted; class 4:  $3 \leq PI < 5$  - strong polluted; class 5:  $PI \geq 5$  - very strong polluted.

The enrichment factor (EF) is an effective tool for determining the origin of heavy metals in the soil [12-15]. Using manganese as reference metal in soil, the calculation formula proposed in this paper is the following:

$$EF = \frac{\left[ \frac{C}{C_{Mn}} \right]_{\text{sample}}}{\left[ \frac{B}{B_{Mn}} \right]_{\text{background}}} \quad (3)$$

where: C – concentration of heavy metal in the soil sample

$C_{Mn}$  - manganese concentration in the analyzed soil sample

B – content of heavy metal in the control soil (background)

$B_{Mn}$  – content of manganese in the control soil (background).

The enrichment of soil classification using this index is:  $EF < 2$  - deficiency to minimal enrichment;  $2 \leq EF < 5$  - moderate enrichment;  $5 \leq EF < 20$  - significant enrichment;  $20 \leq EF < 40$  - very high enrichment;  $EF \geq 40$  - extremely high enrichment.

## 3. RESULTS AND DISCUSSION

Following the analyzes carried out using the three methods presented (XRF, AAS, ICP-MS), various concentrations were determined for a total number of 23 chemical elements (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Pb, Co, B, Cd). 12 chemical elements were quantified by XRF method, the irradiation time of the samples being 120 seconds: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Pb. The XRF analysis scheme and comparison study was completed by employing the AAS method for Co, Cr, Zn, Cu, Ni, Cd and Pb and by ICP-MS method for B, V, Cr, Mn, Ni, Co, Pb, Cd and As.

The main chemical elements (heavy metals and trace elements) determined using the three methods of analysis (XRF, AAS, ICP-MS) are represented in Table 1. Table 2 shows the concentration values of other chemical elements (major, trace) determined only by XRF, after irradiation at 120 s, as highlighted in the spectrum from Figure 2.

Table 1. Heavy metal and trace element content (in ppm) in the soil samples investigated by combined analytical techniques (XRF, AAS, ICP-MS).

Site no.	Zn	As	Ni	V	Cr	Mn	Cd	Pb	Cu	Mo	Sb	B	Co	Sn
1	59.39	35.120	32.648	44.675	62.177	726.499	1.05	26.08	11.66	1.055	2.827	28.221	7.268	nd
2	89.83	30.950	32.816	51.544	62.394	772.660	1.743	33.69	15.86	1.052	3.661	18.223	6.842	nd
3	56.69	26.770	29.881	30.009	61.468	782.405	1.296	28.02	18.97	1.033	0.434	7.923	8.105	2.87
4	102.43	26.050	30.846	39.749	61.853	676.925	1.554	39.05	14.69	1.071	0.200	17.441	7.415	nd
5	110.17	19.580	33.789	67.476	64.374	781.215	1.745	44.38	10.73	1.062	1.908	4.044	5.870	6.08
6	124.87	25.190	38.739	41.100	61.752	748.607	1.759	210.7	13.17	1.046	0.200	0.612	6.618	nd
7	89.5	15.570	43.839	57.456	63.387	763.824	1.244	46.43	11.96	1.039	1.511	<0.15	6.984	9.98
8	97.61	12.500	45.524	28.263	67.619	638.504	1.752	53.5	11.1	1.078	0.200	<0.15	6.607	nd
9	63.04	10.410	34.121	39.580	66.186	729.243	1.457	41.83	96.15	1.048	0.669	<0.15	6.185	0.69
10	83.51	9.350	35.199	31.557	59.190	718.651	0.482	46.19	12.87	1.056	3.585	<0.15	6.381	0.93

nd=not detected

Table 2. Major and trace elements content (in ppm) in the soil samples investigated by XRF

Site	K	Ca	Ti	Fe	Rb	Zr	Sr	Nb	Y
1	19855.1	30718.0	4575.06	28777.2	84.99	366.6	110.2	20.1	36.5
2	20827.6	26827.1	4368.11	28920.6	80.40	362.4	114.9	32.2	38.9
3	19780.6	36051.0	4530.37	29036.5	81.54	363.7	123.9	10.9	40.7
4	19846.8	23321.0	4625.74	29782.7	89.14	369.3	115.2	7.9	37.5
5	18568.2	47888.2	4158.30	28710.7	74.32	341.6	146.4	10.6	55.5
6	19526.6	47142.1	4363.96	29237.8	72.75	316.5	149.3	12.8	55.0
7	20079.6	28919.7	4343.14	28905.0	84.55	345.8	118.9	9.5	39.5
8	19312.7	21719.4	4570.54	29899.0	85.51	366.2	112.7	18.8	38.4
9	20469.6	41227.4	4390.77	28210.1	80.48	350.8	124.4	12.7	42.5
10	20091.4	41366.4	4444.03	28171.2	80.01	332.0	121.4	17.3	42.7

Table 3. Concentration values for traces of chemical elements in soil with sensitive use imposed by the Romanian law [16]

Chemical element	Normal Values [ppm]	Alert limit [ppm]	Action limit [ppm]
As	5	15	25
Co	15	30	50
Cr (total)	30	100	300
Cu	20	100	200
Mn	900	1500	2500
Mo	2	5	10
Ni	20	75	150
Pb	20	50	100
Sb	5	12.5	20
Sn	1	35	50
V	50	100	200
Zn	100	300	600

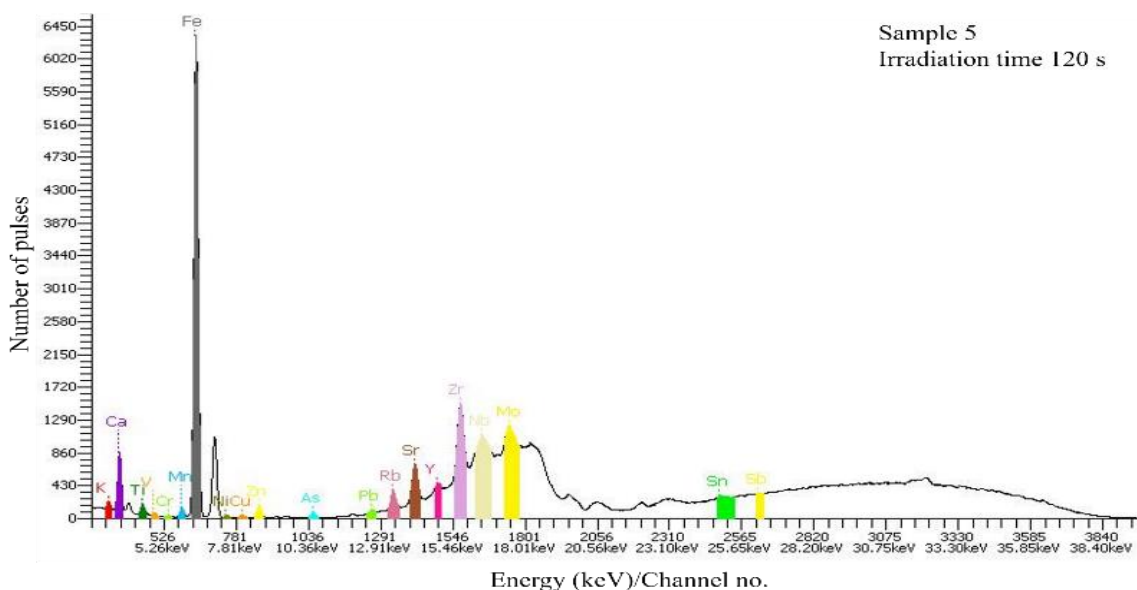


Fig. 2. XRF spectrum obtained for the soil sample no. 5 at 120 s irradiation time

The reference values imposed by the Romanian legislation [16] are shown in Table 3 and, for comparison purpose, in Table 4 we present for a number of fifteen elements [17-19] their mean concentrations found in the surface soil of European continent [17] and in the upper continental crust [18].

All the values of As, Co, Cr, Mn, Ni and V concentrations identified in the ten analyzed soil samples (Table 1) do not exceed the normal value specified in the Romanian law (Table 3). The concentration of Cu in sample 9 exceeds four times the normal value but does not exceed the alert limit value. The concentration of Sn in samples 3, 5 and 7 exceeds several times the normal value for this element in soil. All other concentrations in the network of analyzed samples are below the normal limits. The concentrations of Zn in samples 4, 5, 6 slightly exceed the alert limit value. Pb has a concentration 10% higher than the legal norm only in sample 9.

Table 4. Mean concentration values for trace elements of interest in the European surface soil and composition estimate of the upper continental crust [17-19]

Chemical Element	EU surface soil [ppm]	Upper continental crust [ppm]
Sb	1	0.3
As	11.6	2
Cr	94.8	35
Mn	810	527
Mo	0.9	1.4
Ni	37.3	18.6
V	68.1	53
Zn	68.1	52
Cd	0.284	0.1
Pb	32.6	17
Cu	17.3	14
Co	10.4	11.6
Sn	4.48	2.5
B	-	17
Nb	26	20

Comparing the concentrations of the elements determined in this experimental program with the values of the concentrations in Table 4, we can state that most of the elemental levels do not exceed in a high extent the values of the reference concentrations in soil.

Based on the results obtained from the application of the XRF, AAS and ICP-MS analysis methods (Table 1), and the risk assessment approach, the values of the geoaccumulation index, unique pollution index and enrichment factor indices were calculated using Eqs. (1), (2) and (3) and depicted in Figures 3, 4 and 5.

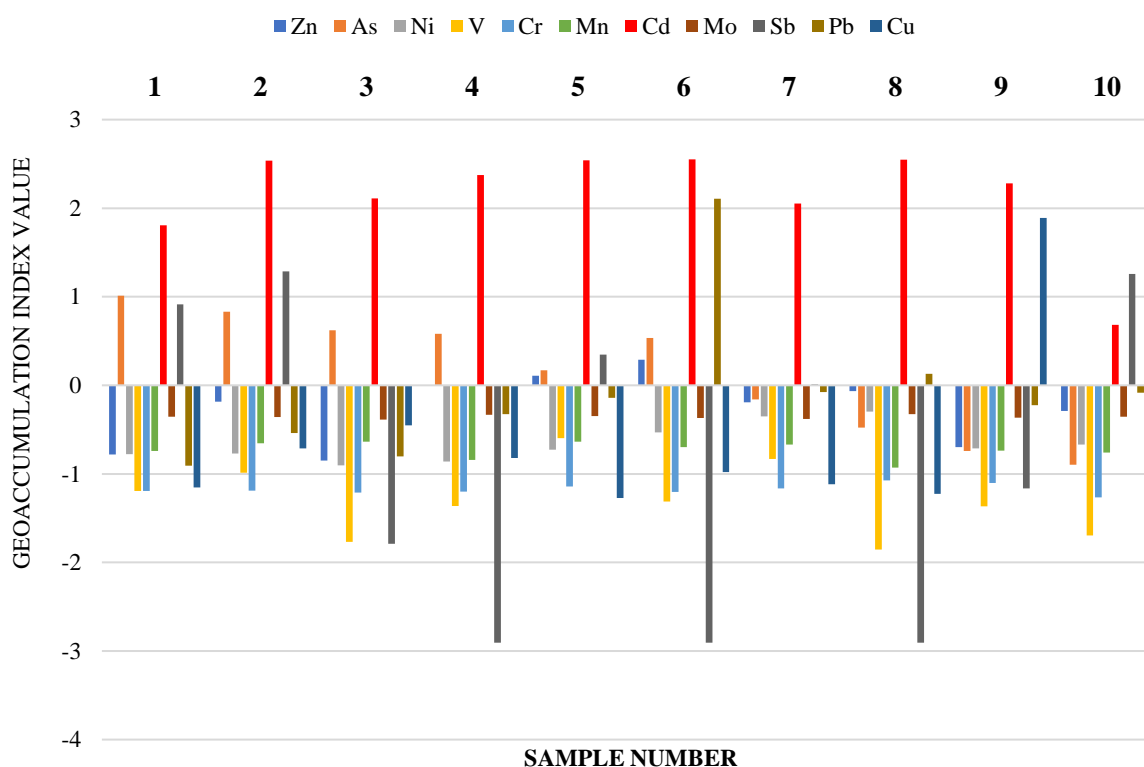


Fig. 3. The variation of the values of the geoaccumulation index of heavy metals in industrial soils

Figure 3 shows that the  $I_{geo}$  values are lower than 0 for the elements Zn (samples 1 - 4 and 7 - 10), As (in samples 7, 8, 9, 10), Ni, V, Cr, Mn, Cd (in samples 2 - 9), Mo, Sb (samples 3, 4, 6, 8, 9), Pb (samples 1 - 5 and 7 - 9) and Cu (samples 1 - 8 and 10). The values for Zn (0.04 - 0.29) from samples 5, 6; As (0.17 - 0.83) from samples 2, 3, 4, 5, 6; Cd (0.68) in sample 10; Sb (0.1 - 0.91) in samples 1, 5, 7 and Pb (2.11) in sample 6 show that the related soils are unpolluted to moderately polluted and are classified in class 1.

The moderately polluted soils classified in class 2 are found in site 1, where the  $I_{geo}$  value for As is 1.01 and the Cd value is 1.81. Also, sites 2 and 10 present  $I_{geo}$  values for Sb of 1.26 and 1.29, respectively, and site 9 a value of  $I_{geo}$  for Cu of 1.89.

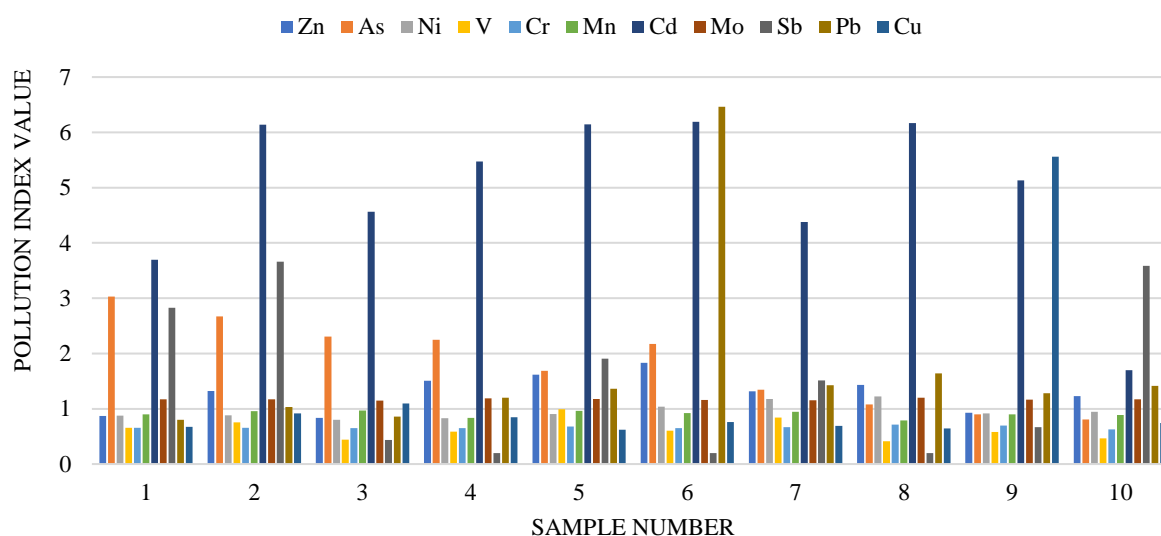


Fig. 4. The variation of the values of the unique pollution index of heavy metals in industrial soils

Figure 4 shows a variation of the PI values from which it can be seen that the indices for the elements V, Cr, Mn are  $PI < 1$ , which means that the soils are of class 1.  $PI < 1$  values are found for Zn (0.83 – 0.93) in samples 1, 3, 9, for As in samples 9 and 10 (0.81 – 0.90), for Ni in samples 1 - 5, 9 and 10 (0.80 – 0.94), for Sb in samples 3, 4, 6, 8, and 9 (0.20 – 0.67), for Pb in samples 1 and 3 (0.8 – 0.86) and Cu in samples 1, 2, 4 – 8 and 10 (0.62 – 0.92).

Lightly polluted soils ( $1 < PI < 2$ , class 2) are found in all sites where the PI value for Mo varies between 1.15 and 1.20; in sites 2, 4 - 8 and 10 where the PI values of Zn are in the range of 1.23 – 1.83; in sites 5, 7, 8 in which PI values between 1.08 and 1.69 were obtained for As; in samples 6, 7, 8 in which Ni has PI values varying between 1.04 and 1.22; in sites 5 and 7, in which PI values for Sb were 1.51 and 1.91, respectively; in sites 2, 4, 5 and 7 - 10 where PI values for Pb vary between 1.03 and 1.64 and in site 3 where the PI value for Cu is 1.1.

The moderately polluted soils of class 3 are found in sites 2, 3, 4, 6 where the PI values for As are between 2.17 and 2.67 and in site 1 where the PI value for Sb is 2.83. Due to the PI values of As (sample 1), Cd (samples 1, 3 and 7) and Sb (sample 2 and 10) which are higher than 2 but lower than 3, the soils corresponding to these sites are highly polluted and classified as class 4.

The soils included in class 5 as highly polluted are specific to samples 2, 4 – 6, 8 and 9 where the PI values for Cd are between 5.13 and 6.47, sample 6 where the PI value for Pb is 6.46 and sample 9 where the PI value is 5.56 for Cu.

Regarding Figure 5, it can be noticed that the EF values for Zn, As (samples 5, 7 - 10), Ni, V, Cr, Mn, Cd (sample 10), Mo, Sb (samples 3 - 9), Pb (samples 1 – 5, 6, 8 and 9), Cu (samples 1 – 8 and 10) are lower than 2, which indicates that the soils are evaluated as deficient to minimally enriched with these metals.

The EF values for As in samples 1 – 4 and 6 varied from 2.17 to 3.03, in samples 1, 3 and 7 the EF values for Cd varied between 4.12 and 4.72, the EF values for Sb were in the range 3.15 – 4.04 in samples 1, 2 and 10, and the EF value for Pb in sample 8 is 2.08. All these EF values indicate a moderate enrichment of the soils.

The highest EF values (5.70 – 7.83) for the elements Cd, Cu and Pb were calculated for samples 2, 4 – 6, 8 and 9, which proves that the industrial soils are significantly enriched with these elements.



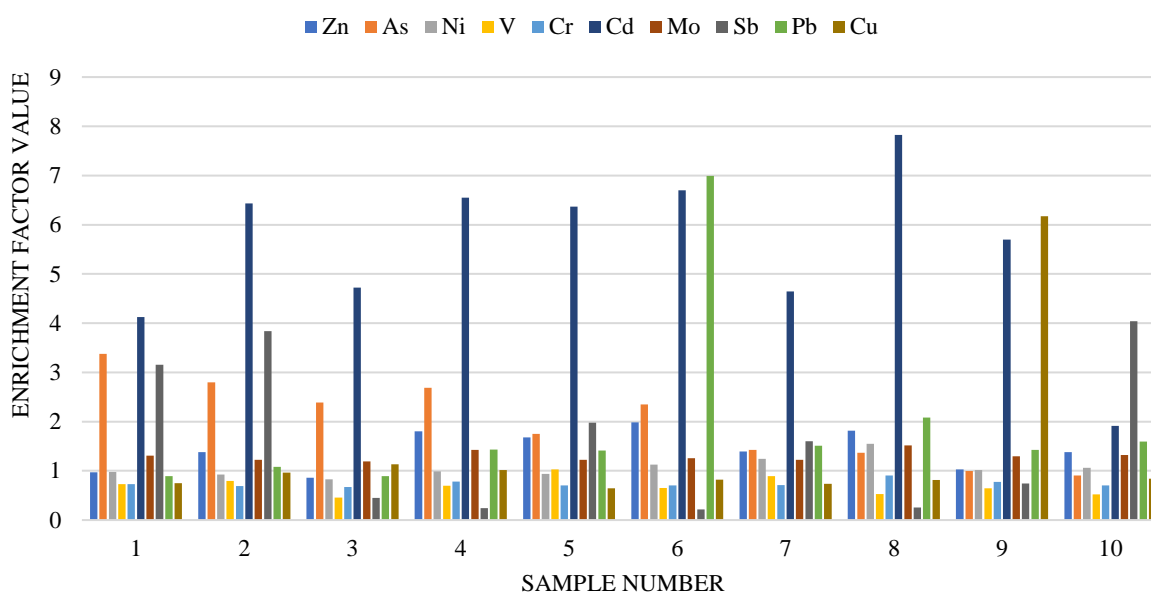


Fig. 5. The variation of the values of the enrichment factor of heavy metals in industrial soils

#### 4. CONCLUSIONS

The recent history of the communist industrial activities at Braila, SE Romania, has left the soil very polluted. The soil around the former chemical plant for obtaining synthetic materials and cellulose derivatives is a permanent threat to local communities, given that the areas are being exploited today and they are located in a large agricultural region of Romania and Danube River basin.

The results of the analyzes obtained by employing the EDXRF, AAS and ICP-MS techniques, presented in this research program, and the calculated risk assessment indices confirm the high pollution level due to the presence of heavy metals in soils adjacent to industrial area.

Due to the fact that for several heavy metals concentrations values above the maximum limit of action limit were obtained, the agricultural activity in the area should be stopped and appropriate remediation measures of this area should be taken.

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