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ENVIRONMENTAL PHYSICS

STUDIES ON ACCUMULATION OF HEAVY METALS IN ACACIA LEAF BY EDXRF

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Abstract. The aim of this work was to determine the heavy metal content of the Acacia leafs and their substrate collected from the south Romania. The concentrations of Fe, Mn, Ni, and Zn in the samples were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry. The coefficient of accumulation of heavy metals was calculated and a highest accumulation of Fe and Zn from substrate was observed for all the analyzed leaf samples. Furthermore, a high accumulation of Fe was observed in Acacia leaf growing in the vicinity of the hydropower.

Key words: heavy metals, acacia leaf, EDXRF, pollution.

1. INTRODUCTION

The pollution represents the environmental contamination with materials that interfere with human health, quality of life or natural functions of ecosystems. For many times, plants and animals can adapt to living in polluted environment if the pollution degree is acceptable, But, if this level is exceeded, the plants get sick or dies. For determining the pollution degree, in addition to physico-chemical determination of pollutants in the ecosystem, is often used the diagnosis of plant diseases induced by this pollutant [1].

All heavy metals analyzed in this study are essential for all vital forms in very small concentrations, their uptake is limited and they are generally bound to proteins in the body as well as in cells. They enter the living cell in the form of cations, but their embedding is strictly regulated, because large amounts of practically all metals are toxic [2]. Heavy metals may be complexed to phenolic compounds, but free ions are available for absorption and this is favoured by the low gastric pH.

It is known that *iron* plays an important role in metabolism and fermentation processes as an enzyme activator, solubilizer and functional component of proteins if is in low concentration. Above trace levels, iron has other roles: altering redox system of the wine in favor of oxidation, participating in the formation of complexes with tannins and phosphates [3–9]. The *manganese,* in plants, activates several enzymes and has an important role in glycolysis and other processes. Also, Mn is necessary for nitrate reduction [10]. The zinc is essential microelements for plants. It is a part of chemical structure enzymes (carbohydrase, phosphatase and many dehydrogenase). A good supply with Zn increasing the tryptophan content, precursor of auxin (hormones essential for body development). Zinc increases the soluble sugar content and action on protoplasm viscosity by the free water content decrease [11]. Also, the nickel stimulates enzyme activity, enhance metabolic processes, cell division, photosynthesis, stimulates plant growth and development, stimulate organs transition from sleep to active state, stimulates absorption etc. [12].

At the beginning it was believed that tolerance of populations to the heavy metals excess was due to their ability to remove those ions. On the contrary, measurements performed have shown that adapted species take from soil heavy metals and accumulate them in amounts that would cause death for most other species, having specific physiological mechanisms to counter the toxic effects of heavy metals, in particular by their isolation in vacuolar juice.

2. METHOD AND MATERIALS

Determination of the heavy metals level from *Acacia greggii* leaves (Fig. 1), collected from three Romanian County was the subject of this study. All parts of plants accumulates certain heavy metals from soil and this is the consequence of many factors, for example, pH.

Fig. 1 – *Acacia greggii* leaves, flower and seeds.

Heavy metals, in small quantity, are very useful in the plant growth. In high quantity, they become toxic. The heavy metals concentrations from leaf, for each sample were determined by EDXRF.

The results to be presented in this work were obtained from samples (*Acacia* leaves and soil) collected in the interval 14^{th}–28^{th} August 2010.

Acacia is a genus of shrubs and trees belonging to the subfamily *Mimosoideae* of the family *Fabaceae*. The genus *Acacia* previously contained roughly 1300 species, about 960 of them native to Australia [13].

2.1. SAMPLES PREPARATION

The samples have been collected from 11 points using a GPS device and the location and geographic coordinates are presented in Table 1 and the Fig. 2.

Table 1

Coordinates of collection points

No.	Location	Coordinates	
		Longitude	Latitude
P_1	Bogati	25.133888	44.825033
P_2	Bradu	24.896086	44.753946
P_3	Vedea	24.591783	44.780206
P_4	Vitomiresti	24.414906	44.881513
P_5	Daesti	24.894556	45.183266
P_6	Berislavesti	24.41805	45.305905
P_7	Racovita	24.303611	45.414097
P_8	Cainenii Mici	24.296016	45.504219
P_9	Bajesti	24.935144	45.020403
P_{10}	Priboieni	24.071883	44.869711
P_{11}	Comisani	25.592794	44.877202

Fig. 2 – Geographic localization of collection points.

All samples were dried for 48 hours at 40ºC and after that were grinded to obtain a fine powder. A small quantity of each sample was put in clean testing chambers covered with Mylar thin film to be studied by the EDXRF method.

2.2. ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry is an analytical technique, nondestructive, used to determine the quantitative and qualitative elemental composition. This method can be successfully applied to a wide range of materials: solids [14, 15], liquids (biological fluids, waste water), and powders [16–22] etc. and combines the precision and the high performance accuracy with the simple preparation of samples.

The concentrations of Fe, Mn, Ni, and Zn in collected samples were determined using the ELVAX spectrometer which has the X-ray tube with Rh anode and operate at 50 kV and 100 µA [17, 18, 23]. 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 [24].

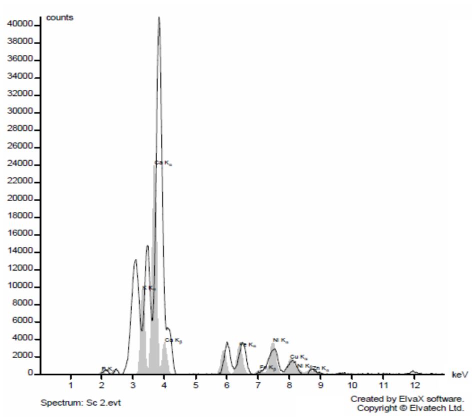

Fig. 3 – EDXRF specter of sample.

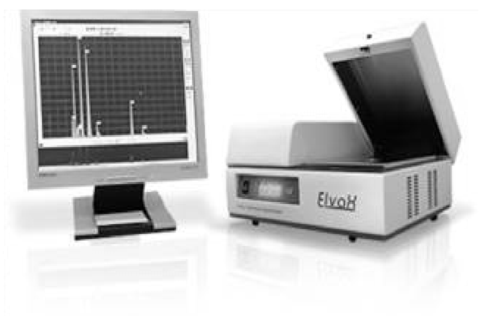

Fig. 4 – ElvaX Spectrometer.

The data acquisition time was set to 30 minutes for soils and 5 minutes for leaves. The precision and accuracy of the results were evaluated by measuring some certified reference samples (NIST SRM 1571 – Orchard leaves; SRM 2711a and SRM 2703 – Soil) and were obtained good agreements between certified values and obtained data, with recoveries ranging from 95 to 105%.

3. RESULTS AND DISCUSSION

The determination of heavy metals concentration in the leaves is essential in environmental studies, because the trees accumulate heavy metals from soils in all seasons and transfer these elements, together with other nutrients, to leaves in the vegetation period. The minerals accumulation is strongly affected by the chemical composition of the soil from which trees get their nutrients.

The heavy metals concentrations of leaves and soils obtained by EDXRF are presented in the Table 2.

Table 2

Heavy metals concentrations [mg/kg w.d.] in *Acacia* leaves and soils obtained by EDXRF

No	Concentrations of heavy metals in leaves				Concentrations of heavy metals in soil			
	Fe	Mn	Ni	Zn	Fe	Mn	Ni	Zn
P_1	226.2	140.94	2.78	19.07	7125.29	619.67	120.51	1089.9
P_2	210.04	222.92	3.03	52.29	7324.68	854.37	121.77	967.77
P_3	258.23	104.73	2.97	45.38	5110.07	497.98	95.72	389.15
P_4	243.93	314.78	2.71	18.89	7624.75	822.75	105.61	1248.06
P_5	200.63	58.01	2.73	41.54	5098.12	316.61	65.13	367.97
P_6	213.75	116.83	2.78	37.73	6120.80	309.31	81.23	520.69
P_7	224.47	102.53	2.81	35.72	6802.77	495.03	125.1	1011.21
P_8	291.82	136.87	2.83	52.35	7055.89	267.43	104.76	1011.6
P_9	290.53	75.39	2.47	35.59	6419.14	230.38	88.04	886.57
P_{10}	256.63	90.35	2.56	41.45	7302.42	314.54	156.41	1162.37
P_{11}	254.97	58.99	2.55	26.45	7055.16	309.75	161.03	1028.99
*ML-IL**	-	-	-	-	4500-7000	2000-4000	200-500	700-1500

* ML-IL = Maximum level – Intervention level mentioned in Order no. 756/1997 (Romanian legislation).

From the wide range of heavy metals we have chosen these four (Fe, Mn, Ni, and Zn) because they are frequently used in pesticides and foliar fertilizers obtaining. The collection points P_1, P_2, P_4, P_7, P_{10} and P_{11} are situated in zones with agricultural activities (fruit growing, viticulture and cereal culture). Near the collection point P_8, functions a hydropower plant and a few gravel pits. All the other points (P_3, P_5, P_6 and P_9) are situated in forest zones.

The highest Fe content in leaves was observed in the sample 8, the higher Mn level was obtained in sample 4 and Ni and Zn was founded in high concentrations in sample 2. For the samples 2 and 4 the heavy metals high concentrations can be explain by the agricultural treatment applied. Intensive agriculture based on mechanization, chemical treatment, irrigation, concentration and specialization was led to the appearance of the pollution in agriculture. A large part of agricultural treatments (pesticides and fertilizers) contain a number of toxic compounds that affect the soil, the air and the water. The high concentration of Fe in sample 8 is the consequence of the gravel pits functioning, because the hydropower plants are apparently non polluting units. Hydropower plants affects the environment through the landscape and ecosystems changes, affects the diversity and number of species and the water quality (the concentration of salts). Due to excessive atmospheric humidity in the area can cause climate disturbances. The pollution resulted from the extracting activities of sand and gravel from river beds is represented by the dust released into the atmosphere, the emissions of noise and vibrations generated by the washing-sorting stations, the transport and the storage of extracted materials.

In the Figs. 5–8 are presented the isoconcentrations curves of heavy metals analyzed in leaves samples and in Figs. 9–12 are presented the isoconcentrations curves of heavy metals analyzed in soil samples.

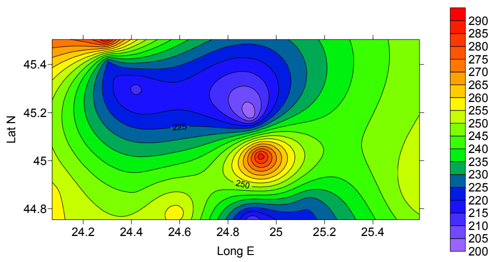

Fig. 5 – Isoconcentrations curves of Fe in leaves.

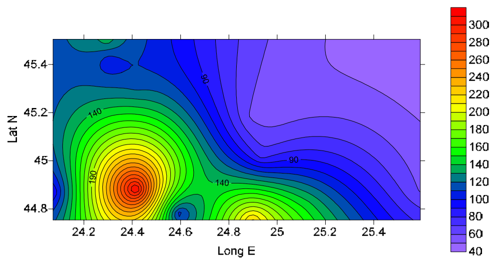

Fig. 6 – Isoconcentrations curves of Mn in leaves.

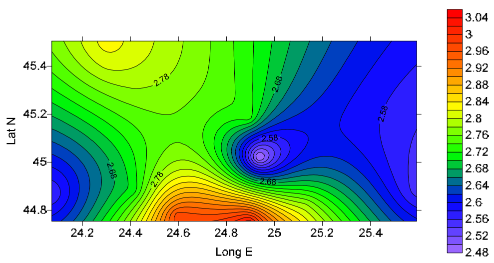

Fig. 7 – Isoconcentrations curves of Ni in leaves.

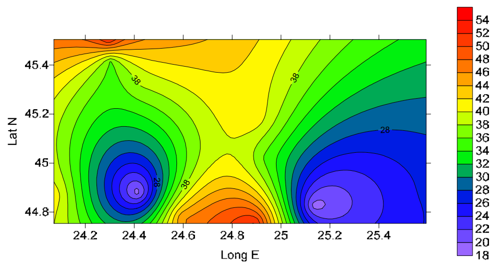

Fig. 8 – Isoconcentrations curves of Zn in leaves.

As can be seen (Table 2), all soil samples have the iron concentration exceeding the maximum level (4 500 mg/kg d.w.), and in 6 soil samples the iron concentration exceeds the intervention level (7 000 mg/kg d.w.). Also, 8 soil samples have the zinc concentration exceeding the maximum level (700 mg/kg d.w.), but none of the samples does not exceed the intervention level (1 500 mg/kg d.w.). In the cases of manganese and nickel are not recorded exceeding of the maximum level (2000 mg/kg d. w. – Mn; 200 mg/kg d.w. - Ni).

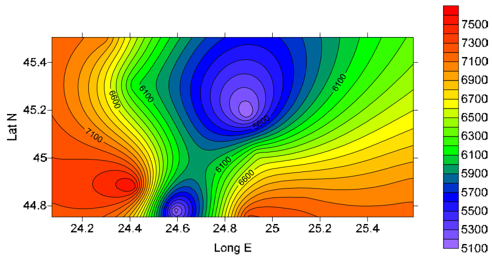

Fig. 9 – Isoconcentrations curves of Fe in soil.

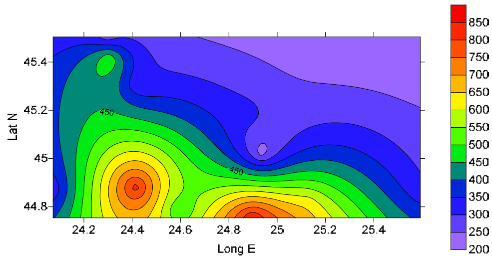

Fig. 10 – Isoconcentrations curves of Mn in soil.

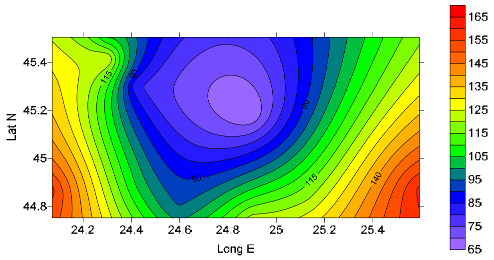

Fig. 11 – Isoconcentrations curves of Ni in soil.

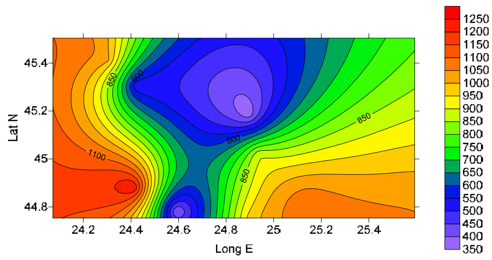

Fig. 12 – Isoconcentrations curves of Zn in soil.

The collection points are placed in zones with different types of activity and so, the transfer degree of heavy metals from soil in leaves is different. This is named, in literature, accumulation coefficient.

The accumulation coefficient has been calculated using the follow equation:

$$K_a = \frac{C_{leaf}}{C_{soil}} \tag{1}$$

with: K_a – accumulation coefficient, C_{leaf} – heavy metal concentration in leaf, C_{soil} – heavy metal concentration in soil.

A plant is considered to be bioaccumulator if the accumulation coefficient (K_a) is at least equal or higher than 1.

The values obtained for accumulation coefficient are presented in Table 3.

Table 3

Accumulation coefficient of analyzed heavy metals in *Acacia* leaves

No.	Accumulation Coefficient			
	K_a Fe	K_a Mn	K_a Ni	K_a Zn
P_1	0.031746	0.227444	0.023069	0.017497
P_2	0.028676	0.260917	0.024883	0.054031
P_3	0.050534	0.21031	0.031028	0.116613
P_4	0.031992	0.382595	0.02566	0.015135
P_5	0.039354	0.183222	0.041916	0.11289

Table 3 (continued)

P_6	0.034922	0.377712	0.034224	0.072462
P_7	0.032997	0.207119	0.022462	0.035324
P_8	0.041358	0.511797	0.027014	0.05175
P_9	0.04526	0.327242	0.028055	0.040143
P_{10}	0.035143	0.287245	0.016367	0.03566
P_{11}	0.03614	0.190444	0.015836	0.025705

As can be seen in Table 3, the heavy metals are not accumulated from soil in leaves. The high values of K_aMn are explained by the fact that manganese and iron is the most important pair of catalysts for oxidation-reducing processes in plants; manganese is a component of chloroplasts and participates in the water photolysis.

4. CONCLUSIONS

EDXRF technique has been employed in order to evaluate the pollution of soil and vegetation with heavy metals (Fe, Mn, Ni, and Zn). The results of this study showed the fact that *Acacia greggi* leaves are not a metal bioaccumulator.

The heavy metals concentration in soil samples was compared with the values reported in Romanian legislation (Order no. 756/1997). From the results can be remarked that all samples (11) have iron concentration higher than the maximum level, and 6 samples contain iron in a concentration higher than the intervention level, 8 soil samples have the zinc concentration higher than the maximum level, but none of the samples does not exceed the intervention level and the manganese and nickel concentration are less than the maximum level.

The highest concentration of Fe in Acacia leaves have been recorded in the collection point P_8; these high values are explained by the presence in the atmosphere of sedimentary powder resulted from activities of gravel pits. In the case of Mn, the highest concentration has been determined in the collection point P_4 where the agriculture is the main activity of the people. Also, the maximum concentrations of Ni and Zn have been reported in the point P_2. In this area the intense agricultural activity is the main factor of pollution and also, the presence of railway and high voltage lines increase the pollution degree.

Acacia is a tree that grows quickly, isn’t pretentious to climate changes because it adapts easily, but is sensitive to high concentrations of heavy metals.

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