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Uptake of Heavy Metals by Different Spontaneous Plant Species Grown Along Lana River, Albania

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Plants absorb a number of elements from soil, some of them are not known for their biological function and some are known to be toxic at low concentrations. The aim of this study is to assess the accumulation of heavy metals (lead, cadmium, nickel, manganese) in some plant species grown in water media. Concentrations of heavy metals were measured also in bottom sediments, near the root of plant species, in one of the most polluted rivers in Tirana *i.e.*, Lana River. Three stations were chosen to assess the effect of growth environment in metal accumulation by each plant depending on water quality and pollution. Beside this, physico-chemical parameters of water samples were measured at time of sampling. Considerable higher contents of Ni and Cd were accumulated especially in species *Typha latifolia* L., (about 254.3 mg/kg Ni) whereas species *Arundo donax* L. accumulated more Mn (about 182.7 mg/kg). Accumulation of Pb and Cd was almost the same in all plant species. Positive correlation was found between the concentrations of Pb and Ni in sediments and in plants for species *Typha latifolia* as well as for *Arundo donax* L. The content of metals accumulated in species *Salix alba* L. was not in good correlation with the content in sediments. All sediment samples sites in the study area basin were generally more or less polluted when compared with the control values. Therefore, all plants can be used as biological indicators while determining environmental situation of a special environment. The results confirm the complexity of factors influencing the efficiency of heavy metal accumulation by plant species. They indicate increasing ion absorption in the case of some metals, while the accumulation of other heavy metal ions was limited.

Key Words: Bioaccumulation, Heavy metals, Polluted water, Atomic absorption spectroscopy.

INTRODUCTION

Plants have a tendency to absorb a number of elements from soil. Some of them are not known for their biological function and some are known to be toxic at low concentrations. Their availability in a soil-plant system depends on a number of factors which include pH of the soil, soil organic matter content, cationic exchange capacity as well as plant species, stage of development, *etc.*[1]. It is known that the availability of some heavy metals decreases with rising pH of the soil, organic matter and clay content[2]. Some of the absorbed elements are referred to as essentials because they are required for plants to complete their life cycle. As plants constitute the foundation of the food chain, some concerns have been raised about the possibility of toxic concentrations of certain elements being transported from plants to higher strata of the food chain. Special attention has been given to the uptake and biotransformation mechanisms occurring in plants and its role in bioaccumulation and impact on consumers, especially human beings. The distribution and behaviour of many aquatic macrophytes are often correlated with water quality[3]. The accumulation of considerable amounts of heavy metals by aquatic macrophytes in their tissues was reported by Kovacs *et al.*[4]. Therefore, aquatic macrophytes were proposed as pollution-monitoring organisms. Metal bioaccumulation depends upon numerous biotic and abiotic factors, such as temperature, pH and dissolved ions in water[5,6].

Heavy metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. They can directly affect plant growth and an excess dietary intake of contaminated plants could also be dangerous for the health of human being and animals. The chemical composition of plants reflects the elemental composition of the soil and the contamination of the plant surface indicates the presence of noxious environmental contaminants in ambient air. There is a need for analytical laboratories to perform rapid, accurate and reproducible analyses of various types of environmental samples. The aim of present work is to the evaluation of metal content in two water plant species using atomic absorption spectroscopy.

EXPERIMENTAL

Sample collection and preparation: *Typha latifolia* L. *Salix alba* L. and *Arundo donax* L. plant species were selected in present studies. *Typha latifoglia* belongs to the Typhaceae family. It is an erect, perennial freshwater aquatic herb which can grow 3 or more meters in height[7]. *Arundo donax* L. is a tall perennial grass grown in freshwaters. Arundo is a tall, perennial, cane-like grass that resembles bamboo[8]. The main stems of *Arundo* reach a height of 3-10 m, a diameter of 1-4 cm and commonly branch during the second year of growth. Once established, *Arundo* forms large, dense clonal rhizome masses that produce a high density of stems. *Salix alba* L. white willow is a large tree that grows in Central and Southern Europe, Asia and North America. Also known as European willow or baywillow, this tree prefers to root near streams and rivers and grows to a height of 35-75 ft (11-25 m). In the spring, the slender branches first sprout tiny, yellow flowers and then long, thin green leaves.

White willow belongs to the Salicaceae family. There are over 300 species of willow, but only several species are used medicinally: white willow (*S. alba*), purple willow (*S. purpurea*), violet willow (*S. daphnoides*) and crack willow (*S. fragilis*).

Plant species were collected in three different stations of one of the most polluted rivers in Albania, the Lana river, beginning from its mouth and going across the city of Tirana, in a certain distance from each other. Species identification was done based on the literature of the Albanian flora[9]. Plant species were cleaned up prior to chemical analyses, washed with deionized water and dried at room temperature for 75 h.

Treatment of plant samples: All plant samples were oven dried at 80 ºC for 24 h. To ensure uniform distribution of metals in the sample, the material was milled in a micro hammer cutter and sieved through 1.5 mm sieve. After homogenization, plant and sediment samples were placed in clear paper bags. pH values of water samples were calculated with a portable pH meter.

About 2 g of dried plant samples was weighted and left in a mixed solution of HNO_3 + HCl in 1:4 ratio for 7 days in closed PTFE vessels. After that, samples were digested for 2 h in 200 ºC, until wet salts were reached. Samples were sent to desired volume with distilled water and analyzed by AAS method.

Treatment of sediment samples: Sediment samples were collected in the same points as the plant species, in a depth of about 10 cm from the surface, using a stainless steel crab. They were dried and passed through a 2 mm sieve. The total metal content was determined after the treatment of samples with 4 mL of aqua regia (HCl/HNO_3, 3:1) in PTFE vessels and digested in a hot plate for 3 h. The digests were made up to 20 mL volume with deionized water, transferred in polyethylene containers and stored at 4 ºC until analysis. All the reagents employed were of Suprapur grade (Merck). The determination of metals was carried out using flame AAS for Ni, Mn determination as well as ETA-AAS for Pb and Cd determination. All measurements were conducted using a Varian SPECTRA 10-Plus atomic absorption spectrophotometer equipped with GTA-96 graphite furnace. Chemical modifier such as $NH_4H_2PO_4$ was used for Cd and Pb determination with ETA-AAS.

SD-M-2TM IAEA certified reference material was used for quality control of the results of heavy metals in sediments. Blank analyses were carried out, showing negligible contamination.

RESULTS AND DISCUSSION

In Table-1 the results of the total metal concentration (mg kg^{-1}) in sediment samples studied are implied. Three subsamples were analyzed for each determination and the values of relative standard deviations are given. The content of all metals resulted to be higher in station 2 and lower in stations 3 and 1. This is because in this point the level of urban and industrial wastes discharge is higher compared especially with the levels in station 1, where the river begins and the quality of water is good (Table-6). Levels of metals in sediments resulted to be low and all the samples belong to the second class according to NIVA classification[10] as moderately polluted.

TABLE-1
CONCENTRATION OF HEAVY METALS IN SEDIMENTS OF RIVER (mg kg^{-1})

Station	Cd	RSD	Mn	RSD	Pb	RSD	Ni	RSD
1	0.10	0.01	301.28	4.53	0.21	0.02	54.42	0.13
2	0.20	0.01	503.51	2.91	0.34	0.03	87.03	0.16
3	0.20	0.01	343.00	12.5	0.26	0.01	70.08	0.10

Results regarding the content of heavy metals in different plant species are given in Tables 2-5. The concentration of heavy metals accumulated varied within different plant species of the same station as well as in different stations for the same plant. Species *Typha latifolia* L. and *Arundo donax* L. resulted to accumulate higher levels of Ni, Pb and Cd metals whereas Mn resulted to be accumulated in higher quantities in *Salix alba* L. and *Arundo donax* L. species.

TABLE-2
CONCENTRATION OF Ni (mg kg^{-1}) IN PLANT SPECIES

Station	1		2		3	
	Conc. (ppm)	RSD	Conc. (ppm)	RSD	Conc. (ppm)	RSD
Salix alba L.	18.61	2.0	32.42	1.6	54.33	3.3
Typha latifolia L.	88.17	2.3	134.45	8.4	249.49	10.43
Arundo donax L.	54.67	8.6	73.24	1.0	39.20	4.3

TABLE-3
CONCENTRATION OF Mn (mg kg^{-1}) IN PLANT SPECIES

Station	1		2		3	
	Conc. (ppm)	RSD	Conc. (ppm)	RSD	Conc. (ppm)	RSD
Salix alba L.	54.23	1.0	93.25	4.3	212.84	13.3
Typha latifolia L.	53.84	1.2	64.42	5.4	43.75	12.3
Arundo donax L.	16.97	1.2	182.73	7.8	150.44	11.2

TABLE-4
CONCENTRATION OF Pb (mg kg^{-1}) IN PLANT SPECIES

Station	1		2		3	
	Conc. (ppm)	RSD	Conc. (ppm)	RSD	Conc. (ppm)	RSD
Salix alba L.	0.19	5.6	0.23	8.9	0.18	6.7
Typha latifolia L.	0.26	5.8	0.32	10	0.18	6.5
Arundo donax L.	0.01	4.5	0.23	9.2	0.25	9.4

TABLE-5
CONCENTRATION OF Cd (mg kg^{-1}) IN PLANT SPECIES

Station	1		2		3	
	Conc. (ppm)	RSD	Conc. (ppm)	RSD	Conc. (ppm)	RSD
Salix alba L.	<0.05	–	0.03	5.9	0.04	6.7
Typha latifolia L.	<0.05	–	0.02	4.0	0.04	6.5
Arundo donax L.	<0.05	–	0.03	6.2	0.05	9.4

TABLE-6
PHYSICO-CHEMICAL PARAMETERS
OF RIVER WATER SAMPLES

Parameter/station	1	2	3
Disolved oxygen (mg L^{-1})	5.7	0.5	0.8
pH	7.8	7.4	7.5
Conductivity (μS cm^{-1})	163	745	687
Temperature (ºC)	14.2	14.8	14.4

Positive correlation was found between the concentrations of Pb and Ni in sediments and in plants for species *Typha latifolia* L. as well as for *Arundo donax* L. (Table-7). The content of Mn and Ni accumulated in species *Salix alba* L. was not in good correlation with the content in sediments.

TABLE-7
CORRELATION COEFFICIENT BETWEEN CONTENT OF
EACH METAL IN PLANT SPECIES AND SEDIMENTS

	Mn	Ni	Pb	Cd
Salix alba L.	-0.09	0.36	0.84	0.97
Typha latifolia L.	0.76	0.26	0.54	0.94
Arundo donax L.	0.79	0.56	0.74	0.50

Determination of heavy metals content in plant species is not sufficient in order to obtain relevant information regarding the accumulation capacity of any plant species. Consequently, values of the Bioaccumulation coefficient "KBA" were calculated as the ratio of the content of metals in plants and in sediments taken in three stations and the average value was used to evaluate the accumulation capacity of each plant species (Fig. 1).

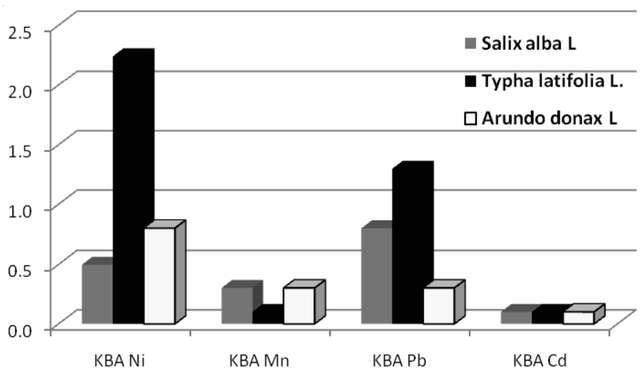

Fig. 1. Values of bioaccumulation coefficient in plant species

Bioaccumulation coefficient values show that species *Typha latifolia* L. is characterized by higher values of the accumulation capacity for Ni and Pb, whereas species *Arundo donax* L. performed high accumulation capacity for Mn. All plant species had the same accumulation capacity for Cd. Accumulation of heavy metals in plant species showed positive correlation with the conductivity values of the water media (Table-8) as well as with temperature.

TABLE-8
CORRELATION COEFFICIENT BETWEEN
METAL CONTENT IN PLANT SPECIES AND WATER
PHYSICO-CHEMICAL PARAMETERS

Salix alba L.	pH	DO	Cond	Temp. (ºC)
Mn	-0.50	-0.65	0.62	0.05
Ni	-0.62	-0.76	0.74	0.20
Pb	-0.54	-0.38	0.41	0.87
Cd	-0.88	-0.96	0.95	0.58
Typha latifolia L.				
Mn	-0.25	-0.07	0.10	0.66
Ni	-0.53	-0.68	0.66	0.09
Pb	-0.16	0.03	0.01	0.59
Cd	-0.84	-0.93	0.91	0.50
Arundo donax L.				
Mn	-1.00	-0.99	1.00	0.86
Ni	-0.29	-0.10	0.14	0.69
Pb	-0.95	-0.99	0.99	0.70
Cd	-0.28	-0.45	0.42	-0.19

Conclusion

Accumulation of heavy metals in three different plant species grown in water media was studied. Results show that the accumulation of heavy metals by plant depends not only on the content of heavy metals in sediments were they grow but also from the kind of plant species and the affinity that plants can have for specific elements. The increase of metal level in sediments was not positively correlated with the content in plants, especially for Mn and Ni in species *Salix alba* L. and *Typha latifolia* L., which is an indicator of the lower affinity of these plants for these metals. From the values of the bioaccumulation coefficient (KBA), it can be shown that different plant species showed higher accumulation capacity for some elements whereas for other elements it resulted very low. Sediments of this river showed low quantity of heavy metals, belonging to the second class of classification, as moderately polluted even though some plants showed high affinity to absorb them.

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