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## THE POTENTIAL OF DIFFERENT PLANT SPECIES FOR NICKEL ACCUMULATION

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### ABSTRACT

Contamination of the environment with toxic heavy metals is a mayor environmental problem. Aimed to find effective and economical attractive solutions for environment cleaning, scientists intensively evolve various phytoremediation techniques. Nickel is one of the essential micronutrients for plants, animals, and humans, but toxic at elevated concentrations. Also, it belongs to a group of heavy metals. In respect of the fact that Ni uptake relies upon plant species and that some of them show hyperaccumulation effects, the aim of our study was to analyse Ni concentration in certain plant species affected by Ni contamination of air and surface soil. Ni deposition in the air was below 60 µg/m<sup>2</sup>/month, while Ni content in the soil was between 42 and 150 µg/g. Average Ni content in plants ranged from 0.1 to 5.0 µg/g. Regardless the analysed locality, the highest Ni (7.1 µg/g) was obtained with the hogweed, whereas the lowest (4.5 µg/g) with the vines. *Ambrosia artemisifolia* and *Taraxum officinale* accumulated the greatest amounts of Ni (10.72 and 10.61 µg/g, respectively). It may be concluded that the analysed plant species exhibit various phytoremediation potential for Ni under the same ecological conditions.

**Keywords:** Pollution, phytoremediation, nickel, plants

**Abbreviations:** D.W. - dry weight; MTC - maximal tolerated concentrations; Ni - nickel.

### Introduction

The role of monitoring of heavy metal pollution is impressive, taking into consideration their toxicity and accumulation events. Calculated per annum, the deleterious effects of heavy metals exceed total harm originating from radionuclides and organic wastes produced each year (20). Their negative effects upon biosphere provoke the increasing attention of scientists, particularly their harmful influence reinforced by a long-term exposure and cumulative effects (10).

Nickel as an essential microelement to plants, animals, and humans belongs to a group of heavy metals. Its amounts exceeding optimum values show a toxic effect. Similar to other heavy metals, excess concentration of Ni causes chlorosis and necrosis, resulting from disturbed Fe uptake and metabolism (34, 35). Elevated concentrations of Ni can inhibit cell division at root meristems in non-tolerant plants (33), and decrease plant growth (32). Also, previous studies showed that Ni has a negative effect on photosynthesis and respiration (31).

Various natural processes and also the human impact may elevate its concentration. An outstanding example is the anthropogenic activity including the combustion of fossil fuels, operation of smelters, and metal refineries. Main source of Ni emission is the combustion of fossil fuels and traffic frequency. For example, total anthropogenic Ni emission into the atmosphere found in California amounts 23-360 t/year (24), whereas in Croatia 20-46 t/year (22). Of the total Ni present in the atmosphere, 20% is associated with traffic.

The average Ni concentration in crude oil amounts 19,690 ppb while in oil fuels 28 ppb (16). As Ni content in the oil relies upon oil deposits, it may amount even up to 93,000 ppb in the South American oil (19). Exhaust gases originated from the combustion of fuel for a diesel engine contain more than 40 air pollutants (21) among which are nickel-oxide, nickel-sulphate, and nickel-subsulphide. All these compounds have a deleterious effect upon vegetation while their genotoxicity and malignancy effects are also recorded (25). In respect of the fact that Ni uptake relies upon plant species and that some of them show hyperaccumulation effects (18), the aim of our study was to analyse Ni concentration in certain plant species affected by a local Ni contamination of air and surface soil along 12 km of M-21 going across the National Park Fruška Gora.

### Materials and Methods

Ni concentration and accumulation in plant species growing in the National Park Fruška Gora, along 12 km of the M-21 (Irig - Iriški Venac - Paragovo) were determined. The analysis of Ni content in air and soil, as well as in vegetative parts of certain herbaceous plants and vines occurring at seven selected sites (**Fig. 1**) was conducted.

Analyzed plant species were vines, clematis (*Clematis vitalba*) and hederia (*Hedera helix*), and herbaceous plants, nettle (*Urtica dioica*), dandelion (*Taraxacum officinale*) and hogweed (*Ambrosia artemisifolia*).

Ni content in plant material was analysed by employing atomic absorption spectrophotometry. Air sampling for the analysis of Ni deposition was performed at two sites (Iriški Venac and the control). Both sites were furnished with sedimentators while samples were analysed in the Laboratory

of the Faculty of Chemistry, University of Belgrade, every 30 days. Sedimentators were mounted during winter (December-February) in the period 2004-2005. Analysis of content and Ni concentration was done by AAS.



Fig. 1. Part of the M-21 (Irig - Iriški Venac - Paragovo section)

Soil sampling for the analysis of the soil Ni content was done by opening the soil profiles where the samples were taken at 0-5 cm, 5-10 cm, 10-20 cm and 20-40 cm soil depth. Ni content and concentration were determined by using atomic

absorption spectrophotometry while “pseudo-total” Ni content was determined according to UNEP-UN/ECE (26).

The obtained results were processed by using the variance analysis and LSD-test for  $p = 0.05$ . The Duncan test was used to determine the significance of mean values. Means designated with the same letter show no significant difference for  $p = 0.05$ . The results are presented in tables and graphs.

## Results and Discussion

It is well known that the Earth crust is composed of about 0.008 % Ni. On the other hand, elevated Ni concentrations are recorded in the air, along the busy lines of communication in particular. The California Air Resources Board and the Department of Health Services estimations show that petrol and diesel engines increase Ni emissions by 54-72 t/year (24). Ni concentration in exhaust pipes of the diesel engines is between 500 and 10.000 mg/l (8). Air contamination by harmful solutions causes physiological, anatomical and morphological changes of plants (6). The effect of gaseous pollutants is readily visible on leaf surface where process of assimilation, dissimilation, and transpiration takes place. Also, extremely high Ni concentrations cause necrosis of the edge of leaf lamina.

The study of the traffic events on the M-21 (Table 1) shows that total vehicles per day amounts 7001, out of which 5647 belongs to the passenger cars using petrol and 1354 diesel fuels. Since the measurement point is situated in the Irig site, a total transport of people and goods moves in a road Irig – Iriški Venac. Half of these vehicles moving in a road Iriški Venac - Paragovo and the other half in the road Paragovo - Iriški Venac possibly cause different contamination rates by heavy metals due to a different number of vehicles and also their different speed. Obtained data show a tendency towards the increase of total vehicles, passenger cars using petrol in particular, and also those with diesel engines.

### Air born nickel deposition intensity

Air pollutants include high concentrations of chemical substances released into the air from different sources. Air pollution may also originate from elevated concentrations of already present air constituents. The pollutants may be divided into the two groups, i.e. primary and secondary.

TABLE 1

Average and expected number of vehicles per day in the period 2004-2008 on the M-21 (Irig – Paragovo)

Year	Vehicles per day										
	Total	PC	B	V <sub>3T</sub>	V <sub>7T</sub>	HV		TC			
						HV <sub>1</sub>	HV <sub>2</sub>	Total TC	TC <sub>1</sub>	TC <sub>2</sub>	TC <sub>3</sub>
2004	7001	5647	180	258	189	153	17	557	155	89	313
2005	7337	5929	186	266	197	159	18	582	162	81	339
2006	7656	6196	192	274	203	166	18	607	169	73	365
2007	7989	6475	197	282	211	172	19	633	176	65	392
2008	8337	6766	203	290	218	178	20	660	184	57	420

Where: PC = passenger car; B = bus; V<sub>3T</sub> = vehicle for carrying freight (up to 3t); V<sub>7T</sub> = vehicle for carrying freight (7t); HV = heavy vehicle for carrying freight; HV<sub>1</sub> = heavy vehicle for carrying freight (one shaft drive); HV<sub>2</sub> = heavy vehicle for carrying freight (two shaft drives); TC = freight train; TC<sub>1</sub> = freight train carrying cars; TC<sub>2</sub> = freight train carrying cars (two shaft drives); TC<sub>3</sub> = freight train carrying cars (three shaft drives)



Former includes the chemical substances produced by different chemical processes, i.e. in metal smelters, domestic disposal sites, and traffic. The latter group is made of chemical substances introduced into the air by either different chemical reactions or physico-chemical processes associated with the primary pollutants (27).

The World Health Organization (29), in its instructions specifying the air quality for Europe, quoted As, Cd, Cr, Pb, Mn, Hg, Ni, Ru and V as highly dangerous trace metals. These pollutants are found in soil, minerals, and fuels. Some of them are main ore constituents. They occur in surface soil and water and also in plants even if they are not present in the air (7).

The analysis of the effect of the air pollution upon plants is primarily concerned with plant cells absorbing pollutants via stomata and cuticle, thus affecting the plant metabolism (28).

Wet and dry deposition processes are used to remove air particles. A mean total deposition value is used to calculate the deposition rate. Receptors are surface soil, vegetation, and surface waters, i.e. all the surfaces being in contact with the atmosphere.

It may be concluded that the Ni values point to a moderate course at the analysed sites (Table 2). A total Ni deposition is below 60 µg/m<sup>2</sup>/month at all the analysed sites, i.e. 260 µg m<sup>-2</sup>/day. On the other hand, mean annual deposition intensity at Iceland amounts 0.5 µg/m<sup>2</sup> while in the Great Britain 30 µg/m<sup>2</sup> (1). No enforced regulations for Ni deposition intensity and its limitations are defined in this country.

**TABLE 2**

Mean values of the Ni deposition intensity (mg/m<sup>2</sup>/month)

December 2004	
Site	mg/m <sup>2</sup>
Site III	<0,06
Site VII	<0,06
January 2005	
Site	mg/m <sup>2</sup>
Site III	<0,06
Site VII	<0,06
February 2005	
Site	mg/m <sup>2</sup>
Site III	<0,06
Site VII	<0,06

#### Ni accumulation in soil

According to Klocke (15), the most frequently recorded soil Ni content is between 10 and 50 mg/kg<sup>1</sup> while maximum value amounts 100 mg/kg<sup>1</sup>. Other authors found that the total Ni content ranges from 5 to 100 µg/g while in serpentine soils 500 µg/g, frequently even up to 600 µg/g (17). The reported results (Table 3) of soil properties at the analysed sites point to the alkaline soils reaction with pH ranging from 7.67 to 8.58. As an established standard, increase of Ni content is followed by an increase of soil depth.

The analysed soil is rich in humus where the surface layer (0-5 cm) shows the highest values. Humus content amounts between 0.49 and 14.81%, gradually decreasing as soil depth BIOTECHNOL. & BIOTECHNOL. EQ. 21/2007/4

decreases. Total clay content ranges from 11.10 to 65.80%. Carbonate content is between 1.40 and 39.10% indicating a carbonated soil type. The two main parameters indicating the Ni distribution between solid phase and soil solution are pH value and clay content. Hydroxyl Ni complex prevails at pH > 8, whereas in the case of higher carbonate amounts (the analysed soil) Ni carbonates (NiCO<sub>3</sub>, NiHCO<sub>3</sub>) are also recorded (11). A correlation between Ni content and humus and clay contents was found, where the correlation coefficient amounts 0.654.

**TABLE 3**

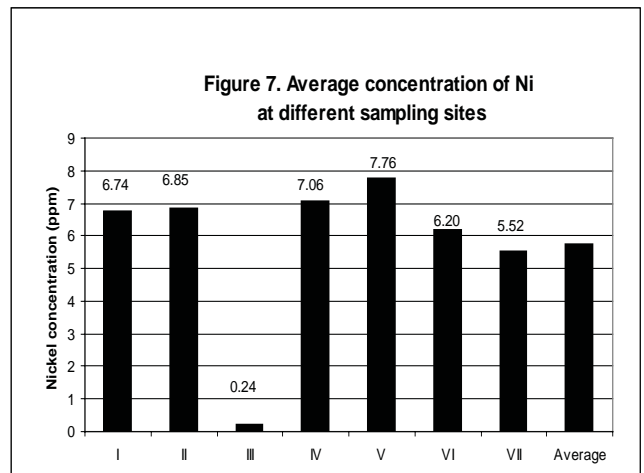
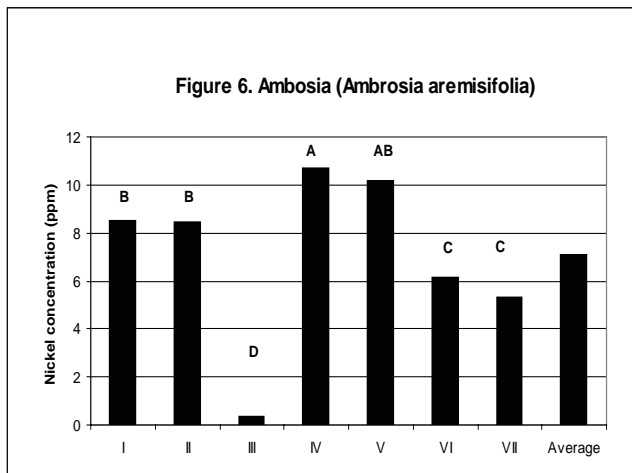
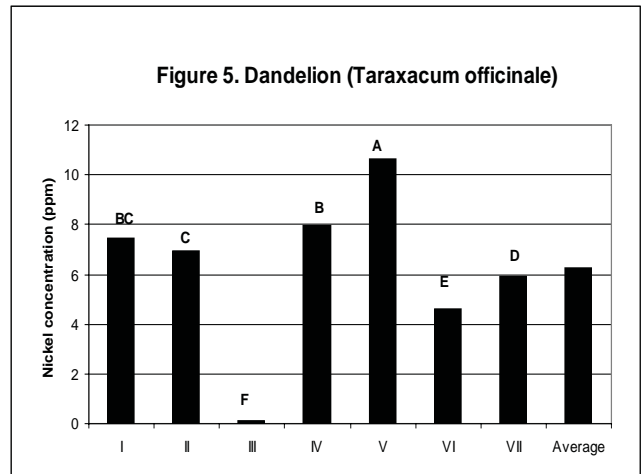
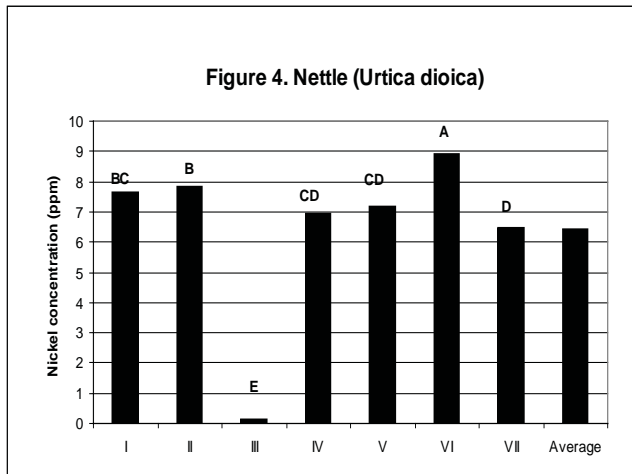
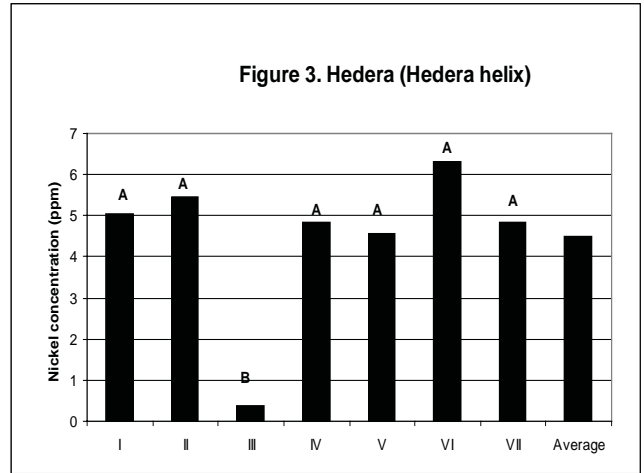
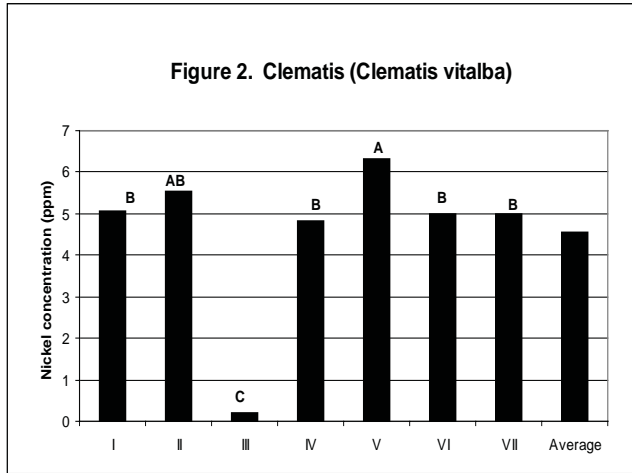
Ni concentration in soil

Site	Depth (cm)	Ni mg/kg	pH		% CaCO <sub>3</sub>	Humus (%)	Clay+silt (%)
			H <sub>2</sub> O	CaCl <sub>2</sub>			
I	0-5	99	7.86	7.20	8.35	14.81	42.90
	5-10	120	8.1	7.30	10.43	4.67	50.60
	10-20	120	8.2	7.30	11.48	2.44	53.40
	20-40	140	8.3	7.32	10.85	1.68	55.20
II	0-5	42	7.80	7.15	15.44	7.18	19.50
	5-10	62	7.90	7.23	11.68	2.57	11.10
	10-20	66	8.03	7.35	12.52	4.14	15.70
	20-40	91	8.20	7.50	19.20	1.74	47.80
III	0-5	83	8.05	7.30	39.10	11.27	39.50
	5-10	120	8.24	7.43	20.16	8.60	49.30
	10-20	120	8.36	7.50	12.40	1.48	62.70
	20-40	89	8.58	7.52	12.00	0.49	65.80
IV	0-5	64	7.82	6.97	11.64	8.27	30.90
	5-10	64	7.88	7.12	12.00	7.74	28.20
	10-20	73	7.9	7.20	10.90	7.66	24.10
	20-40	68	7.9	7.25	6.50	6.20	26.70
V	0-5	87	7.67	7.13	1.90	6.05	26.50
	5-10	79	7.75	7.19	1.60	3.70	21.00
	10-20	120	7.86	7.20	1.67	3.16	26.70
	20-40	150	8.06	7.18	1.40	3.34	28.40
VI	0-5	95	7.78	7.22	5.17	3.40	40.20
	5-10	79	7.92	7.32	8.35	5.15	38.20
	10-20	83	8.00	7.40	7.60	6.20	40.00
	20-40	89	8.00	7.42	7.00	4.70	38.40
VII	0-5	140	7.80	7.25	7.25	6.85	54.70
	5-10	150	7.87	7.32	6.23	3.86	52.90
	10-20	150	7.97	7.37	5.00	2.58	54.20
	20-40	150	7.96	7.39	5.40	1.70	50.00

The lightest soils are recorded at site 2, 4 and 5. Ni content was between 42 and 150 µg/g. These elevated concentrations exceed the permitted values of 50 µg/g tolerated by legislation (13).

#### Ni content in plants

Ni represents an essential microelement to higher plants (5, 12), animals and men (23). On the other hand, higher Ni



Figs. 2-7. Nickel concentration in different plant species in depending of site

concentrations tend to be toxic to plants (30). Its chemical properties are similar to those of Fe and Co. Plants take up this microelement in the form of Ni<sup>2+</sup> ions that produce a stable complex with certain organic molecules like cysteine and citrate. Also, Ni plays an important role in N metabolism (14). Ni transport through xylem and phloem is rapid and efficient while its considerable accumulation into plant fruits and seed is also known.

The uptake of heavy metals by plants relies upon their genetic background, root surface area, root capacity for ion absorption, root exudates, and the evapotranspiration rate (2).

The highest Ni concentration was recorded in plant leaves at site 5 (2.5 km of Iriški Venac in the Paragovo direction) and, also, at site 4 (at 500 m of Venac to Paragovo). The latter represents the spot where a smaller vehicle speed is recorded due to a curve that points out a direct relationship between Ni concentrations and the traffic density.

The lowest Ni concentration was found at site 3 (Iriški Venac) where an average value amounts only 0.25 µg/g. This accounts for the carbonate nature of soil highly rich in CaCO<sub>3</sub>, rich in humus, and with high clay content resulting in the occurrence of inaccessible Ni deposited on vegetative plant organs only.

By discussing the analysed plant species (Figs. 2-7) one may conclude that the hogweed contains 10.72 µg/g while the dandelion 10.61 µg/g Ni. Regardless the analysed locality, the highest Ni (7.1 µg/g) was obtained with the hogweed, whereas the lowest (4.5 µg/g) with the vines. A comparison between the recorded Ni concentrations and the available literature data shows that they are below a critical level. Critical toxicity levels are > 10 µg/g D.W. in sensitive and > 50 µg/g in moderate tolerant species (3). Beckett and Davis (4) defined the upper critical level as the concentration that causes a 10% yield reduction.

Capability for Ni accumulation varies between species. Average Ni content in plants ranges from 0.1 to 5.0 µg/g dry matter while its toxic values exceed 10 µg/g dry matter (12). Plants containing more than 1 mg Ni g<sup>-1</sup> in dry matter of their aerial parts are classified as hyperaccumulators, and these plants have been studied as interesting examples of evolution and adaptation and as useful indicators of metal contaminated areas. Although there are hyperaccumulators for other metals, plants that accumulate large amounts of Ni are the most numerous, with a total number of 318 taxa distributed in regions with Ni-rich soils (36). The present study's results indicate that, regarding Ni content in studied plants, they could not be labeled as hyperaccumulator species. Nickel phytotoxicity varies with its external concentration as well as with the plant species (38). Some plant species are tolerant to the nickeliferous soils so that accumulation of large quantities of Ni in their aerial parts produces no adverse effect (34, 39). Although Ni is an essential nutrient, the requirement for this element by non-hyperaccumulator plants is so low that Ni deficiency has never been reported in field-grown crops (37).

The deficiency in Ni content in the growing medium and the low activity of urease could upset nitrogen metabolism and leads to the accumulation of toxic urea levels (40).

When average Ni content of all the analysed plant species by the investigated sites (Fig. 7) is compared, a remarkable range of the obtained values is observed. Also, it may be concluded that the average values amount between 0.13 and 10.72 µg/g. Our results show that the analysed plant species exhibit varied potential for Ni under the same ecological conditions being in agreement with the data quoted by Guo and Marschner (9).

## Conclusions

Heavy traffic on the M-21 (Irig - Iriški Venac - Paragovo section) shows the tendency to increase its intensity in next years. Total air born Ni deposition was below 60µg/m<sup>2</sup>. Soil Ni content exceeded MTC, ranging from 42 to 150 µg/g. Average content of Ni in plants by localities was between 0.13 and 10.72 µg/g. In all the analysed plant species, the lowest Ni was recorded at site 3 (Iriški Venac). Ni hyperaccumulation was obtained with *Ambrosia artemisifolia* (10.72 µg/g) and *Taraxum officinale* (10.61 µg/g). On the M-21 this heavy metal is produced by the exhaust gasses of traffic moving on this busy road section.

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