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NICKEL CONTENT IN DECIDUOUS TREES NEAR COPPER MINING AND SMELTING COMPLEX BOR (EAST SERBIA)

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Abstract: Excessive amounts of nickel (Ni) in the environment may represent a potential risk for all living organisms, including humans. Regions with massive mining, smelting and other industrial activities are especially endangered. One of such regions is the Bor region (East Serbia), which is known for its copper mine, but also as one of the most polluted industrial and urban centers of the whole Balkan peninsula. A long-term monitoring of air-quality parameters in this area gives evidence of extremely high pollution by heavy metals such as: Cu, Zn,Pb, Cd and As. High levels of these elements are recently detected in soil and plant biota, but the knowledge of Ni levels is still missing. In this study, spatial soil and organs of lime and birch were collected from polluted zones and analyzed by ICP-OES to determine Ni accumulation. The results from the data analysis showed that there was no severe pollution by this trace element. Also, it was noticeable that the uptake and behavior of Ni in trees was regulated in a different way than for other heavy metals. Lime and birch gave us very useful information about the state of the environment of Bor and its surroundings and proved themselves to be suitable candidates for biomonitoring purposes. Unfortunately, the values of biological accumulation coefficients (BCF<1, MR<1) show that both plants have a very low rate of uptake, which limits their use in phytoremediation.

Key words:Nickel, trees, lime, birch, biomonitoring, phytoremediation

1. INTRODUCTION

Nickel (Ni) is a transition metal usually found in natural soils as atrace element, except in ultramafic or serpentinic soils, in which its levels may reach up to 2000mg/kg (Kabata-Pendias, 2011). Nickel concentrations in soils have enlarged worldwide during the previous century due to mining, smelting, industrial and other anthropogenic activities such as combustion of coal and oil (Yadav, 2010; Nagajyoti et al., 2010; Yusuf et al., 2011).With increasing Ni contamination, Ni excess is universally found in the living organisms. This may represent a potential risk for human health, as a correlation between nickel compounds and the incidence of lung and nasal cancer wasrecognized (Yaman, 2000).

On the other hand, nickel has been confirmed to be essential for the basic metabolism of soil microbes, plants and animals, even thoughts precise role has not been resolvedyet (Babula et al., 2008). Nickel concentrations in plantsrange usually from 0.05-10mg/kg DW (dry weight) (Gonnelli & Renella, 2012). This metal is involved in hydrolysis of urea into carbon dioxide and ammonia, and is required in higher plants for urease, the nickel-containing enzyme (Kabata-Pendias, 2011; Nagajyoti et al., 2010; Vamerali et al., 2010). For normal plant metabolism, a very small amount of Ni is needed. Symptoms of Ni deficiency, such as chlorosis and necrosis are seldom found in plants. The symptoms are a result of the lack of urease, which leads to urea accumulation to toxic levels and to deficiency of nitrogen (Gonnelli & Renella, 2012; Nagajyoti et al., 2010). Under Ni excess exposure, plants may exhibit reduced biomass, leaf chlorosis, morphological alterations, changes in water balance, inhibited root growth, membrane disintegration, ion leakage, lipid peroxidation, and eventually cell death

(Kabata-Pendias, 2011; Nagajyoti et al., 2010; Yadav, 2010; Yusuf et al., 2011).

Plants'responds to Ni toxicity vary significantly among plant species. Factors such asphase of growth, cultivation conditions, Ni concentration in soil and the time of exposure are very important in this process. Soil Ni toxicity thresholds to plants are difficult to estimate, but they are generally reported to be in the order of 100mg/kg. In sensitive plant species, critical toxicity levels are usually>10 µg/gDW and in moderately tolerant species>50 µg/gDW (Gonnelli & Renella, 2012). However, there are some plant species, so called hyperaccumulators, which can accumulate Ni concentrations higher than 1,000 mg/kg, DW in their shoots, without any toxic symptoms. Actually, the very first metal hyperaccumulator discovered was the Tuscan nickel plant *Alyssum Bertolonii.* Members of *Alyssum* family can accumulate over 400 kg Ni/ha. Another successful Ni accumulator is a member of *Brasicaceae*family:*Brassica juncea* (Indian mustard). Native vegetation of serpentine soils may contain up to 19,000 mg/kg (AW) (Gonnelli & Renella, 2012; Kabata-Pendias, 2011;Yusuf et al., 2011).

Biological factors, which represent indices of accumulative capabilities of plants, are usually very high for Ni accumulators. Biological factors are defined as(Alagić et al., 2013; Mingorance et al., 2007; Nagajyoti et al., 2010):

- Biological Concentration Factor, BCF (metal concentration ratio of plant roots to soil);
- Mobility Ratio, MR (ratio of heavy metal in above ground plant partto that in soil);
- Translocation Factor, TF (ratio of trace metal in the above ground plant part to that in plant root).

It is a well known fact that hiperaccumulating plants may be very useful for clean-up of polluted environment (Alagić et al.,2013; Maric et al., 2013; Marques et al., 2009), in particular for the mining waste rehabilitation (Damian & Damian, 2006), but also for phytomining. It should be noted that the phytomining of Ni has more potential thanother metals since most of the known hyperaccumulators are capable to concentrate1–3% Ni in dry matter, providing 12% to >20% in the residue; these values are anorder of magnitude higher than lateritic ores (Gonnelli & Renella, 2012).

In general, Ni is easily extracted from soil by plants (Gonnelli & Renella, 2012; Yusuf et al., 2011). Excessive amounts of Ni are accumulated in the cell walls and vacuoles as well (Rascio &Navari-Izzo, 2011). Yusuf et al., (2011) noted a controversy about the target plant organ: some investigations pointed that Ni tends to accumulate in newly formed plant parts as well as the seeds, while some other studies observed that Ni accumulation was more preferential in roots than in shoots. The investigators agree that the transport and storage of Ni is metabolically controlled in a way which allows this metal to behighly mobile in xylem and phloem, so that Ni is proficient to reach even the seeds, with leaves being the major target organs (Kabata-Pendias, 2011; Yusuf et al., 2011).

Leaves may also assimilate Ni into plant tissue through stomata (Yusuf et al., 2011). This way of assimilation may contribute significantly to the total metal content in above-ground plant organs. This particularly occurs when the plant is exposed to massive pollution of atmospheric origin (Alagić et al., 2013). It has been noticed that the metal content in leaves (especially tree leaves) represents a very specific evidence of spatial and temporal history of the polluted area. Trees can be particularly useful as biomonitors of trace metal pollution as they often are naturally growing in urban/industrial areas, and the content of trace metals in their tissues is very easy and cheap to establish (Alagić et al., 2013; Dmuchowski & Bytnerowicz, 2009; Mingorance & Rossini, 2006; Mingorance et al., 2007; Nkongolo et al., 2008; Samecka-Cymerman et al., 2009a; Unterbrunner et al., 2007).

The concept of utilization of various biological materials as indicators of the state of the polluted environment is well known for more than one hundred years (Čechakova et al., 2014). For processing plant samples from industrially contaminated areas, the element enrichment factor (EF) was usually calculated as: EF=Cpolluted/Ccontrol, where the Cpolluted and Ccontrol are the metal concentrations in plant parts (leaves, roots) from the polluted sampling site and the control site, respectively. Element enrichment factor is usually evaluated by using the local background values. Values of EF>2, point to the enriched samples (Mingorance et al., 2007).

Since trees are appropriate for biomonitoring and phytoremediation purposes, a large number of tree species have been examined. Among them, birch (*Betulaspp.*) and lime (*Tilliaspp.*) were of special interest, as species tolerant to effects of industrial pollution (Alagić et al., 2013; Kosiba, 2008; Kuzovkinaet al., 2004; Piczak et al., 2003; Reimann et al., 2001; Samecka-Cymerman et al., 2009b). Both mentioned tree species from contaminated sites in Bor (East Serbia) and its surroundings were examined in this study, to determine the accumulation of Ni.

The primary pollution sources in the environment of Bor are the mining and metallurgical processes. They are a source of sulfur-dioxide emission, dust with high content of heavy metals (copper, zinc, lead, arsenic, cadmium, nickel etc.), soot, carbon-dioxide and other pollutants. One hundred years of mining activities on the territory of Bor and its surroundings resulted in numerous ecological problems and enormous consequences as an inheritance.Due to the fact that the town was built in the close vicinity ofthe mine belonging to the Mining and Smelting Complex Bor (RTB Bor), the town itself represents an environmental hotspot of Serbia. The mining operations in Bor have affected the relief, microclimate, plant and animal biota and, most importantly,the health and existence of human population (Serbula et al., 2012).

The high concentrations of Cu, Pb, and Zn have been found in many plant species from Bor region (Antonijevic & Maric, 2008; Maric et al., 2013; Serbula et al., 2012), but the knowledge of the levels of trace elements such as As, Cd and Ni is still quite poor. Recently, a first investigation on the bioaccumulation of highly toxic As and Cd in birch and lime from this region was realized (Alagić et al., 2013). In present work, an investigation of Ni content has been done, with similar goals as follows: to establish the greatest concentrations of Ni in plant parts and soils; to investigate the correlation of metal concentrations in soils and plants; to evaluate the accumulation potential of adult trees in the most endangered sites; and to determine to what extent the studied metal is enriched in plant parts from the contaminated zone compared with those in the control zone.

2. MATERIAL AND METHODS

2.1 Description of the sampling area

The town of Bor, with the Bor Copper Mine, is situated in eastern Serbia, 220 km away from Belgrade and about 30 km away from the Bulgarian border. Geographic coordinates of the town of Bor are 44°25'N latitude and 22°06'E longitude. Bor is surrounded by mountains: Stol, VelikiKrs, and CrniVrh, with the peaks over 1000 m and the sea level of 378 m. The climate is moderately continental with the annual average temperature of 10.2°C, and the annual average rainfall of 688mm/m^2. The air humidity in Bor and its surrounding is 76%. High temperature oscillations and rapid changes of weather are the characteristics of this region. The dominant winds in this region are: the northwest (NW), the west-northwest (WNW) and the west (W). Wind direction influences the distribution of pollutants from the industrial facilities to the town of Bor and its surrounding areas.

In this study, the concentrations of Ni were determined in soils and plant parts of lime and birch from the most endangered zones (Fig. 1). The urban-industrial (UI) zone included two sampling sites: the centre of Bor town (area of the town park) and the hospital, both very close to the copper smelter, a dominant source of pollution, whereas the rural (R) zone included two rural settlements: Slatina and Ostrelj (Table 1). The control (C) zone was an unpolluted area in a tourist zone Zlot which is known for impressive characteristics of its intact nature. The main factors which influenced the selection of the representative sites for measuring the concentrations of Ni were: position of the industrial plants, volume and character of the emission, meteorological and topographic parameters, and the type of settlement.

2.2 Experimental

2.2.1 Sample Collection and Preparation

Plant material and spatial soil samples of *Tillia sp.* And *Betula sp.* were prepared for analysis as it was described in our previous paper (Alagić et al., 2013) samples of leaves and roots of *Tillia sp.* and *Betula sp.* were taken from three to five adult treesat each sampling site (Fig. 1). Fresh leaves were sampled in the quantity of about 200 g and were divided into two subsamples: washed and unwashed. The samples of soil were taken from the topsoil, from which root samples of both plants were taken, too. Root samples were washed with tap water followed by distilled water.

Table 1. Positions of sampling sites in relation to the source of pollution

Sampling site	Zone	Distance (km)	Wind direction
Bor center (town park)	UI	0.5	ENE
Bor hospital	UI	1	ESE
Ostrelj	R	4.5	WNW
Slatina	R	6.5	NW
Zlot	C	13	NE

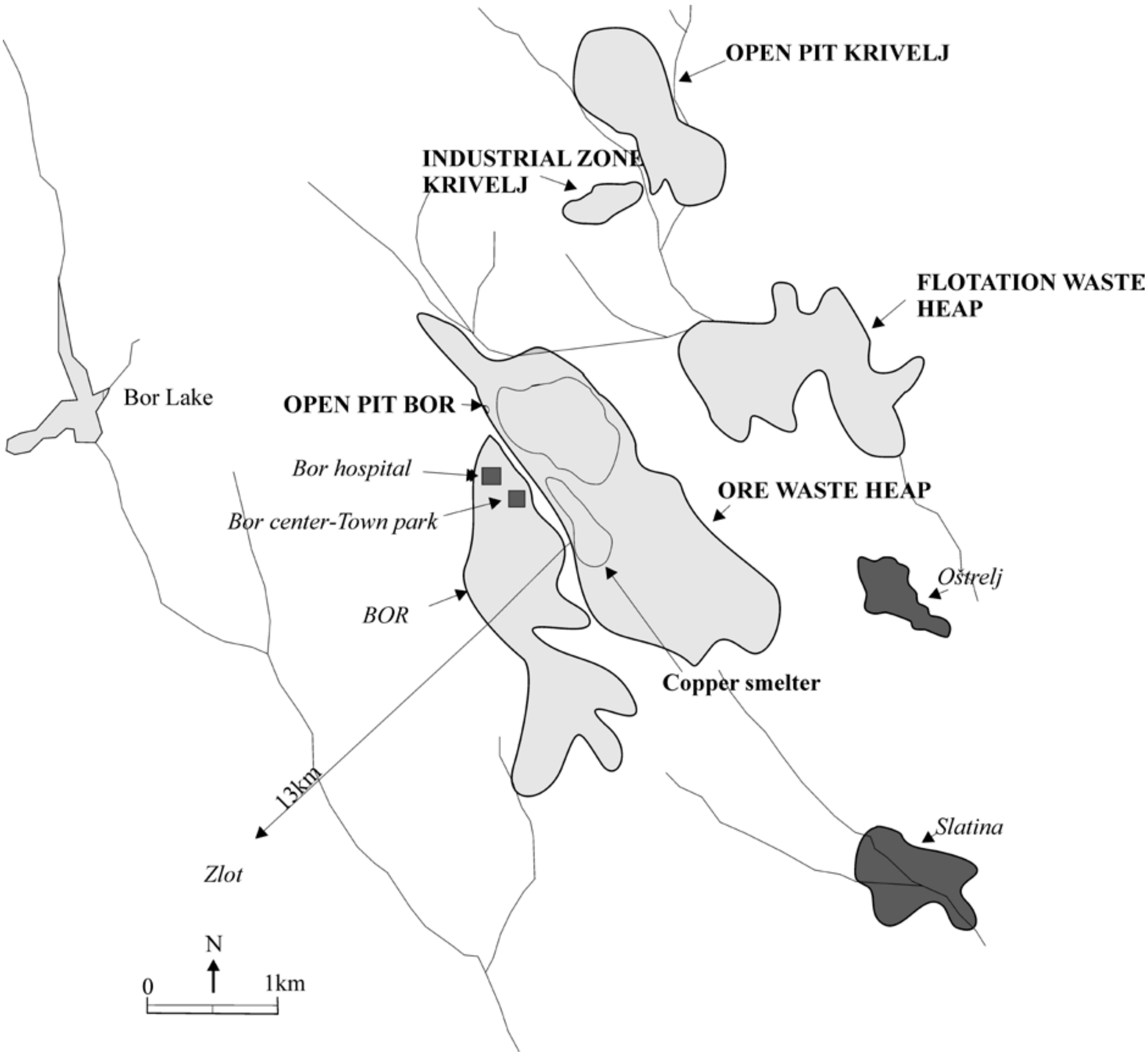

Figure 1. Study area with sampling sites in Bor and its surroundings

All of the samples were dried to a constant weight at room temperature, and after that homogenized in a laboratory mill and griddled through 0.2 mm sieve. 0.5g of each dried plant sample was measured (Precisa XR125 SB, semi-micro balance with a minimum 0.01 mg mass resolution), for the process of digestion.

Microwave digestion method with 65% HNO_3 (Merck, Darmstadt), and 10% H_2O_2 (Merck, Darmstadt) was used to achieve the complete decomposition of the organic matrix. The digestion was performed in the microwave digestion system MARS 5 CEM (CEM corp., USA) equipped with sealed containers (XP-1500 plus). The conditions wereas follows: 1200 W, up to 800 psi, with the temperature program: ramping time 15 min up to 180°C, and holding time 15 min at 180°C (const).

Obtained solutions were filtered and diluted to 25mL with ultra-pure waterand stored in polyethylene bottles at 4^{o}C previously treated with 5% nitric acidto avoid contamination of the samples, and washed with ultra-pure water (conductivity 0.05 μS/cm) which was obtained using MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH.

2.2.2 Instrumentation and Validation

iCAP 6000 inductively coupled plasma optical emission spectrometer (Thermo Scientific, Cambridge, United Kingdom) with an Echelle optical design and a charge injection device (CID) solid state detector was used for determination of Ni content in plant samples under the operate conditions as follows:

- Flush Pump Rate - 100 rpm
- Analysis Pump Rate - 50 rpm
- RF Power - 1150 W
- Nebulizer Gas Flow - 0.7 L/min
- Coolant Gas Flow - 12 L/min
- Auxiliary Gas Flow - 0.5 L/min

- Plasma View – Axial

The chosen wavelength for Ni, based upon tables of known interferences, baseline shifts and the background correction (the highest signal-to-background ratio) which was manually selected for the quantitative measurements was 231.604nm. The limit of detection (LOD), limit of quantification (LOQ) and correlation coefficient (r) were: 0.2233 ppm, 0.7443ppm and 0.9991, respectively. Detection and quantification limits were expressed as: LOD = 3xSD/m and LOQ = 10xSD/m, where SD is the standard deviation of blank responses and m is the slope of the calibration graph. The multi-element standard solution of about 20.00±0.10mg/L (Ultra scientific, USA) was used as a stock solution for calibration.

The soil samples were analyzed as it was described in our previous work (Alagić et al., 2013): the soil pH was determined by dissolving 5.0g of the soil samples in 25 mL of 1 mol/dm^3 solution of KCl, whereas the content of Ni in soil samples, was determined on a simultaneous inductively coupled plasma atomic emission spectrometer (ICP-AES, model "SpektroCiros Vision"). Previously, the soil samples (1g) were dissolved using a strong acid digestion method which dissolves all elements that could become environmentally available: after repeated additions of HNO_3 and H_2O_2 the resultant solutions are reduced in volume while heating and then diluted to a final volume of 100 mL. All results were calculated on a dry weight basis (mg/kg DW).

2.3 Statistical Analysis

In order to establish the effects of soil pH and the distance from the source of pollution on Ni content in plants' parts, as well as the correlations between Ni content in soil and plants' parts, the Pearson's correlation study was applied (Miller & Miller, 2005). All of statistical analyses were done using a statistical package IBM SPSS 20, United States.

3. RESULTS AND DISCUSSION

The content of trace metal Ni was analyzed at all the sampling sites in spatial soil, roots, and leaves of lime and birch. The detected concentrations are given in table 2, whereas the biological coefficients and factors are given in tables 3 and 4.

The fate of trace metals in soils is a result of many processes such as: dissolution, sorption and desorption processes, precipitation, complexation, diffusion, ageing, etc. All these processes are governed by several soil properties, of which soil pH is very important, influencing the metal solubility and availability to plant roots. The mobility of most metal ions usually decreases with the increase of pH and it is the highest in acid media (pH<5) (Unterbrunner et al., 2007). Soil at the examined sampling sites is moderately acid up to middle alkaline (Table 2). The lowest pH values were measured in the UI (site Bor center) and C zone whereas the highest pH value was recorded in the R zone.

According to Kabata-Pendias (2011), terrestrial background concentrations of Ni are: 5-20mg/kg in granites, and 1400-2000 mg/kg in serpentinic soils. Ni content in polluted soil can reach 20- to 30-fold (200–26,000 mg/kg) higher than the overall range (10–1000 mg/kg) found in natural soil (Nagajyoti et al., 2010; Yadav, 2010). The greatest contents of Ni in this work were found in soils from the control site Zlot and the sampling site Bor hospital from UI zone. But still, Ni concentrations at all sites were lower than maximal allowed concentration (MAC) recommended by Serbian regulation: 50 mg/kg (The Official Gazette of Republic of Serbia, no. 23/94) and were also lower than soil toxic levels for plants: 100 mg/kg (Gonnelli & Renella, 2012) (Table 2).

Naturally elevated Ni content in the soil from the control site Zlot was reflected in increased concentrations of Ni in plants from this site (Table 2). For example, among all plant samples, the greatest Ni concentration was recorded in birch root from Zlot: 9.936 mg/kg, which is very close to the toxic range in sensitive plant species (10 mg/kg DW) (Gonnelli & Renella, 2012). All the rest of Ni concentrations measured in plants' parts were much below the toxic range. The greatest Ni concentration in washed leaves was found in birch also from the control zone Zlot: 1.848 mg/kg. However, the greatest Ni concentrations in unwashed leaves were recorded in birch samples from the U/I zone: 2.580 mg/kg (Bor center) and 2.552 mg/kg (Bor hospital). All the concentrations in unwashed birch leaves from Bor region were lower than Ni concentrations in unwashed birch leaves from Monchegorsk region, on the Kola Peninsula, Russia having the nickel smelter and refinery, being the most important industrial point source emitter of metals on the area: 3.9-109 mg/kg (Reimann et al., 2001). These concentrations were also lower than Ni concentrations in unwashed birch leaves from polluted area of Wrocław, Poland: 4.9 mg/kg mean value (Samecka-Cymerman, 2009b). The contents of Ni in washed lime leaves were lower than Ni content in washed lime leaves from polluted areas of Province of Lower Silesia, Poland: 0.26-10.21 mg/kg (Kosiba, 2008), and also from different urban areas in Poland: 2.29-7.63 mg/kg (Piczak et al., 2003).

Table 2. Concentrations of Ni (mg/kg DW) in plant and soil samples∗ and soil pH

Sampling site	Plant	Material	Ni content	
Zlot (C)	Lime	Soil	23±2	pH=6.77
		Root	2.982±0.384	
		Leaves (washed)	1.704±0.196	
		Leaves (unwashed)	2.008±0.166	
	Birch	Soil	42±3	pH=6.30
		Root	9.936±0.408	
		Leaves (washed)	1.848±0.192	
		Leaves (unwashed)	2.104±0.372	
Ostrelj (R)	Lime	Soil	7.0±0.9	pH=7.91
		Root	1.868±0.062	
		Leaves (washed)	1.052±0.024	
		Leaves (unwashed)	1.950±0.122	
	Birch	Soil	8±1	pH=7.73
		Root	1.760±0.136	
		Leaves (washed)	0.788±0.042	
		Leaves (unwashed)	2.072±0.238	
Slatina (R)	Lime	Soil	5.0±0.8	pH=7.70
		Root	1.012±0.036	
		Leaves (washed)	0.744±0.088	
		Leaves (unwashed)	1.680±0.082	
	Birch	Soil	4.0±0.7	pH=7.59
		Root	1.976±0.128	
		Leaves (washed)	1.072±0.152	
		Leaves (unwashed)	1.072±0.248	
Bor hospital (UI)	Lime	Soil	20±3	pH=6.28
		Root	1.712±0.044	
		Leaves (washed)	0.868±0.024	
		Leaves (unwashed)	1.288±0.156	
	Birch	Soil	17±2	pH=7.21
		Root	1.152±0.204	
		Leaves (washed)	0.780±0.096	
		Leaves (unwashed)	2.552±0.368	
Bor center (UI)	Lime	Soil	13±1	pH=5.16
		Root	1.976±0.036	
		Leaves (washed)	0.928±0.088	
		Leaves (unwashed)	1.680±0.082	
	Birch	Soil	15±1	pH=4.95
		Root	3.244±0.352	
		Leaves (washed)	1.072±0.072	
		Leaves (unwashed)	2.580±0.036	

∗ Data are presented as the mean ± standard deviation (SD) for triplicate determinations

Calculated BCF and MR values for lime and birch from the Bor region, point that the uptake of Ni from soil was not significant (Table 3), but all thesevalues are higher than those for As and Cd (Alagić et al., 2013), which means that both plants extracted Ni more easily. The mean TF values for Ni are: 0.57 for lime and 0.44 for birch, while for Cd, the TF values were: 0.67 and 0.96, respectively, and for As were≈1 for both plants (Alagić et al., 2013). These amounts may suggest that the translocation of assimilated Ni was less successful than the translocation of non-essential As and Cd but it should be kept in mind that the TF is not so valuable tool for estimating metal translocation from root to leaves in the environments with high concentrations of contaminants of the atmospheric origin (Alagić et al., 2013). The calculation of EF for Ni gives some dissimilar information than in the case of As and Cd. All EF values for Ni in plants which grow in polluted zones of Bor regionare lower than 2 (Table 4) which may indicate that there is no serious enrichment by this metal.

Table 3. Biological coefficients (Biological Concentration Factor, BCF; Mobility Ratio, MR; Translocation Factor, TF)

Sampling site	Plant	TF	MR	BCF
Zlot	Lime	0.57	0.07	0.13
	Birch	0.19	0.05	0.24
Ostrelj	Lime	0.56	0.15	0.27
	Birch	0.45	0.10	0.22
Slatina	Lime	0.74	0.15	0.20
	Birch	0.54	0.27	0.49
Bor hospital	Lime	0.51	0.04	0.08
	Birch	0.68	0.05	0.07
Bor center	Lime	0.47	0.07	0.15
	Birch	0.33	0.07	0.22
Mean values	Lime	0.57	0.10	0.17
	Birch	0.44	0.11	0.25

BCF=Croot/Csoil,
MR=Cwashed leaves/Csoil,
TF=Cwashed leaves/Croot,

Table 4. Element enrichment factors (EF)

Sampling site	EF		
	Root	Washed leaves	Unwashed leaves
Ostrelj	0.62	0.62	0.97
	0.18	0.43	0.98
Slatina	0.34	0.44	0.84
	0.20	0.42	0.51
Bor hospital	0.57	0.51	0.64
	0.12	0.42	1.21
Bor center	0.66	0.54	0.84
	0.33	0.58	1.23

EF=Cpolluted/Ccontrol

But as plants' parts from the control zone contain increased amounts of Ni, maybe the calculation of EF cannot offer secure information in the case of Ni. The greatest EF values were calculated for birch unwashed leaves from the U/I zone: 1.21 (Bor hospital) and 1.23 (Bor center). Also, it should be noted that all EF values for roots are higher in the case of lime.

To avoid confusion which arises after calculation of biological and enrichment factors for As, Cd and Ni, in birch and lime from Bor region, the Pearson's correlation study was made. Unlike As and similarly to Cd, the values of Pearson's correlation coefficients between distance from the source of pollution and Ni concentrations in soil and plants' parts for subsamples "birch"and "lime", do not show significant negative correlations which indicate that the content of Ni in soils is not caused by atmospheric pollution solely, but it is more of natural origin. These observations support findings obtained from calculated EF for Ni. Also, in the case of Ni, negative correlations between soil pH and Ni concentrations in roots and leaves are not significant. On the basis of this, it can be concluded that this factor was not so decisive in Ni assimilation from soil, as it was in the case of Cd and As (Alagić et al., 2013).

The study of the correlations between amounts of Ni in the soil and parts of birch, as well as between the individual parts of the plant shows the significant positive correlations in fallowing cases: soil/root (0.91795), soil/washed leaves (0.84797) and root/washed leaves (0.97576). For the subsample "lime", significant correlation exists in the cases:soil/root (0.75400), soil/washed leaves (0.64712) and root/washed leaves (0.94058).

Ni content in unwashed leaves from both plants does not correlate well with other plants' contents which indicate the effect of atmospheric pollution.

4. CONCLUSIONS

Nickel concentration varied among examined plants' samples from the Bor region but all measured concentrations were belowthe toxic range, and also lower than in related birch and lime organs from other polluted regions in Europe. The greatest

Ni concentration was recorded in birch root from the control site Zlot: 9.936 mg/kg. The greatest Ni concentration in washed leaves was found in birch from the same site: 1.848 mg/kg. However, the greatest Ni concentrations in unwashed leaves were recorded in birch samples from the U/I zone: 2.580 mg/kg (Bor center) and 2.552 mg/kg (Bor hospital). The greatest contents of Ni in soils from this work were found at the control site Zlot and the sampling site Bor hospital from UI zone, but all soil concentrations were lower than Serbian MAC: 50 mg/kg.

The values of biological accumulation coefficients for Ni:BCF<1, MR<1, are greater than in the case of As and Cd, but still much lower than for accumulator plants,which confirm lime and birch as excluders of these three trace elements. The average translocation of metal (TF) from root to leaves was found to be 0.57 for lime, and for birch: 0.44, which is slightly lower than in the case of As and Cd. The greatest EF values were calculated for birch unwashed leaves from the U/I zone: 1.21 (Bor hospital) and 1.23 (Bor center), but all EF values for Ni in plants which grow in polluted zones of Bor region are lower than 2. This gives a first relevant clue that there was no serious enrichment by Ni, which is in the opposite to As and Cd.

The final confirmation of this observation was found in the results of the Pearson’s correlation study. Namely, these results showed that there was no significant negative correlation between distance from the source of pollution and the content of Ni in soils, which means that geology contributes significantly to this content, not pollution from the atmosphere. Also, the content of Ni in plants’ parts was not in negative correlation with distance, which additionally confirms that there was no noticeable atmospheric pollution. It can be said that Ni was assimilated mainly from the soil, thorough roots. This is additionally supported by the study of the correlations between amounts of Ni in the soil and parts of plants, as well as between the individual parts of plants. All these correlations were significantly positive, with the best correlations between roots and washed leaves. Similarly to previous work, birch expressed slightly better correlations than lime.

In the opposite to previous work, the results of the Pearson’s correlation study showed that soil pH was not decisive factor for metal uptake from soil in the case of Ni. It seems that plants assimilated this essential element according to their individual requirements.

The final conclusion of this work is that lime and birch from Bor region, can’t be useful for phytoextraction of Ni, but can be of interest for the phytostabilization purposes, as it was concluded in the caseof As and Cd, also. Once again, interacting actively with their local environment, these two native plant species gaveus very useful information about the state of the environment of Bor and its surroundings and prove themselves to be suitable candidates for biomonitoring purposes. In the case of Ni, lime and birch illustrated that there was no severe pollution of atmospheric origin.

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REFERENCES

Alagić, S.Č., Šerbula, S.S., Tošić, S.B., Pavlović, A.N. & Petrović, J.V., 2013. *Bioaccumulation of Arsenic and Cadmium in Birch and Lime from the Bor Region.* Archives of Environmental Contamination and Toxicology, 65(4), 671-682.

Antonijevic, M. & Maric, M., 2008. *Determination of the content of heavy metals in pyrite contaminated soil and plants.* Sensors-Basel, 8(9), 5857–5865. doi: 10.3390/s8095857.

Babula, P.,Adam, V., Opatrilova, R., Zehnalek, J., Havel, L. & Kizek, R., 2008. *Uncommon heavy metals, metalloids and their plant toxicity: a review.* Environmental Chemistry Letters, 6(4), 189-213.

Čechakova, K., Motyka, O., Valova, E., Macečkova, B. & Stalmachova B., 2014. *Investigation of the influence of nickel in precipitation through the surface properties of moss Pleurozium schreberi.* Carpathian Journal of Earth and Environmental Sciences, 9(2), 153–158.

Damian, F. & Damian, Gh., 2006. *Geochemical characterization of some old mine waste dumps from Baia Mare area and their influence on the natural vegetation*. Carpathian Journal of Earth and Environmental Sciences, 1(2), 63–72.

Dmuchowski, W. & Bytnerowicz, A., 2009. *Long-term (1992–2004) record of lead, cadmium, and zinc air contamination in Warsaw, Poland: Determination by chemical analysis of moss bags and leaves of Crimean lime.* Environmental Pollution, 157, 3413-3421.

Gonnelli, C. & Renella, G., 2012. *Chromium and Nickel.* In Alloway BJ (ed) Heavy Metals in Soils. Trace Metals and Metalloids in Soils and their Bioavailability. Environmental Pollution (22). Third Edition, Springer Dordrecht Heidelberg New York London, pp 313-334.

Kabata-Pendias, A.,2011.*Trace elements in soils and plants.* Fourth edition, CRC Press,Taylor and Francis Group, LLC, Boca Raton,London, New

York, pp. 237-246.

Kosiba, P., 2008. *Variability of morphometric leaf traits in small-leaved linden (Tilia cordata mill.) under the influence of air pollution.* Acta Societatis Botanicorum Poloniae, 77(2), 125-137.

Kuzovkina, Y.A., Knee, M. & Quigley, M.F.,2004.*Cadmium and Copper Uptake and Translocation in Five Willow (Salix L.) Species.* International Journal of Phytoremediation, 6(3), 269–287.

Maric, M., Antonijevic, M. & Alagic, S., 2013. *The investigation of the possibility for using some wild and cultivated plants as hyperaccumulators of heavy metals from contaminated soil.* Environmental Science and Pollution Research, 20(2), 1181-1188.

Marques, A.P.G.C., Rangel, A.O.S.S. & Castro, P.M.L., 2009. *Remediation of Heavy Metal Contaminated Soils: Phytoremediation as a Potentially Promising Clean-Up Technology.* Critical Reviews in Environmental Science and Technology, 39, 622–654.

Miller, J.N. & Miller, J.C.,2005. *Statistics and Chemometrics for Analytical Chemistry*, Pearson Education Limited, Prentice Hall, Londonpp. 107-147.

Mingorance, M.D. & Rossini Oliva, S., 2006. *Heavy metals content in N. Oleander leaves as urban pollution assessment.* Environmental Monitoring and Assessment, 119, 57-68.

Mingorance, M.D., Valdés, B. & Oliva, R.S., 2007. *Strategies of heavy metal uptake by plants growing under industrial emissions.* Environmental International, 33, 514–520.

Nagajyoti, P.C., Lee, K.D. & Sreekanth, T.V.M., 2010. *Heavy metals, occurrence and toxicity for plants: a review.* Environmental Chemistry Letters, 8, 199–216.

Nkongolo, K.K., Vaillancourt, A., Dobrzeniecka, S., Mehes, M. & Beckett, P., 2008. *Metal Content in Soil and Black Spruce (Picea mariana) Trees in the Sudbury Region (Ontario, Canada): Low Concentration of Arsenic, Cadmium, and Nickel Detected near Smelter Sources.*Bulletin of Environmental Contamination and Toxicology, 80(2), 107-111.

Piczak, K., Leśniewicz, A.L. & Żyrnicki, W., 2003. *Metal concentrations in deciduous tree leaves from urban areas in Poland.* Environmental Monitoring Assessment, 86, 273–287.

Rascio, N. & Navari-Izzo, F., 2011. *Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting?* Plant Science, 180, 169-181.

Reimann, C., Koller, F., Kashulina, G., Niskavaara, H. & Englmaier, P., 2001. *Influence of extreme pollution on the inorganic chemical composition of some plants.* Environmental Pollution, 115, 239-252.

Samecka-Cymerman, A., Stankiewicz, A., Kolon, K. & Kempers, A.J.,2009a. *Bioindication of Trace Metals in Brachythecium rutabulum Around a Copper Smelter in Legnica (Southwest Poland): Use of a New Form of Data Presentation in the Form of a Self-Organizing Feature Map.* Archives of Environmental Contamination and Toxicology, 56, 717–722.

Samecka-Cymerman, A., Kolon, K. & Kempers, A.J., 2009b. *Short shoots of Betula pendula Roth. As bioindicators of urban environmental pollution in Wrocław (Poland).* Trees-Structure and Function, 23, 923-929.

Serbula, S.M., Alagić, S.Č., Ilić, A.A., Kalinović, T.S. & Strojić, J.V., 2012. *Particulate Matter Originated From Mining-Metallurgical Processes.* In Knudsen H, Rasmunssen N (ed) Particulate Matter: Sources, Emission Rates and Health Effects. Nova Science Publishers US, New York, pp 91-116.

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Yadav, S.K., 2010. *Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.* South African Journal of Botany, 76, 167–179.

Yaman, M., 2000. *Nickel Speciation in Soil and the Relationship with Its Concentration in Fruits.* Bulletin of Environmental Contamination and Toxicology, 65, 545-552.

Yusuf, M., Fariduddin, Q., Hayat, S. & Ahmad, A., 2011. *Nickel: An Overview of Uptake, Essentiality and Toxicity in Plants.* Bulletin of Environmental Contamination and Toxicology, 86(1), 1-17.

Unterbrunner, R., Puschenreiter, M., Sommer, P., Wieshammer, G., Tlustos, P., Zupan, M. & Wenzel, W.W., 2007. *Heavy metal accumulation in trees growing on contaminated sites in Central Europe.* Environmental Pollution, 148, 107-114.

Vamerali, T., Bandiera, M. & Mosca, G., 2010. *Field crops for phytoremediation of metal-contaminated land. A review.* Environmental Chemistry Letters, 8, 1-17.

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