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Elder, linden and pine biomonitoring ability of pollution emitted from the copper smelter and the tailings ponds

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ABSTRACT

This study aims to evaluate and compare the ability of elder, linden and pine for biomonitoring purposes in the zones affected by emissions from a copper smelter and the tailings ponds of open pit mines. Concentrations of Al, As, Cd, Cu, Fe, Pb and Zn were determined in foliar parts of plants and in soils.

The effects of leaves/needles water washing on the concentrations of the studied elements were examined. The bioaccumulation coefficient (BAC) and correlations between element concentrations in leaves and soil were calculated in order to find out if a plant absorbs a certain element from the soil. In the conditions of the increased environmental pollution, elder soil had the highest As, Cu, Pb, Zn and Cd concentrations, compared to pine and linden soil. Elder leaves are a better choice for detection of the analyzed elements in the atmospheric deposition (proved by water washing), and for biomonitoring in the conditions of high environmental pollution. However, all the three plants can serve for biomonitoring purposes. It has been concluded that Cu and Pb in leaves/needles originate from the soil and the air. Pine, linden and elder uptake As predominantly from the air. Copper smelter is a dominant source of pollution, especially in the case of Cu, As and Pb, compared to the tailings ponds of open pit mines.

1. Introduction

Pollution emitted from pyrometallurgical copper production poses a serious risk to the biota environment. During the processes of pretreatment of ore and smelting of the concentrate, large quantities of fugitive dust and gasses are released, affecting all natural resources (Ettler et al., 2011; Medyñska-Juraszek and Kabała, 2012; Serbula et al., 2014a). The biggest concern the world is facing today is that human beings, after plants and animals, are the final recipient of toxic and carcinogenic substances (EC, 2004).

Detection and monitoring of pollutants play an important role in the environmental protection. Passive biomonitoring by using plants is a tool for obtaining reliable analytical information of the environmental quality. The abilities of plants to absorb, deposit (conjugate), and degrade pollutants, and to mineralize organic and accumulate inorganic pollutants within its cells determine the ecological potential of the plant (Kvesitadze et al., 2006). High level of certain elements in plant parts can be indicative of (1) atmospheric pollution via incorporation through the stomata or (2) soil pollution taken up via roots and transported to leaves (Rucandio et al., 2011). However, it is sometimes difficult to distinguish between the amounts of a metal taken up from soil and the amounts deposited from the air. This is because long-lived organisms reflect cumulative effects of environmental pollution both from soil and the atmosphere (Sawidis et al., 2012).

Concentrations of the selected elements in/on the leaves are usually in accordance with the trends in the bulk atmospheric deposition (Aničić et al., 2011; Samecka-Cymerman et al., 2006). Because of that, plants could be used as biological filters accumulating particulate matter on their foliage, thus reducing its concentration in the air. The ability of plants to accumulate pollutants from the air might be successfully used for biomonitoring purposes (Hu et al., 2014; Przybysz et al., 2014; Singh and Verma, 2007).

The results of many researches confirmed that deciduous as well as evergreen trees can be applied for biomonitoring of metals in the environment (Bertolotti and Gialanella, 2014; Chrzan, 2015; Kocić et al., 2014; Piczak et al., 2003; Rucandio et al., 2011; Sawidis et al., 2011; Samecka-Cymerman et al., 2006; Sun et al., 2010). There are also various good examples of shrubs/bush species used for evaluation of air and soil pollution level (Li-qiang et al., 2004; Madejón and Lepp, 2007; Reyes et al., 2013; Yanqun et al., 2004). Evergreen and deciduous trees like pine (*Pinus* spp.) and linden (*Tillia* spp.) are considered as good choice for biomonitoring of air and soil pollution around the copper smelter

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in Bor (Serbia) (Alagić et al., 2013; Serbula et al., 2013a). However, elder (*Sambucus nigra*) has not been examined for those purposes in this area, until now. Abilities of these three species to accumulate certain elements in the same conditions of environmental pollution have not been compared in recent world publications. Therefore, the aim of this study is to compare the ability of pine (*Pinus nigra*), linden (*Tilia grandifolia*) and elder (*Sambucus nigra*) to reflect the air and soil pollution in the zones affected by emissions from the copper smelter and the tailings ponds of the open pit mines.

2. Material and methods

2.1. The study area description

The town of Bor is situated in a mountainous and forested area in Eastern Serbia (Southeastern Europe), close to the Bulgarian and Romanian borders and approximately 200 km away from the capital city of Belgrade. The climate on the territory of the Bor area is moderately continental. Dominant winds are in the W, WNW and NW direction. Winds less frequent are in the direction of E, ENE and ESE, whereas the least frequent winds are in the direction of S and SSW. Although winds are frequent in the area of Bor, their strength is usually weak to moderate.

Bor and the surroundings are well-known for copper deposits, which are among the largest in Europe (Serbula et al., 2013b). Mining production in Bor has existed for over 100 years. Within the Bor Copper Mines, two open pit mines (Cerovo and Veliki Krivelj) operate, one for underground mining (the mine "Jama" in the town of Bor) and two plants for mineral processing (flotations in Veliki Krivelj and Bor) (EIA Study, 2010). The copper smelter, located on the northeastern border of the town, processes sulfide copper concentrate with the accompanying elements Fe, Pb, As, Cd, Ni, Zn, Mn and precious metals. Every year the copper smelter emits 5–8 kg of Zn, 6–25 kg of Pb and 5–20 kg of As per inhabitant of the Bor region. The town of Bor is considered to be one of the most polluted regions with As, not only in Serbia, but in Europe as well. Also, there is a historical pollution with significant exceedances of maximum allowed concentration of total atmospheric depositions, according to the Serbian Regulation (Serbula et al., 2013a). The highest air pollution was detected in the urban–industrial and rural areas of the Bor region. More detailed discussions about air pollution in Bor and its surroundings are given in Serbula et al. (2013b) and Serbula et al. (2014a).

2.2. Sampling and chemical analyses

Naturally present and naturally distributed deciduous tree (linden, *T. grandifolia*), deciduous shrub (elder, *S. nigra*) and evergreen tree (pine, *P. nigra*), were selected for analyses. The sampling was carried out under calm weather conditions, after a prolonged rainless period, and in days without wind.

Plant material and soil samples were collected from September to mid October 2013 (just before shedding, to assure maximum metal accumulation), in the eight sampling zones (Fig. 1 and Table 1). It should be noted that impacts of pollution sources in most of the sampling zones are overlapping, because of close vicinity of the mining and smelting facilities.

From each particular sampling zone, leaves/needles and soil were sampled from three to five plants of each species (depending on the availability). These subsamples were mixed into one composite sample (Piczak et al., 2003; Yanqun et al., 2004; Rossini Oliva and Mingorance, 2004), representing linden leaves, elder leaves, pine needles and soil from the particular sampling zone. Therefore, concentrations of elements, presented in the paper, were obtained from total of eight composite samples of washed, eight samples of unwashed leaves/needles and eight soil samples of particulate plant species. The total number of sampled plants was about 40.

The methodology of sampling the plant material followed the usually defined orientations. Samples of leaves and current year needles were collected at 1.5 to 2 m height above the ground from outer branches of the canopy at south, west, east, and north directions. In the laboratory, the foliar samples were divided into two halves. One half was retained as an unwashed sample. The second half was thoroughly washed with running distilled water for about 1 min at room temperature, to remove the fraction deposited on the leaves/needles surfaces (Dmuchowski et al., 2011; Sun et al., 2010). About 500 g of soil from the rhizosphere (10–20 cm depth) was collected around each plant at four directions. After air drying at room temperature, plant and soil samples were ground to a fine powder and stored at room temperature until analysis.

All chemical analyses were conducted by accredited chemical laboratory, at the Institute of Mining and Metallurgy Bor (Serbia). Leaves, needles and soil samples were digested according to the U.S. EPA method 3050B (U.S. EPA, 1996), in a microwave oven. The samples of plant material were digested with a mixture of H_2O_2 and HNO_3 (1:5). Soil samples were digested with a mixture of HNO_3 and HCl (1:3).

Concentrations of Al, As, Cd, Cu, Fe, Pb and Zn in extracts were determined by simultaneous dual view inductively coupled plasma atomic emission spectrometer (ICP-AES) with axial and radial plasma observation produced by Spectro model Blue. The quality of the analytical data was checked by replicate analysis of the same samples. The relative standard deviations for the concentration measurements were up to 10%. The concentrations of all the measured elements are expressed as μg/g dry mass. The most sensitive and recommended wavelengths of the analyzed elements, as well as the achievable detection limits (DL) are shown in Table 2. Limits of quantification (LOQ) were evaluated as ten times the detection limits.

Soil pH values (Table 3) were determined according to the ISO standard 10390:2005 (ISO, 2005). Soil organic matter (OM) contents were obtained by loss in weight on ignition (Maisto et al., 2004).

2.3. Data analysis

A statistical processing of the data was carried out using the SPSS 17.0 for Windows version. Since statistical distribution of most variables determined by chemical analyses did not exhibit a normal distribution with Shapiro–Wilk test, nonparametric statistic methods were employed. In order to compare the element concentrations in unwashed and washed leaves sampled in the zones under the influence of copper production processes, a paired Wilcoxon Signed Rank test was performed. All significant differences were at $P < 0.05$ level. The existence of correlations between different parameters was tested by calculating the Spearman rank coefficient.

The bioaccumulation coefficient (BAC) was calculated in order to find out if a plant absorbs a certain element from soil. The BAC represents the ratio of element concentration in aboveground plant parts (foliage) to its concentration in soil.

3. Results and discussion

3.1. Soil properties and concentrations of elements in soil

Most of the sampled soils are slightly acid to neutral, with a few exceptions of strongly acid and slightly alkaline soils, according to the suggested soil pH classification in Sparks (2003) (Table 3). According to the ΔpH which in most cases was <1, it can be said that the sampled soils had low ability of acidification (Zseni et al., 2003). This could be a good property of soil, due to the fact that metals have a low mobility in less acid soils. Also, the positive ΔpH values for all the soil samples indicate that the cation exchange capacity is higher than the anion exchange capacity, which increases the ability to hold onto cations at negatively charged sites within the soil (Pansu and Gautheyrou, 2006). Organic matter content is relatively high, especially in the linden