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ORIGINAL PAPER

Heavy metal contamination of topsoil and parts of peach-tree growing at different distances from a smelting complex

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Abstract This paper reports on the content of six heavy metals (Cu, Zn, Pb, As, Cd and Ni) in topsoil and parts of peach-tree, sampled from eight locations in urban–industrial and rural areas located at various distances from the Bor copper smelter, Serbia. Topsoil samples were analyzed for physical and chemical properties, while the content of heavy metals in all samples was determined using an inductively coupled plasma optical emission spectrometer (iCAP 6000). The enrichment factor showed that the topsoil was enriched by heavy metals (except for nickel), at all locations. An extreme enrichment by copper was found at six locations ($EF_{soil} = 86–101$). The enrichment factors of heavy metals in peach-tree parts were highest in roots and leaves. The most extreme enrichment by copper was found to occur in the roots ($EF_{plant} = 68.80$) from the flotation tailing pond. Among the studied heavy metals, only the content of zinc was within normal limits for plants. Calculated biological concentration factors ($BCF < 1$) indicated a limited soil-to-root transfer of heavy metals. Moreover, the leaf/branch ratio as well as numerous and very strong Pearson's correlations between elements in the peach-tree parts confirmed that leaves represent the best indicators of pollution originating from atmospheric deposition. Principal component analysis identified sources of heavy metals in soil and parts of peach-tree.

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Introduction

Metal extraction, i.e., mining, mineral processing and smelting, generates various waste materials (waste rocks, mill and flotation tailings, smelting slag, waste solutions, flue gases and dust) (Moore and Louma 1990; Stüben et al. 2001; Bianchini et al. 2015). These waste materials pollute soil, surface and underground water, as well as air even far from the source of pollution (Li et al. 2006; Malmstrom et al. 2006; Anju and Banerjee 2012).

Toxic metals are usually accumulated in topsoil and can enter the food chain through plants. These metals contaminate the environment by affecting soil properties, biomass and crop yields, and ultimately human health (Mudgal et al. 2010). Toxicity of the heavy metals (HMs) that are absorbed by vegetation or retained in the soil depends on their concentration, type of metallic compound present in the soil and bioavailability, which in turn depends on the pH of the soil and the content of the organic matter (Alvarez et al. 2003).

It can be said that plants represent important components of ecosystems as they can transfer elements (including toxic metals) from abiotic to biotic environments (Chojnacka et al. 2005). Generally, HMs such as Cd, Pb, Hg and As are phytotoxic at extremely low concentrations (metalloid As is often included in HM category due to its toxic potential). The essential metals such as the micronutrients Cu, Zn, Ni and Fe service certain biochemical and physiological functions in plants, but they are also phytotoxic above certain threshold levels (Nagajyoti et al. 2010; Ayari et al. 2010; Alagić et al. 2015).

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Numerous investigations have confirmed that some plants grow successfully even in the soil that is heavily polluted by heavy metals. HM concentrations in these plants are often considerably elevated due to their high ability to absorb them from soil, water or air (Alvarez et al. 2003; Gonzalez and Gonzalez-Chavez 2006; Li and Yang 2008; Arnetoli et al. 2008; Tian et al. 2009; Agyarko et al. 2010; Mudgal et al. 2010; Antonijević et al. 2012). Usually, these are wild-growing species, which have developed successful strategies for HM tolerance. Therefore, plants with high tolerance to HMs are the subject of intensive research in terms of their use for phytoremediation and biomonitoring around mineral-ore mines and smelters (Gonzalez and Gonzalez-Chavez 2006; Mingorance et al. 2007; Antonijević et al. 2008; Rashed 2010; Ashraf et al. 2011; Balabanova et al. 2012; Mehes-Smith et al. 2013; Saba et al. 2015).

More than 100 years of the mining and smelting operations around the town of Bor (Serbia) has had a strong impact on the environment and public health. In view of the fact that Bor is situated near one of the mines and the copper smelter belonging to the Bor Mining and Smelting Complex (RTB Bor), the town represents an environmental hot spot of Serbia and Europe (Dimitrijević et al. 2009). According to the Local Environmental Action Plan (LEAP 2003), from the extraction processes in the RTB Bor complex, 5–20 kg As, 5–8 kg Zn, 6–25 kg Pb and ≥3.5 t SO_2 per capita are emitted each year and 11,300 t of waste rocks and tailings are dumped. Waste gases released from the smelter smokestacks (SO_2 and toxic elements in particulate matter such as As, Cd, Pb) devastated agricultural soil around the town of Bor in an area of approximately 22,000 ha. Despite this gloomy picture, the town, which is exposed to this extreme pollution, is still rich in vegetation. This indicates that different plant species have adapted to the existing pollution. It is especially interesting to note that the soil surrounding the old flotation tailing pond (agricultural soil in the past), which is within the boundaries of the RTB complex and close to the smelting plant, has been overgrown by various wild-growing plant species. Among them, peach and apple trees, as well as blackberry and grapevine shrubberies can be also found. Unfortunately, these plants bear fruits that are contaminated by HMs.

Plants usually accumulate larger quantities of metals in their leaves than in their fruits or seeds. On the other hand, some studies have shown that heavy metals significantly contaminate the fruit (Matei et al. 2013; Radwan and Salama 2006). Therefore, in this paper the concentrations of heavy metals (Cu, Zn, Pb, As, Cd and Ni) in peach-trees' parts (root, branch, leaf, fruit) and physical and chemical characteristics of the topsoil, in which peach-trees grow, have been determined, correlated and compared with the control site (unpolluted area). Experiments were carried out during autumn 2012 on the authentic sort of a peach-tree, Prunus persica L. Batech, which produces fruit with white pulp. The distance of the sampling sites from the copper smelter, which is considered to be the main pollution source in the Bor region, was taken into account in the analysis of the heavy metal content and statistical analysis. The obtained results are evaluated in terms of peach-trees' use for phytoremediation and biomonitoring of areas polluted by HMs produced by copper smelter activity. The risks involved with using the peach-tree fruit as food is estimated by comparing the obtained results with the recommended levels in the Serbian and European regulations.

Materials and methods

Description of the sampling sites

The municipality of Bor is located in the mountain and forest area of the central part of Eastern Serbia (area of 856 km²), <50 and 100 km far from the Bulgarian and Romanian border, respectively. The population density is 58.4 inhabitants per km². The majority of population lives in the urban area of the town of Bor, while the remainder of the population lives in the rural zones (12 rural settlements). The geographic coordinates of Bor are: 44°25′N latitude and 22°06′E longitude. The altitude of Bor is 378 m above sea level, which is low compared to the surrounding tall mountains (Stol 1156 m, Veliki Krš 1146 m and CrniVrh 1043 m). Thus, Bor is located in the valley of the Bor River. The main industrial activities in Bor are mining and metallurgy, where one of the copper mines and the smelting complex are located on the northeastern edge of the town. The climate of the Bor area is moderately continental. The average annual values of meteorological parameters in 2012 were: air temperature 11.34 °C, atmospheric pressure 971.6 mbar, relative humidity 65.75 %, precipitation 673.5 mm/m², wind speed 0.62 m/s and the wind calm period 57.6 %. The dominant winds in this region are in the west (W), the west-northwest (WNW) and the northwest (NW) direction. Winds less frequent are in the direction of east (E), east-northeast (ENE) and east-southeast (ESE). The least frequent winds are in the direction of south (S) and south-southwest (SSW) (Fig. 1). Wind direction influences distribution of pollutants from the industrial zone to the town and surrounding areas.

In this study, the concentrations of investigated heavy metals were determined in soil and parts of P. persica L. Batech, sampled from eight sampling sites differing in distance from the smelter smokestacks (120 and 150 m high), as given in Table 1.
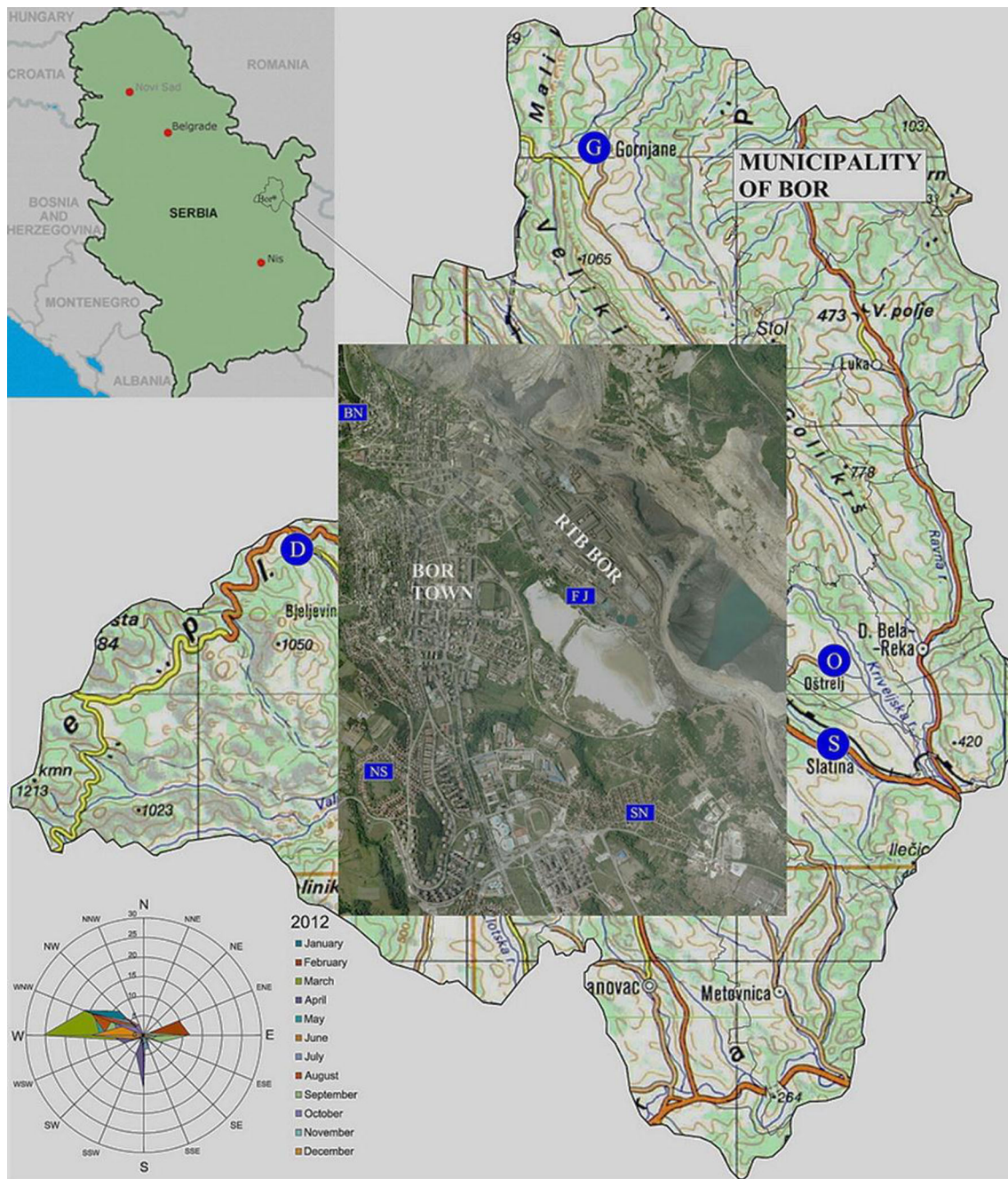
Fig. 1 Map of the study area showing measuring sites in the town of Bor and its surroundings

The selection of the representative sampling sites was based on the presence of investigated plant species primarily in the dominant wind directions from the smelting complex. The urban–industrial (UI) zone included four sampling sites as follows: the old flotation tailing pond (FJ, Flotacijsko jalovište), the hospital settlement (BN, Bolničko naselje), a part of the town which is situated near the city hospital, and the two other suburbs: the settlement "Sun" (NS, Naselje

Sunce) and Slatina settlement (SN, Slatinsko naselje). All the sites in the UI zone are located very close to the copper smelter. The rural zone (R) included three rural settlements: Oštrelj (O), Slatina (S) and Dubašnica (D). The control zone (C) was in an unpolluted area of the rural settlement Gornjane (G) which is located 19 km from the town of Bor. The Gornjane area is naturally protected from pollution by the Veliki Krš mountain (Fig. 1).

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Table 1 Distance of the sampling sites from the main pollution source and dominant wind directions

Sampling site	Zone	Distance (km)	Wind direction
Flotation tailing pond (FJ)	UI	0.7	WNW, NW
Hospital settlement (BN)	UI	2.2	E, ESE
The settlement "Sun" (NS)	UI	2.5	E, ENE
Slatina's settlement (SN)	UI	2.3	WNW, NW
Oštrelj (O)	R	4	W, WNW
Slatina (S)	R	7	NW, WNW
Dubašnica (D)	R	17	E, ESE
Gornjane (G)	C	19	S

Sample collection, preparation and analysis

Samples of peach-tree parts (*P. Persica* L. Batech) together with the associated soil samples were taken from selected sites in September 2012, when the maximum HM enrichment was expected. At each site, samples of roots, branches, leaves and fruits were taken from three to five peach-trees. Leaves were taken from different quarters of the canopy (branches at a height 2.5 m above the soil). Soil samples were taken from the rooting zone (0–30 cm). Root samples were thoroughly washed with tap water followed by distilled water, whereas the aboveground plant parts remained unwashed. Each plant part and soil sample was a composite of 3–5 subsamples. All the samples were dried to a constant weight at room temperature, pulverized and passed through a 2-mm sieve for subsequent chemical analysis in triplicate. Mineralization of all samples was done according to US EPA method 3052 (USEPA 1996), as described in a previous work (Alagić et al. 2015).

Analyses were carried out using an iCAP 6000 inductively coupled plasma optical emission spectrometer (Thermo Scientific, Cambridge, UK) with an Echelle optical design and a charge injection device (CID) solid-state detector (Alagić et al. 2015). All results were calculated on a dry weight basis (mg/kg DW).

The pH and electrical conductivity (EC) values (solid:distilled water = 1:2.5) of the soil samples were measured using a pH meter (3510 Jenway, UK) and an EC meter (4510 Jenway, UK), respectively. The soil organic matter (OM) was determined by the loss-on-ignition (LOI) method at 550 °C (Jolivet et al. 1998).

Data processing and statistical analysis

The enrichment factor for elements in soils, EF_{soil}, is used to assess the level of pollution and the possible anthropogenic influence. The enrichment factor (Eq. 1) is the relative abundance, with respect to iron, of one element, [M], in a soil compared to its relative abundance [M/Fe] in the local control site (Oliva and Espinosa 2007):

$$EF_{soil} = [M/Fe]_{soil} / [M/Fe]_{control} \qquad (1)$$

In this equation, the content of metal M was normalized to iron. Iron was used as a metal for normalization since its anthropogenic sources are small compared to natural sources. Five contamination categories were recognized on the basis of the enrichment factor values: depletion to minimal enrichment (EF < 2), moderate enrichment (EF = 2–5), significant enrichment (EF = 5–20), very high enrichment (EF = 20–40) and extremely high enrichment (EF > 40). As the EF value increases, the contribution of the anthropogenic origin also increases (Sutherland 2000).

The enrichment factor of a plant, EF_{plant}, was calculated using Eq. (2) (Kisku et al. 2000):

$$EF_{plant} = \frac{[\text{Metal}] \text{ in plant parts at polluted site}}{[\text{Metal}] \text{ in plant parts at unpolluted (control) site}} \qquad (2)$$

The biological concentration factor, BCF, was calculated as the ratio of the metal concentration in roots to that in soil, as follows:

$$BCF = [\text{Metal}]_{root} / [\text{Metal}]_{soil} \qquad (3)$$

Values of BCF > 1 indicate the accumulation of a particular trace metal in roots (Alagić et al. 2013).

The ratios of concentrations between plant parts, R, were estimated using Eqs. (4)–(6) (Oliva and Mingorance 2006):

$$R_{leaf/branch} = [M]_{leaves} / [M]_{branch} \qquad (4)$$

$$R_{fruit/leaf} = [M]_{fruit} / [M]_{leaves} \qquad (5)$$

$$R_{fruit/branch} = [M]_{fruit} / [M]_{branch} \qquad (6)$$

These three ratios give information concerning the different accumulation in each part and indicate whether there is a free movement of the elements between the parts. Values of R > 1 indicate pollution via atmosphere.

Data obtained in instrumental analysis are presented as mean values including standard deviation. Pearson's correlation coefficients were used to express associations between soil and plant quantitative variables, considering two-tailed statistical significance at the 95 % confidence interval. PCA was applied for the purpose of identifying the origin of HMs in soil and plant samples (Doležalová Weissmannová et al. 2015). All data were analyzed using a SPSS statistical program package (release 17.0).

Results and discussion

Soil properties and heavy metal concentrations in soil and plant parts

The topsoil characteristics from the eight sampling sites demonstrated considerable differences in terms of pH, EC and OM (Table 2). Soil at the site FJ is extremely acidic (pH is 4.39), probably due to the weathering oxidation of pyrite in the soil, over many decades. Moreover, soil at the same site and in comparison with other sites has the highest electrical conductivity of 1371 µS/cm and very low content of organic matter (6.2 %). Soil at the site BN is strongly acidic (pH = 5.22), while sites D and G, and NS, SN, O and S are slightly acidic and neutral, respectively. The overall electrical conductivity of the samples at the studied sites is low since the EC values vary from 89.9 up to 176.4 µS/cm. Conductivity in natural soil varies between 200 and 800 µS/cm, and this is necessary for the optimum plant growth (Sadhu et al. 2012). Although the content of OM varies in a wide range (5.2–21.2 %), the analyzed soil samples have a predominantly lower OM content, especially in rural areas. The soil with 21.2 % of OM was sampled at the site NS which represents a border of the urban area of Bor and is located on the former agricultural soil.

The content of HMs in the analyzed soil varies within wide ranges (Table 2).

It can be seen in Table 2 that the concentrations of investigated HMs in soil decrease in the following order: Cu > Zn > Pb > As ≥ Ni > Cd (Fe was not considered, and it was used only for estimation of EF_{soil}). It is clear that the soil is mostly polluted by Cu and except for the controlling site (G); the range of Cu concentrations is 141.5–1586 mg/kg. The maximum content of Cu is over 40 times higher than the maximum allowable concentrations (MAC) in Serbia, or 30–50 times higher than the normal values in the soil (Table 2) (Kabata-Pendias and Mukherjee 2007; Alloway 2013). Only at sites G and D, Cu concentration is lower than the MAC for agricultural soil (150 mg/kg). It should be noted that in all UI areas, soil Cu content is higher than 1000 mg/kg which is a direct consequence of the copper mine tailings existence in this area (Antonijević et al. 2012).

The Zn content in the soil is increased relative to the maximum allowable concentration (MAC) in Serbia at all UI locations, and the highest value of 465 mg/kg was recorded at site SN, most likely due to the nearby foundry for copper and copper alloys. Furthermore, a considerably higher concentration of lead (238.4 mg/kg) when compared to the MAC in Serbia was determined location NS. This can be explained by the proximity of the main road with dense traffic as a source of lead released through

Table 2 Total concentrations of HMs (mg/kg DW) in soil samples (mean ± SD) and soil pH, EC and OM

Sampling site and distance	Cu	Zn	Pb	As	Cd	Ni	Fe	pH	EC (µS/cm)	OM (%)
FJ (0.7 km)	1369 ± 19	322 ± 2	108.1 ± 0.9	36.7 ± 0.4	4.38 ± 0.03	14.8 ± 0.2	16,375 ± 45	4.39	1371	6.2
BN (2.2 km)	1586 ± 15	177 ± 2	128 ± 2	67.6 ± 0.7	5.85 ± 0.04	21.3 ± 0.2	19,245 ± 130	5.22	105.1	9.2
NS (2.5 km)	1465 ± 24	327 ± 2	238.4 ± 0.5	43 ± 0.4	4 ± 0.02	34.17 ± 0.04	15,710 ± 115	6.86	117.4	21.2
SN (2.3 km)	1141 ± 10	465 ± 2	129.2 ± 0.8	13.2 ± 0.2	4.03 ± 0.02	26.4 ± 0.2	14,365 ± 160	7.15	163.1	10.0
O (4 km)	991 ± 2	144.8 ± 0.3	109 ± 2	23.5 ± 0.2	3.61 ± 0.02	24.7 ± 0.2	16,241 ± 275	6.98	168.7	13.2
S (7 km)	206 ± 2	93.8 ± 0.3	41.86 ± 0.07	10.2 ± 0.2	3.1 ± 0.02	45.5 ± 0.3	18,090 ± 170	6.79	176.4	8.6
D (17 km)	141.5 ± 0.8	127 ± 0.7	66.6 ± 0.3	32 ± 0.2	4.45 ± 0.02	32 ± 0.2	19,100 ± 120	6.24	96.4	14
G (19 km)	9.2 ± 0.01	43.4 ± 0.2	21.99 ± 0.07	2.62 ± 0.09	1.255 ± 0.01	16.78 ± 0.08	10,010 ± 165	6.50	89.9	5.2
MAC[a] (Serbian)	36	140	85	29	0.8	35				
Normal range in soils	20–30[b]	10–300[b]	15–28[b]	0.5–80[b]	0.06–1.1[b]	19–22[b]				
	2–50[c]	10–100[c]	17[c]	0.1–55[c]	0.1–1.0[c]	0.03–51[c]				
MAC in agricultural soil[d]	60–150	100–300	20–300	15–20	1–5	20–60				

[a] The Official Gazette of Republic of Serbia, no. 88/2010 (MACs—maximum allowable concentrations in Serbian non-agricultural soil)

[b] Kabata-Pendias and Mukherjee (2007)

[c] Alloway (2013)

[d] Kabata-Pendias (2011)

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usage of leaded gasoline in the cars and trucks. A similar average concentration of Pb (202 mg/kg) was determined in the urban soils of Palermo Italy (Salvagio Manta et al. 2002). The highest As concentration of 67.6 mg/kg was recorded at site BN; some increased concentrations (higher than the MAC in Serbia) were found at sites FJ, BN, NS and D. However, all As concentrations fall into the range of normal values found in soil (Kabata-Pendias and Mukherjee 2007). Excluding the control site G, the Cd concentration is increased at all sites by 4–5 times regarding the MAC in Serbia and normal values in soil (Kabata-Pendias and Mukherjee 2007; Alloway 2013). The highest value of 5.85 mg/kg for Cd was recorded at site BN. One of the interesting findings is that the highest soil pollution by Cu, As and Cd is recorded at site BN, where the public hospital is located. This site is exposed to high concentrations of SO_2 and particulate matter in wind calm periods ($\sim$60 %) or under E and ESE winds ($\sim$10 %) (Dimitrijević et al. 2009), essentially, during whole year, regardless of wind activity (a simple consequence of the close proximity of the main source of pollution). In addition, Ni concentration in soil at all sites, except for site S, is lower than the MAC in Serbia (35 mg/kg).

The data in Table 2 show that the UI area is more polluted by Cu, Zn and Pb, than area R, while this trend is not observed for As, Cd and Ni. This supports the conclusion that Cu, Zn and Pb are concentrated in more coarse fractions, which are deposited closer to the emitting source, while As, Cd and Ni could be found in finer fractions, which under the influence of wind can be spread over longer distances. For instance, higher concentrations of Cu and Zn in PM_{10} than in $PM_{2.5}$ have been confirmed at a street location in Rotterdam, the Netherlands (Keuken et al. 2013). Additionally, more than 30 years of air quality control in Bor indicates consistently increased concentrations of As, Cu, Cd and Zn, and periodically increased concentrations of Pb and Ni, in ambient particulate and deposited matter (Dimitrijević et al. 2009; Serbula et al. 2012; Kovačević et al. 2010).

The content of HMs in parts of peach-trees sampled from eight sites is given in Fig. 2. However, while considering the obtained results, it should be kept in mind that all aboveground parts were analyzed as unwashed, so that the detected concentrations do not represent a real accumulation in these cases. The detected contents of HMs in peach parts decreased as follows: leaf > root > branch > fruit. All values are compared with normal and critical values for plants/mature leaves in Table 3.

Leaves accumulate HMs not only from soil but also from atmospheric deposition, and they can often be the best indicator of pollution. Extreme contents of Cu in all parts of peach (root 608 mg/kg, branch 344 mg/kg, leaf 306 mg/kg and fruit 117 mg/kg) are recorded only at site FJ, where

soil is very acidic, with a very low content of OM and high EC. In a recently published work by Antonijević et al. 2012, the high concentrations of Cu in branches, leaves and fruit of peach-trees that grow on the dam of tailings pond have also been found. At several locations, the Cu concentration in leaves (BN 276 mg/kg, SN 212.5 mg/kg and S 175 mg/kg) was above the upper limit of toxic values in mature leaves (20–100 mg/kg, Table 3). Only at the control site G, the Cu concentration of 13.37 mg/kg was within the normal range (5–20 mg/kg). Although Cu is an essential micronutrient for plant growth, it can also be phytotoxic at high concentrations. The excessive content of Cu can lead to inhibition of plant growth, lowering the biomass and root elongation (Francini and Sebastiani 2010, Weng et al. 2005; Xu et al. 2006). Despite the high concentration of Cu, these symptoms were not observed in the studied peach-trees.

The Zn content in leaves is within normal values (27–150 mg/kg), at all sites. The Pb contents determined in leaves are at FJ 36 mg/kg, BN 43.9 mg/kg, NS 13.6 mg/kg, SN 14.4 mg/kg, O 8.58 mg/kg, S 32.9 mg/kg, D 13.7 mg/kg and G 1.9 mg/kg. These values are higher than the normal values in leaves (5–10 mg/kg), except for locations O and G. At sites FJ and BN, the Pb content is within the critical range for leaves (30–300 mg/kg). The toxic concentrations of As in leaves (5–20 mg/kg) are recorded at FJ 18.8 mg/kg, BN 21.3 mg/kg and S 12.8 mg/kg. At all other sites, As concentrations were above the normal range in leaves. The highest Cd concentrations in leaves were found at FJ 1.28 mg/kg, BN 1.78 mg/kg and S 1.255 mg/kg. At other sites, Cd concentration was less than 1 mg/kg but still above the normal range in leaves (0.05–0.2 mg/kg). The normal range of Ni in leaves is 0.1–5 mg/kg. Only leaves from the sites FJ 5.44 mg/kg and BN 6.52 mg/kg were found to be far above this range. Compared with concentrations determined at site FJ (flotation tailing pond), some similar concentrations of Pb and Cd were found in a peach-trees on the reclaimed tailing dam in the manganese mine wasteland, China (Li and Yang 2008).

With regard to the peach fruits, there is some risk associated with their consumption at all investigated sites, especially in the rural areas where unwashed fruits are often eaten. The recommendable maximum limits for HMs concentrations in fruit per net weight are 5 mg/kg for Cu and Zn, 0.1 mg/kg for Pb and 0.05 mg/kg for Cd (EC no. 1881/2006; Matei et al. 2013). The Official Gazette of Republic of Serbia, no. 11/92 and 32/2002, recommends the following MAC in fruit: Pb 3 (1), As 1 (0.1) and Cd 0.3 (0.05) mg/kg d.w. (w.w.). According to this, even at the control site, which is considered as an unpolluted location, the As content in unwashed fruit (1.6 mg/kg) is above the recommended limit. At other locations, concentrations of studied HMs in unwashed fruits are significantly higher than MACs in Serbia. It is

Fig. 2 Heavy metal content in parts of peach-trees against studied sampling sites
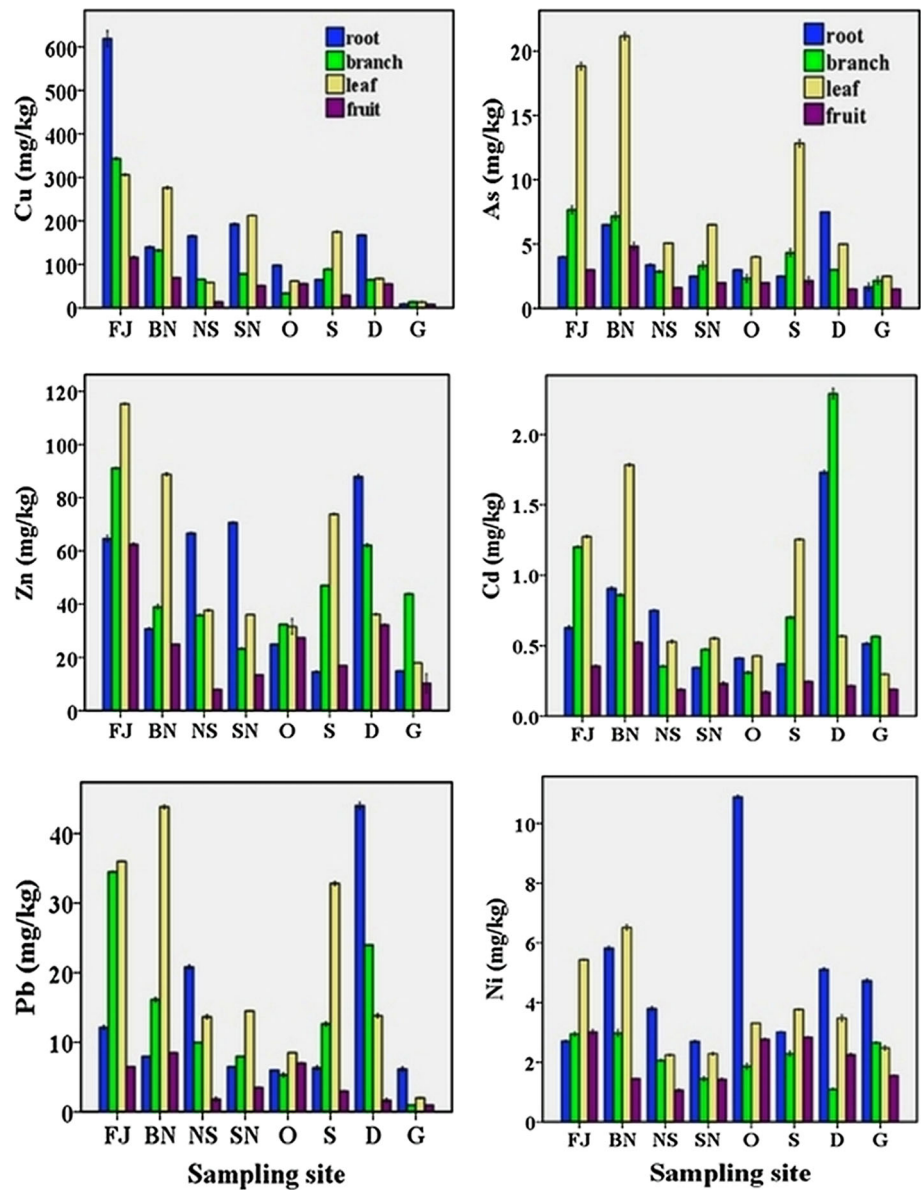
Table 3 Normal and toxic concentrations of heavy metals (mg/kg) in plants/mature leaves

Heavy metal	Cu	Zn	Pb	As	Cd	Ni
Normal range in plants[a]	5–20	1–400	0.2–20	0.02–7	0.1–2.4	0.02–5
Sufficient or normal range in mature leaves[b]	5–30	27–150	5–10	1–1.7	0.05–0.2	0.1–5
Excessive or toxic concentrations in mature leaves[a,b]	20–100	100–400	30–300	5–20	5–30	10–100

[a] Agyarko et al. (2010)

[b] Kabata-Pendias (2011)

noteworthy that this kind of peach does not undergo any pesticide treatments. In an orchard, in Bursa (Turkey), which was irrigated using river water polluted by HMs, it was found that Ni and Pb were accumulated to the toxic levels in different parts of the fruit (pulp and peel) (Basar and Aydinalp 2005). At the same time, concentrations of HMs in the soil of the orchard were considerably lower than the ones given in this study. According to the record of the Environmental Working Group, peach is one of the most polluted fruits (Crinnion 2010).

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Quantification of the level of pollution of soil and peach-tree parts

Soil enrichment

The normalized element enrichment factors for soil from the studied sites, EF_{soil}, are shown in Table 4. EF_{soil} between 0.5 and 2 could be considered as natural variability, while values higher than 2 indicate some enrichment corresponding mainly to the anthropogenic impact (Hernandez et al. 2003). According to this, the soil samples are not enriched with Ni and in some cases by Zn, Pb and Cd (bolded values in Table 4). All soil samples are enriched by Cu, and at six sites, there was an extremely high enrichment (86.42–101.46). EF_{soil} for Zn (1.53–7.47), Pb (1.05–7.47), As (2.15–13.42) and Cd (1.77–2.42) varied from moderate to significant levels. This indicates the anthropogenic influence on HM enrichment, i.e., the impact of smelting gases as a predominant source of pollution in the municipality of Bor.

Enrichment of plant parts (EF_{plant})

High values of EF_{plant} (Table 5) indicate increased HMs concentration in parts of the peach-trees at the polluted sites. The highest enrichment by HMs was in the root and the leaf. At only two sites, FJ and D, the Pb enrichment was higher in branches. At site FJ, fruit was enriched by Ni. Generally, values of EF_{plant} for all plant parts decreased as follows: Cu > Pb > Zn > As > Cd > Ni. Maximum values of EF_{plant} determined for specific HMs are as follows: $Cu_{r/r} = 68.80$ (FJ), $Zn_{l/l} = 6.45$ (FJ), $Pb_{b/b} = 30.97$ (FJ), $As_{l/l} = 9.05$ (BN), $Cd_{l/l} = 5.95$ (BN) and $Ni_{f/f} = 7.06$ (FJ).

Biological concentration factor

Biological concentration factor, BCF, shows a differing ability of the plant to accumulate or limit the accumulation of particulate metals from soil to the root. Calculated values of BCF (Table 5) for the studied sites were less than 1, except for site D where an increased accumulation of Cu in the root was observed (BCF = 1.187). Although at some sites, the uptake of HMs in the root of a peach-tree was relatively high, BCF values showed a tendency toward restricted soil-to-root transfer of HMs.

It can be said that the branched root of peach-trees can grow in the surface layers of the soil at a depth of 20–60 cm and can accumulate significant concentrations of HMs in its tissues. Therefore, the studied peach-tree could be applied for phytoremediation of shallow soils polluted with HMs. It is likely that the peach-tree will grow and develop even in tailings ponds covered with a very thin layer of humus. However, it should be kept in mind that the fruits from the trees planted for phytoremediation purposes are not safe for consumption. Namely, it is obvious from the obtained results that peach-tree fruits are susceptible to the retention of airborne particulate matter with high contents of HMs.

Ratios of heavy metal concentrations between plant parts

As explained above, the aboveground parts of peach-trees were not washed in order to assess the direct effect of atmospheric pollution (Oliva and Mingorance 2006). Table 6 shows the mean values of the three ratios (R) for six HMs, at all sampling sites. $R_{1/b}$ for all examined sites, except for the control one, are higher than 1, $R_{f/l}$ are less than 1, while $R_{f/b}$ is higher than 1 only at site O. The highest value for $R_{l/b}$ was determined at sites BN = 2.38 and S = 2.09, while the lowest value was determined at the controlling site G = 0.94. This situation is not unexpected because the sites BN and S are in the direction of predominant winds, which transfer the pollutants emitted from the copper smelter smokestacks. Additionally, as a simple consequence of the closeness to the smokestacks, site BN is constantly exposed to severe contamination. These results demonstrate that the level of contamination of peach-tree leaves corresponds to the level of atmospheric pollution. The results show that the leaves of deciduous trees such as peach-trees may also be a good indicator of atmospheric pollution in areas that lack evergreen trees, well known as an excellent indicator of pollution (Oliva and Mingorance 2006).

Statistical analysis

Relationship between concentration of HMs in soil, physical and chemical parameters of soil and distance from the source of pollution are evaluated by Pearson's correlation coefficients given in Table 7.

Table 4 Element enrichment factors (EF_{soil}) for soil

Site	Cu	Zn	Pb	As	Cd	Ni
FJ	90.96	4.53	3.00	8.56	2.13	**0.54**
BN	89.66	2.12	3.03	13.42	2.42	**0.66**
NS	101.46	4.80	6.91	10.46	2.03	**1.30**
SN	86.42	7.47	4.09	3.51	2.24	**1.10**
O	66.39	2.05	3.05	5.53	**1.77**	**0.91**
S	12.39	**1.19**	**1.05**	2.15	**1.37**	**1.50**
D	8.06	**1.53**	**1.59**	6.40	**1.86**	**1.00**

Bold values—not enriched

Table 5 Element enrichment factors for peach-tree parts (EF$_{plant}$) and biological concentration factors (BCF)

Sampling site	EF$_{plant}$	Cu	Zn	Pb	As	Cd	Ni
FJ	r/r	68.80	4.32	1.93	2.38	1.21	0.57
	b/b	24.81	2.07	30.97	3.49	2.11	1.11
	l/l	22.91	6.45	18.98	8.02	4.25	2.19
	f/f	13.71	6.20	6.93	1.82	1.87	7.06
BCF		0.444	0.202	0.111	0.113	0.144	0.184
BN	r/r	15.83	2.05	1.28	3.69	1.74	1.23
	b/b	9.58	0.88	14.43	3.29	1.51	1.12
	l/l	20.68	4.96	23.09	9.05	5.95	2.63
	f/f	8.20	2.47	9.05	3.00	2.76	0.93
BCF		0.088	0.173	0.063	0.095	0.154	0.273
NS	r/r	18.73	4.44	3.33	1.95	1.44	0.80
	b/b	4.75	0.81	9.14	1.31	0.62	0.78
	l/l	4.39	2.11	7.18	2.16	1.77	0.91
	f/f	1.62	0.81	1.86	1.01	1.00	0.69
BCF		0.113	0.203	0.088	0.079	0.187	0.111
SN	r/r	21.84	4.71	1.03	1.38	0.66	0.57
	b/b	5.67	0.53	7.14	1.50	0.83	0.55
	l/l	15.89	2.01	7.57	2.72	1.85	0.92
	f/f	6.05	1.33	3.72	1.24	1.24	0.92
BCF		0.169	0.152	0.049	0.182	0.086	0.102
O	r/r	11.10	1.68	0.98	1.82	0.80	2.30
	b/b	2.42	0.73	4.76	1.02	0.54	0.71
	l/l	4.62	1.77	4.52	1.74	1.42	1.34
	f/f	6.55	2.72	7.29	1.13	0.89	1.78
BCF		0.099	0.173	0.056	0.135	0.115	0.441
S	r/r	7.41	0.97	1.00	1.46	0.71	0.64
	b/b	6.43	1.07	11.41	1.94	1.24	0.86
	l/l	13.08	4.12	17.33	5.43	4.18	1.52
	f/f	3.45	1.70	3.29	1.38	1.29	1.82
BCF		0.318	0.156	0.150	0.250	0.119	0.066
D	r/r	18.96	5.87	7.00	4.27	3.34	1.08
	b/b	4.71	1.41	21.71	1.44	4.03	0.41
	l/l	5.07	2.02	7.20	2.10	1.90	1.40
	f/f	6.57	3.19	1.81	0.94	1.13	1.45
BCF		1.187	0.693	0.659	0.231	0.391	0.160
G BCF		0.961	0.345	0.285	0.664	0.414	0.282

r root, *b* branch, *l* leaf, *f* fruit

Table 6 Mean values of the three ratios (R) for all HMs at studied sampling sites

Ratio (R)	Sampling site							
	FJ	BN	NS	SN	O	S	D	G
R$_{l/b}$	1.43	2.38	1.27	1.79	1.57	2.09	1.20	0.94
R$_{f/l}$	0.35	0.29	0.29	0.37	0.71	0.27	0.53	0.67
R$_{f/b}$	0.48	0.58	0.37	0.61	1.11	0.51	0.68	0.56

l leaf, *b* branch, *f* fruit

A large number of metal pairs such as Cu–Zn, Cu–Pb, Cu–As, Cu–Cd, Zn–Pb, Zn–Cd, Pb–As, Pb–Cd and As–Cd showed a significant positive correlation in soil ($r = 0.684$), ($r = 0.813$), ($r = 0.716$), ($r = 0.692$), ($r = 0.677$), ($r = 0.411$), ($r = 0.573$), ($r = 0.504$) and ($r = 0.862$), respectively. Very strong and positive correlations were found between Cd and As. In the case of all HMs (with the exception of Ni), a significant negative correlation with respect to the distance is observed. This indicates that the concentration of HMs decreases with the

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Table 7 Pearson's correlation coefficients between determined soil parameters and distance from main pollution source ($N = 24$)

	Cu	Zn	Pb	As	Cd	Ni	pH	OM	EC	D
Cu	1									
Zn	0.684**	1								
Pb	0.813**	0.677**	1							
As	0.716**	0.184	0.573**	1						
Cd	0.692**	0.411*	0.504*	0.862**	1					
Ni	−0.296	−0.120	0.054	−0.172	−0.008	1				
pH	−0.351	−0.025	0.050	−0.564**	−0.453*	0.556**	1			
SOM	0.292	0.255	0.752**	0.328	0.281	0.462*	0.429*	1		
EC	0.429*	0.470*	0.215	0.077	0.166	−0.229	−0.533**	−0.167	1	
D	−0.883**	−0.681**	−0.668**	−0.469*	−0.593**	0.018	0.215	−0.189	−0.589**	1

OM organic matter; *EC* electrical conductivity; *D* distance from smelter

** Correlation is significant at the 0.01 level (two-tailed); * Correlation is significant at the 0.05 level (two-tailed)

distances from the source of pollution. Moreover, a very weak correlation is observed in the case of Ni. It means that Ni does not originate from the same anthropogenic source of pollution; it is more likely that Ni is of a geological origin (Alagić et al. 2015). A significant correlation was found between As, Cd and Ni content and pH of the soil, while Pb and Ni significantly correlated with OM.

Correlations between HMs in peach-tree parts are given in Table 8. A significant number of metal pairs show positive and very strong correlations as it is observed in soil. The highest number of these correlations is determined between certain HMs in leaves: PbL–ZnL ($r = 0.927$), AsL–ZnL ($r = 0.950$), AsL–PbL ($r = 0.976$), CdL–PbL ($r = 0.987$), CdL–AsL ($r = 0.972$) and NiL–AsL ($r = 0.921$). Additionally, all HMs in leaves show excellent correlations with As in branches. Correlations of As and Cd in the fruit with Zn, Pb, As and Cd in the leaves are also significant. The least significant correlation is between NiR, NiB, PbF and NiF and HMs in plant parts.

Table 9 displays some additional significant correlations. Significant negative correlations are found between pH and the content of HMs in peach-tree parts, with the exception of Zn, Pb, Cd and Ni, in the root and Ni in the fruit. Significant positive correlations are found for Cu, As and Cd in the soil relative to HMs content in leaves and fruit, with the exception of Zn and Ni in the fruit. Additionally, a larger number of positive correlations are observed between EC and HM in peach-tree parts, as well as a higher number of negative correlations relative to the distance from the source of pollution.

Principal component analysis (PCA) was performed using the varimax rotation and Kaiser criterion (eigenvalues > 1) and taking into consideration the loading coefficients ≥0.40. The loadings having a value greater than 0.71 (typically regarded as excellent, Garcia et al. 2004) are marked bold in Table 10.

It was obvious from PCA results that the first four of the six principal components extracted explained the 86.3 % of the total variance (Table 10). PCA1–PCA4 are related to the contents of HMs in soil, roots and aboveground parts of peach. PCA1 accounts for 45.8 % of the total variance, while heaving high loadings in leaves indicates high influence of atmospheric deposition on this plant part. PCA2, PCA3 and PCA4 explain 17.5, 12.6 and 10.5 %, respectively, of the total variance with high loadings in branches, roots and soil. It can be said that first four principal components PCA1–PCA4 explain the contribution of metals from local anthropogenic activities (copper smelting). PCA5 and PCA6 correlated strongly only with Ni. Loading of −0.900 for Ni in soil suggests that the principal source of this metal is dissimilar regarding other metals, i.e., is lithogenic.

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Table 8 Correlation analysis between concentrations of HMs in peach-tree parts ($N = 24$)

	CuR	ZnR	PbR	AsR	CdR	NiR	CuB	ZnB	PbB	AsB	CdB	NiB	CuL	ZnL	PbL	AsL	CdL	NiL	CuF	ZnF	PbF	AsF	CdF	NiF
CuR	1																							
ZnR	0.511*	1																						
PbR	0.102	0.723**	1																					
AsR	0.206	0.475*	0.704**	1																				
CdR	0.061	0.579**	0.924**	0.885**	1																			
NiR	−0.356	−0.338	−0.069	0.129	0.026	1																		
CuB	0.942**	0.277	−0.051	0.217	−0.006	−0.402	1																	
ZnB	0.757**	0.275	0.334	0.340	0.343	−0.308	0.785**	1																
PbB	0.835**	0.540**	0.450*	0.609**	0.482*	−0.345	0.848**	0.865**	1															
AsB	0.679**	0.063	−0.140	0.409*	0.068	−0.320	0.861**	0.572**	0.732**	1														
CdB	0.292	0.553**	0.819**	0.785**	0.876**	−0.161	0.259	0.622**	0.699**	0.238	1													
NiB	0.264	−0.551**	−0.571**	−0.149	−0.361	−0.110	0.498*	0.321	0.144	0.641**	−0.302	1												
CuL	0.652**	0.114	−0.298	0.219	−0.152	−0.397	0.798**	0.356	0.604**	0.905**	0.082	0.445*	1											
ZnL	0.708**	0.008	−0.169	0.296	−0.032	−0.331	0.893**	0.636**	0.758**	0.958**	0.196	0.617**	0.879**	1										
PbL	0.447*	−0.070	−0.169	0.394	0.026	−0.299	0.684**	0.382	0.607**	0.920**	0.167	0.546**	0.869**	0.927**	1									
AsL	0.529**	−0.090	−0.237	0.368	−0.012	−0.265	0.758**	0.439*	0.619**	0.973**	0.140	0.655**	0.900**	0.950**	0.976**	1								
CdL	0.340	−0.176	−0.211	0.403	0.030	−0.232	0.605**	0.322	0.523**	0.902**	0.143	0.602**	0.826**	0.885**	0.987**	0.972**	1							
NiL	0.438*	−0.131	−0.099	0.567**	0.195	0.041	0.653**	0.476*	0.615**	0.905**	0.299	0.615**	0.742**	0.847**	0.873**	0.921**	0.902**	1						
CuF	0.840**	0.333	0.034	0.443*	0.144	−0.014	0.849**	0.639**	0.803**	0.769**	0.388	0.243	0.761**	0.753**	0.593**	0.674**	0.532**	0.714**	1					
ZnF	0.856**	0.293	0.166	0.406*	0.224	−0.014	0.855**	0.854**	0.865**	0.674**	0.500*	0.271	0.561**	0.713**	0.472*	0.555**	0.407*	0.633**	0.922**	1				
PbF	0.371	−0.203	−0.399	0.287	−0.170	0.400	0.492*	0.104	0.301	0.672**	−0.127	0.464*	0.669**	0.634**	0.643**	0.712**	0.660**	0.789**	0.712**	0.522**	1			
AsF	0.246	−0.213	−0.314	0.413*	0.009	−0.016	0.477*	0.117	0.328	0.839**	0.006	0.647**	0.761**	0.720**	0.843**	0.893**	0.897**	0.897**	0.515*	0.311	0.785**	1		
CdF	0.343	−0.076	−0.182	0.500*	0.133	−0.146	0.560**	0.247	0.462*	0.894**	0.162	0.614**	0.797**	0.765**	0.865**	0.916**	0.907**	0.914**	0.571**	0.389	0.708**	0.978**	1	
NiF	0.384	−0.155	−0.030	0.032	−0.076	0.189	0.436*	0.594**	0.470*	0.244	0.282	0.070	0.223	0.437	0.257	0.245	0.204	0.317	0.524**	0.685**	0.308	−0.049	−0.047	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed)

Table 9 Correlation between selected soil parameters and HM concentrations in peach-tree parts (N = 24)

	CuR	ZnR	PbR	AsR	CdR	NiR	CuB	ZnB	PbB	AsB	CdB	NiB
CuS	0.487*	0.245	−0.237	0.143	−0.176	0.023	0.465*	−0.075	0.230	0.518**	−0.335	0.308
ZnS	0.537**	0.622**	−0.069	−0.111	−0.212	−0.413*	0.379	−0.092	0.206	0.204	−0.205	−0.181
PbS	0.238	0.440*	0.088	0.084	−0.011	−0.031	0.110	−0.254	0.035	0.074	−0.322	−0.060
AsS	0.313	0.262	0.233	0.717**	0.438*	0.115	0.377	0.142	0.453*	0.623**	0.204	0.301
CdS	0.411*	0.459*	0.267	0.741**	0.411*	0.026	0.435*	0.111	0.563**	0.631**	0.318	−0.007
NiS	−0.414*	−0.008	0.230	−0.026	0.058	−0.162	−0.373	−0.277	−0.139	−0.313	0.020	−0.452*
pH	−0.737**	−0.129	−0.056	−0.478*	−0.262	0.206	−0.857**	−0.786**	−0.793**	−0.891**	−0.420*	−0.645**
SOM	−0.166	0.444*	0.492*	0.212	0.313	0.196	−0.344	−0.339	−0.118	−0.396	−0.053	−0.507*
D	−0.484*	−0.098	0.416*	0.073	0.432*	0.050	−0.504*	0.077	−0.221	−0.507*	0.439*	−0.261
EC	0.890**	0.221	−0.182	−0.160	−0.304	−0.303	0.863**	0.646**	0.628**	0.542**	−0.036	0.347

	CuL	ZnL	PbL	AsL	CdL	NiL	CuF	ZnF	PbF	AsF	CdF	NiF
CuS	0.561**	0.451*	0.445*	0.498*	0.405*	0.394	0.461*	0.233	0.649**	0.558**	0.516**	−0.250
ZnS	0.457*	0.170	0.106	0.122	0.000	−0.122	0.327	0.107	0.126	0.044	0.077	−0.284
PbS	0.102	0.044	0.069	0.051	0.008	−0.077	0.025	−0.116	0.157	0.101	0.074	−0.478*
AsS	0.439*	0.505*	0.603**	0.617**	0.615**	0.687**	0.435*	0.301	0.591**	0.721**	0.733**	−0.223
CdS	0.629**	0.546**	0.661**	0.632**	0.628**	0.645**	0.615**	0.392	0.637**	0.658**	0.685**	−0.043
NiS	−0.213	−0.148	0.043	−0.172	0.002	−0.304	−0.463*	−0.430*	−0.380	−0.308	−0.325	0.076
pH	−0.668**	−0.827**	−0.683**	−0.792**	−0.677**	−0.841**	−0.777**	−0.808**	−0.536**	−0.665**	−0.751**	−0.290
SOM	−0.421*	−0.365	−0.278	−0.384	−0.327	−0.386	−0.326	−0.330	−0.228	−0.333	−0.355	−0.357
D	−0.661**	−0.552**	−0.543**	−0.541**	−0.472*	−0.349	−0.471*	−0.250	−0.660**	−0.471*	−0.406*	−0.050
EC	0.562**	0.676**	0.393	0.448*	0.277	0.288	0.671**	0.731**	0.341	0.105	0.142	0.538**

** Correlation is significant at 0.01 level (two-tailed); * Correlation is significant at 0.05 level (two-tailed)

Table 10 PCA factors and loadings for heavy metals contents (mg/kg/, d.w.) in soil and parts of peach-tree

Variables	PCA 1	PCA 2	PCA 3	PCA 4	PCA 5	PCA 6	Communality
Cu root		**0.856**					0.994
Zn root			0.630	0.598			0.984
Pb root			**0.938**				0.983
As root	0.401		**0.881**				0.997
Cd root			**0.997**				0.999
Ni root					**0.960**		0.991
Cu branch	0.494	**0.797**					0.991
Zn branch		**0.805**					0.942
Pb branch		**0.755**	0.480				0.991
As branch	**0.858**	0.460					0.999
Cd branch			**0.868**				0.975
Ni branch	0.650		−0.451			0.492	0.902
Cu leaf	**0.764**	0.462					0.921
Zn leaf	**0.795**	0.571					0.983
Pb leaf	**0.935**						0.999
As leaf	**0.938**						1.000
Cd leaf	**0.975**						1.000
Ni leaf	**0.895**						0.999
Cu fruit	0.443	**0.800**					0.960
Zn fruit		**0.908**					0.996
Pb fruit	0.683				0.592		0.990
As fruit	**0.957**						0.981
Cd fruit	**0.949**						0.973
Ni fruit		**0.765**		−0.440			0.990
Cu soil	0.457			**0.823**			0.980
Zn soil				**0.898**			0.954
Pb soil				**0.904**			0.850
As soil	0.680		0.437	0.447			0.939
Cd soil	0.626		0.439	0.554			0.992
Ni soil						**−0.900**	0.944
Eigenvalue	13.73	5.26	3.78	3.14	1.98	1.31	
Variance (%)	45.76	17.53	12.59	10.46	6.60	4.38	
Cumulative (%)	45.76	63.29	75.88	86.34	92.94	97.32	

Variables with loadings ≥ 0.70 were identified as significant variables and they are in bold

The structure of relations among the contents of HMs in soil and parts of peach-tree is illustrated in three-dimensional (3D) space (Fig. 3).

PCA revealed a strong correlation between the contents of heavy metals, especially in the aboveground parts of the peach-tree, as can be seen in Fig. 3 where the largest grouping exists in the case of variables related to the aboveground parts.

Conclusion

Results of the present study revealed that the copper smelter activity brings to soil pollution by Cu, Zn, Pb, As, Cd, as follows: UI areas were more polluted than the rural ones by Cu, Zn and Pb, while for As and Cd, this was not observed; the soil in UI areas was extremely polluted by Cu; the soil pollution by HMs followed a trend:
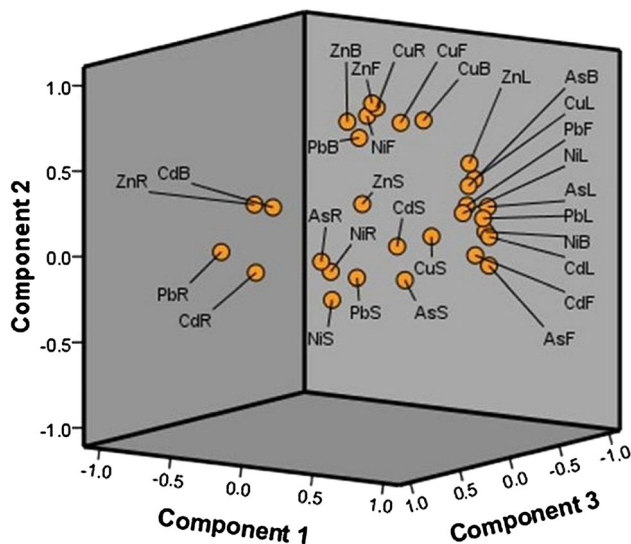
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Fig. 3 PCA 3D plot for HM contents in soil and parts of peach-tree

Cu > As > Zn > Pb > Cd. Computed EF_{soil} also showed that the soil was enriched by the mentioned HMs (except Ni). The highest enrichment was by Cu. For the examined HMs (except Ni), significant negative correlations in relation to the distance from the pollution source were determined which means that pollution from the RTB Bor metallurgical complex decreased with increasing distance from the smelter. The concentrations of HMs in many plant parts of peach-trees were above the normal ones, that is, at the levels of phytotoxicity, and the highest contents were determined for Cu. EF_{plant} showed that the highest metal enrichment was in the root and the leaf of peach-trees close to the smelter. On the other hand, the low values of BCF indicated the peach's tendency to restrict massive transfer of HMs from soil to the root. The results obtained from statistical analysis (Pearson correlation analysis and PCA) confirmed that the contents of HMs in the aboveground plant parts originated mainly from the atmosphere, i.e., from the copper smelter. The content of Ni in the soil is demonstrated to be of geogenic origin. The three ratios ($R_{l/b}$, R_{fl} and R_{flb}) demonstrated that the leaves were the best indicators of pollution by atmospheric deposition. This was additionally confirmed by high positive correlations between metals in the leaves. At all examined sites, the concentrations of HMs in the fruit of the peach-trees were above the allowed limits so that the fruits were not safe for consumption. Even at the controlled location G, 19 km away from the copper smelter, an increased content of As in fruits was found.

It can be concluded that the peach-tree *P. persica* L. Batech may be classified as a metallophyte since it can grow in soils with high concentrations of HMs that are toxic for most of the other plants. It is demonstrated that peach-trees are tolerant to extremely high concentrations of Cu when the concentrations of other HMs are also high. Therefore, the studied peach-tree can be considered as a potential plant for phytoremediation, in particular for phytostabilization of soil that is contaminated by various HMs. Additionally, analysis of peach-tree leaves revealed their potential to be used as an excellent biomonitor for atmospheric pollution in industrial zones.

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