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Evaluation of urban contamination with trace elements in city parks in Serbia using pine (*Pinus nigra* Arnold) needles, bark and urban topsoil

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Abstract

Urban environments are strongly influenced by anthropogenic activities, which are often reflected by a high degree of contamination in relation to the natural environment. Concentrations of five trace elements (B, Cr, Cu, Mn and Zn) were determined in the surface layers of soil (0-10 cm), bark, and 1-year and 2-year-old needles of *Pinus nigra* Arnold in urban parks in four cities in Serbia exposed to different pollution sources. The sampling locations in parks were chosen based on their proximity to industrial complexes and heavy traffic. Soil indices such as the contamination factor and the degree of contamination were used to assess the potential ecological risk in urban topsoil. Although some metal concentrations (Cr, Cu, Mn and Zn) occasionally exceeded the background values, they posed no threat to the environment. The content of the selected metals in needles varied depending on the metal, the age of the needles, and the site. It is evident from this study that pine needles do not accumulate trace elements in large (mg kg^{-1}) quantities. The highest metal accumulation was observed in the soil and needles at sites with heavy industry and heavy traffic, such as Smederevo and Belgrade, which were the two most polluted sites.

Key words: urban environment, trace metals, indices of pollution, background, *Pinus nigra*, needles

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1. Introduction

Urban areas are specific areas with a dominant human impact. They suffer from considerable pollution due to a wide array of substances that contaminate soil and air, an increase in concentrations of substances of anthropogenic origin, heavy traffic, coal combustion, various industrial facilities, and waste disposal sites (Craul 1999; Buszewski et al. 2000; Rucandio et al. 2011; Parzych and Jonczak 2014).

Soils are more sensitive to the effects of pollution than other components of the natural environment, given the fact that contaminants in air/water are dispersed/diluted by air/water circulation, unlike contaminants in soils which persist for a long time after their introduction (Adriano 2001). In urban and industrial areas they are regarded as continuous recipients of various pollutants and hazardous elements (Islam et al. 2015), particularly heavy metals as one of the most persistent contaminants, since they are not biodegradable and can stay in soil for a long time (Schuurmann and Markert 1998; Adriano 2001). Background metal content in soil is determined by the geological substrate and reflects various environmental and geological processes in the past (Parzych and Jonczak 2013). Assessment of soil contamination is mostly based on the degree of contamination using various pollution indices. These indices can show the relative enrichment in any contaminant when compared to pre-industrial soils from the same environment (Islam et al. 2015). Distribution and identification of hazardous elements is essential in determining the pollution status of urban soils (Yuan et al. 2014; Islam et al. 2015).

Using plant material as an indicator of long-term soil contamination and air pollution in urban environments is a widely-used tool, especially in areas where the sampling and chemical analysis may be challenging and expensive (Kozlov 2005; Samecka-Cymerman et al. 2009; Madejon et al. 2013). Various types of lichens, mosses and parts of higher plants (leaves and bark) have been used to detect the deposition, accumulation and distribution of metal pollution (Bargagli et al. 1998; Markert et al. 2003; Tomašević et al. 2008; Aničić et al. 2011; Rucandio et al. 2011; Sawidis et al. 2011; Šerbula et al. 2013; Pavlović et al. 2017a). The main advantages of using plants are the greater availability of biological material, the simplicity of species identification, sampling and treatment, and the ubiquity of some genera, which makes it possible to cover large areas (Berlizov et al. 2007). With regard to this, Austrian pine (*Pinus nigra* Arnold) meets many requirements in terms of environmental monitoring (Šerbula et al. 2013). It is resistant to drought and wind and tolerates urban conditions well. It is also one of the most tolerant species in terms of habitat, in the sense that *P. nigra* is a pioneer species capable of surviving extreme soil and slope conditions, on almost completely vertical limestone, dolomite and serpentine cliffs (Jovanović, 1985). Furthermore, its needles have a thick epicuticular wax layer and are particularly sensitive to environmental pollution, with pine needles frequently used as biomonitors of air pollution because of passive and active uptake (Sun et al. 2009; Sun et al. 2010; Kuang et al. 2011) by needle tissue from the atmosphere (Mingorance et al. 2007; Šerbula et al. 2013).

In order to investigate pollution derived from industrial cities on soils and plants, samples from Pančevo, Smederevo, Obrenovac and Belgrade in Serbia were compared and discussed in relation to the control site - Topčider Park. Boron, copper, manganese and zinc represent essential elements for living organisms. Boron in very small quantities is necessary for all living beings, Cu is involved in many physiological processes in plants, Mn is included in metabolic processes in plants, since it represents a component of an enzyme included in photosynthesis, and Zn has a fundamental role in plant metabolism. Unlike the other examined elements, Cr does not represent an essential element; however, in small quantities it can have a beneficial effect on plant growth, but in large quantities it becomes highly toxic (Shanker et al. 2005). The objectives of this study were: 1) to determine the physical and chemical properties of topsoil from urban parks in relation to the control site, 2) to investigate the contamination factor and degree of contamination in urban topsoil and thus to assess the extent of the anthropogenic contribution and the potential risk of soil contamination, 3) to estimate the trace metal content in urban topsoil, bark, as well as in 1-year and 2-year-old needles from *Pinus nigra*, 4) to determine the difference between 1-year and 2-year-old needles in terms of their accumulation ability, and 5) to compare pollution levels in the four cities in relation to trace metal accumulation in soil and plant material.

2. Materials and methods

2.1 Study area

The research sites were municipal parks in four cities in central Serbia, within 50 km of each other, exposed to airborne and trace element pollution from industrial activities, municipal and industrial waste disposal, and heavy traffic – in Pančevo the dominant sources of pollution are the NIS-RNP Oil Refinery, HIP-Azotara d.o.o. (the Nitrogen Fertilizer Plant), and HIP-Petrohemija (the Petrochemical Complex) and sampling was performed in the National Garden (Narodna Bašta)

(44°51'54" N, 20°39'23" E); in Smederevo the dominant pollution source is the Smederevo Steelworks (Železara Smederevo) and sampling was performed in the National Heroes Park (Park Narodnih heroja) (44°40'22" N, 20°55'67" E); in Obrenovac the dominant sources of pollution are two thermoelectric power plants - 'Nikola Tesla A' and 'Nikola Tesla B', as well as two ash disposal sites generated by coal combustion, with a total surface area of 1000 ha, and sampling was performed in the City Park (Gradski park) (44°39'17" N, 20°12'30" E); in Belgrade the dominant source of pollution is heavy traffic and sampling was performed at Pioneer Park (Pionirski park) (44°48'53" N, 20°29'70" E). Topčider Park (Topčiderski park) (44°46'59" N, 20°26'19" E), which is located in a zone of mixed oak forest (*Quercetum farinetto cerris* Rud.), was chosen as the control site for this research (Fig. 1). The control site was selected in order to compare differences in elemental content in plant tissues that are under the direct influence of pollution sources and those that are isolated.

The research was carried out in October 2012. This year was characterized by extremely high summer temperatures and low precipitation, with 62 days of tropical daily temperatures of +30 °C (40 days more than the annual average) and 52 days of tropical nights with average temperatures of +20 °C. During 2012, the daily average and the maximum and minimum air temperatures in Serbia were mostly above the average values for the reference period (1981-2010). The annual precipitation sum in Serbia for the year 2012 ranged from 30.9 mm to 112.3 mm, which represents 17-69 % of the annual average for the reference period (1981-2010) (Smailagić et al. 2012).

Fig. 1 Selected urban sampling sites in Serbia: 1) Pančevo, 2) Smederevo, 3) Obrenovac, 4) Belgrade, and 5) Belgrade - control site

2.2 Sampling and element concentration analysis

2.2.1 Soil samples

Composite topsoil samples at a depth of 0–10 cm were collected from around each plant at five random locations with a stainless steel shovel. Stones and foreign objects were removed by hand, while soil samples were stored in clean polyethylene bags. Each soil sample was first air dried for 10 days, then in a dryer at a temperature of 105 °C (Binder, Tuttlingen, Germany), and afterwards sieved through a stainless steel sieve with a mesh diameter of 2 mm. The following were then determined: particle size distribution, active acidity (pH_{H2O}) and potential acidity (pH_{KCl}), organic carbon content (OC), nitrogen content (N), and carbon/nitrogen (C/N) ratio.

The physical properties of the soils were determined by combined pipette and sieving techniques with 0.4 N solution of sodium pyrophosphate. Fractionation was carried out according to Atteberg. Soil pH in an aqueous solution was measured using a glass electrode (1:2.5 soil-water ratio), as well as in 1 M KCl (1:2.5 soil-KCl ratio) after agitating samples for approximately 30 min (Dick et al. 2000). Organic carbon and nitrogen concentrations in soil samples were determined with a CNS analyzer, Vario model EL III (Elemental Analysis systems GmbH, Hanau, Germany), and the C/N ratio by computing.

In order to determine total element concentrations, soil samples (0.3 g) were digested in a microwave (CEM, 39 MDS-2000), using the USEPA 3051A method (USEPA 1996). Element concentrations were determined with inductively coupled plasma optical emission spectrometry (ICP-OES) (SpectroGenesis Genesis Fee, Spectro-Analytical Instruments GmbH, Kleve, Germany). Five replicates were performed for each sample. Quality control for soil was performed using standard soil reference material – ERM-CC141 loam soil obtained from the IRMM (Institute for Reference Materials and Measurements, Geel, Belgium) and certified by the EC-JRC (European Commission-Joint Research Centre). The concentrations obtained were within 95-105 % of the certified values for all the elements measured. The limits of detection for B, Cr, Cu, Mn and Zn were: 0.000634 mg kg^{-1}, 0.000315 mg kg^{-1}, 0.00069 mg kg^{-1}, 0.000157 mg kg^{-1} and 0.00348 mg kg^{-1} respectively. Concentrations of all the measured elements are expressed in milligrams per kilogram of dry weight (mg kg^{-1} d.w.).

For assessing and quantifying the level of contamination in urban soil samples, the following contamination indices were used: contamination factor (C_f) and degree of contamination (C_{deg}).

C_f is determined by the following equation:

$$C_{f=}C_m/B_m$$

where C_f represents the contamination factor of the element of interest, C_m is the concentration of the element in the sample, and B_m is the background concentration in soil. It has been established that a C_f of less than 1 refers to low contamination, $1 \leq C_f \leq 3$ means moderate contamination, $3 \leq C_f \leq 6$ considerable contamination, while $C_f \geq 6$ represents very high contamination (Hakanson 1980).

C_{deg} represents the sum of all the contamination factors in a soil sample and is determined by the following equation:

$$C_{deg} = \Sigma\ (C_m/B_{m)}$$

where C_m is the concentration of the element in the soil sample and B_m is the background concentration. Hakanson (1980) defined different categories for the degree of contamination: $C_{deg} \leq 8$ refers to a low degree of contamination, $8 \leq C_{deg} \leq 16$ means a considerable degree of contamination, and $C_{deg} \geq 32$ a very high degree of contamination.

The arithmetical median method was used for calculating the background concentrations for each city in Serbia (MAD - median of absolute deviations from data median) proposed by Reimann et al. (2005) and Mrvić et al. (2011).

2.2.2 Plant samples

Element content was determined on the needles and bark of *P. nigra* collected from five randomly chosen trees at each sampling site. The trees were about 20–30 years old. Needle samples were taken uniformly from each tree from different quarters of the tree crown in all directions around the tree with stainless-steel scissors. The samples from each tree in every location were mixed into a composite sample (10-20 g), taking into consideration the age of the needles (separate 1-year-old and 2-year-old samples), resulting in one composite needle sample per sampling site. Flakes of the bark layer from each tree, about 4–5 mm in thickness and an initial quantity of about 30 g, were carefully cut with a stainless steel knife at 1.2–1.5 m above ground level (in all directions around the tree) and mixed into a composite bark sample, resulting in one composite bark sample per sampling site.

All plant samples were first washed and then air dried for 10 days at room temperature and then dried to a constant weight at 65 °C (Binder, Tuttlingen, Germany). For the element concentration analysis, plant samples (0.3 g) were digested in a microwave (CEM, 39 MDS-2000), using the USEPA 3052 method (USEPA 1996). Five replicates were performed for each sample. Quality control for leaves was performed using standard leaf reference material – BCR-100 beech leaves obtained from the IRMM (Institute for Reference Materials and Measurements, Geel, Belgium) and certified by the EC-JRC (European Commission-Joint Research Centre). The concentrations obtained were within 95-105 % of the certified values for all the elements measured. All the limits of detection for plant samples were the same as for soil samples. Element concentrations were expressed in milligrams per kilogram of dry leaf/bark weight (mg kg^{-1} d.w.).

2.3 Data analysis

One-way analyses of variance (ANOVA) were performed to test differences in trace metal accumulation in the soil samples, pine needles and bark, both from the urban sampling sites and the control site. Statistical processing of the data was carried out using the Minitab 17. Pearson's correlation coefficients were calculated in order to study the relationship between element concentrations in soil samples, as well as between soil and plant tissues at all the sampling sites. Data on potential similarities or differences between the sampling sites in relation to the elements tested was obtained by principal component analysis (PCA).

3. Results

3.1 Selected physical and chemical soil properties

Particle size distribution, active and potential acidity, organic carbon, nitrogen and the carbon/nitrogen ratio are shown in Table 1.

Table 1 Selected physical and chemical soil properties

Sampling site	Depth (cm)	Granulometric composition %							
		Total sand	Silt	Clay	pH		Organic C	N	C/N
		2.0-0.02 mm	0.02-0.002 mm	<0.002 mm	H_2O	KCl	%	%	
Pančevo	0 - 10	45.83	27.96	26.21	8.44	6.84	3.00	0.31	9.67
Smederevo	0 - 10	53.13	25.95	20.92	8.51	6.87	2.68	0.23	11.65
Obrenovac	0 - 10	36.27	34.71	29.02	8.44	6.99	2.10	0.18	11.66
Belgrade	0 - 10	52.23	27.43	20.34	8.47	7.00	5.56	0.40	13.90
Control site	0 - 10	35.57	37.29	27.14	8.61	6.93	2.71	0.28	9.67

Given values are mean, n=5

The lowest total sand content (fine and coarse fraction) was measured at the control site (35.57 %), while the highest was recorded in Belgrade (52.23 %) and Smederevo (53.13 %). The silt fraction varied from 25.95 % in Smederevo to 37.29 % at the control site, while the clay content was relatively uniformly distributed and ranged from 20.34 % in Belgrade to 27.14 % at the control site (Table 1). The chemical reaction of the soil (pH_{H2O}) was alkaline (Soil Survey Division Staff 1993), given the fact that results showed a narrow range from 8.44 in Pančevo to 8.61 at the control site (Table 1). The pH_{KCl} solution also showed consistency and ranged from 6.84 in Pančevo to 7 in Belgrade, classifying these soils as practically neutral. OC varied from 2.10 % in Obrenovac to 5.56 % in Belgrade, while N content ranged from 0.18 % in Obrenovac to 0.40 % in Belgrade (Table 1). The C/N ratio varied from 9.67 % in Pančevo and at the control site to 13.90 % in samples from Belgrade.

3.2 Element concentration in topsoil

All the results obtained for soil exhibited elevated concentrations of B in relation to the average content for worldwide sandy soils of 134 mg kg^{-1} described by Kabata-Pendias and Pendias (2001) and the average content for soils in Serbia of 25-40 mg kg^{-1} (Aubert and Pinta 1977, Table 2). Boron content ranged from 155.01 mg kg^{-1} in Pančevo up to 175.35 mg kg^{-1} in Obrenovac. No significant differences were found between Pančevo and Smederevo in relation to the control site, while Obrenovac and Belgrade showed significant differences ($p<0.001$) (Table 3).

The lowest amount of Cr was found in samples from Belgrade (72.08 mg kg^{-1}), while the highest was measured in soil from Smederevo (126.01 mg kg^{-1}). All results for Cr in soil were well above the background values for the selected sampling sites (Table 2). No significant differences were found in soil samples from Pančevo and Belgrade when compared to the control site, while samples from Obrenovac exhibited differences ($p<0.05$) together with samples from Smederevo, which showed significant variations ($p<0.001$) in Cr accumulation ability (Table 3).

Copper levels in soil samples from Pančevo, Obrenovac and Belgrade fell within the range of average values described for worldwide soils of 12-23 mg kg^{-1} (Kabata-Pendias and Pendias 2001) and below the background values (Table 2). The highest Cu concentrations were recorded in samples from the control site (36.98 mg kg^{-1}) and Smederevo (64.12 mg kg^{-1}), which were slightly above the respective background values. All the examined sites exhibited significant differences ($p<0.001$) in relation to the control site (Table 3).

Although Mn concentrations in soils from the selected sampling sites were significantly higher in relation to the average values for worldwide sandy soils of 270-525 mg kg^{-1} (Kabata-Pendias and Pendias 2001), all the recorded results were below the background values, except for samples from Belgrade (523.94 mg kg^{-1}) and the control site (593.11 mg kg^{-1}), which were somewhat elevated. All the samples, except for the one from Smederevo (no differences), exhibited significant differences ($p<0.001$) in relation to the control site (Tables 2 and 3).

The zinc content in soil ranged from 54.73 mg kg^{-1} in Pančevo to 151.26 mg kg^{-1} in Smederevo. Samples from Smederevo and Belgrade (72.41 mg kg^{-1}) exceeded the background values (Table 2). Furthermore, all the obtained results, aside from Obrenovac (no differences), exhibited significant differences in Zn accumulation ability in relation to the control site ($p<0.001$) (Table 3).

3.3 Indices of soil pollution

Selected soil pollution indices, as well as background concentrations in samples from the urban parks examined, are presented in Table 2. Due to the absence of data on background concentrations of B at all the selected sampling sites, we were compelled to use data on average B content in Serbian soils from Aubert and Pinta (1977). The lack of background data and publications on this element is due to the fact that it is not considered hazardous.

Table 2. Selected soil indices and trace element background content at the selected sampling sites

Indices	C_f					C_{deg}	[a] Background concentration [b] Average content in Serbian soils				
site | element	B	Cr	Cu	Mn	Zn		B[b]	Cr[a]	Cu[a]	Mn[a]	Zn[a]
Pančevo	3.87	1.83	0.55	0.98	0.56	7.79	25-40	47.50	37.79	689.55	96.45
Smederevo	4.05	1.82	1.09	0.84	1.31	9.11	25-40	69.00	58.50	700.94	115.00
Obrenovac	4.38	1.18	0.74	0.80	0.88	7.98	25-40	79.00	28.00	863.70	74.00
Belgrade	3.72	1.18	0.65	1.07	1.06	7.68	25-40	61.00	30.00	489.28	68.00
Control	3.95	1.21	1.23	1.21	0.97	8.57	25-40	61.00	30.00	489.28	68.00

[a] Data for Cr, Cu, Mn and Zn obtained from Mrvić et al. 2011, [b] Data for B from Aubert and Pinta 1977

Contamination factors for the selected elements are given in Table 2. It should be noted that the C_f for B was calculated on the basis of the upper average value of 40 mg kg^{-1}, which is why it suggested considerable contamination at all sites. The C_f for Cr indicated moderate contamination and ranged from 1.18 in Obrenovac and Belgrade to 1.83 in Pančevo. For the rest of the elements, low contamination (<1) was exhibited. The assumption that Topčider Park, as the control site, situated in a large green area on the periphery of Belgrade, was a suitable site appeared to be disputable due to moderate contamination factors for Cr, Cu and Mn in soil samples.

Assessment of overall soil contamination by the elements tested was based on C_{deg}, which varied from 7.68 in Belgrade to 9.11 in Smederevo.

3.4 Element concentrations in needles of *Pinus nigra*

Concentrations of B, Cr, Cu, Mn and Zn in needles of *Pinus nigra* from each sampling site are given in Table 3. Trace element content in plant tissues varied depending on the element, the age of the needles, and the sampling site. Of the tested elements, B had the highest levels, followed by Zn, Mn, and Cu, with Cr exhibiting the lowest levels (B>Zn>Mn>Cu>Cr) in 1-year-old needles. In 2-year-old needles, the order was slightly different, since Mn concentrations were higher than Zn (B>Mn>Zn>Cu>Cr). At all the examined sites, higher levels of B, Cr and Mn were found in 2-year-old needles, while 1-year-old needles contained more Cu and Zn.

Boron concentrations in pine needles ranged from 22.02 to 50.87 mg kg^{-1} in 1-year-old needles and from 29.08 to 65.72 mg kg^{-1} in 2-year-old needles (Table 3). The lowest B content was recorded in Pančevo for both needle types, while the highest levels for 1-year-old needles were measured in Smederevo (50.87 mg kg^{-1}) and for 2-year-old needles in Belgrade (65.72 mg kg^{-1}). Significant differences in B content ($p<0.001$) were recorded between the control site and all the other examined sites, apart from 2-year-old needles from Obrenovac ($p<0.05$) (Table 3).

The lowest Cr concentrations were measured in Obrenovac in 1-year-old needles (0.89 mg kg^{-1}) and at the control site (1.53 mg kg^{-1}) in 2-year-old needles (Table 3). The highest concentrations of Cr in both types of needles were measured in Smederevo (2.45 mg kg^{-1} for 1-year-old and 2.87 mg kg^{-1} for 2-year-old needles). Significant differences ($p<0.001$) for one and two-year-old needles were recorded in Smederevo (2.87 mg kg^{-1}) and Belgrade (2.77 mg kg^{-1}) in relation to the control site. It should be noted, however, that all the obtained results are well above values that are sufficient for normal plant development as suggested by Kabata-Pendias and Pendias (2001), but are not within the toxic range.

The lowest Cu concentrations for both needle types were measured in Obrenovac (2.08 mg kg^{-1} for 1-year-old and 1.70 mg kg^{-1} for 2-year-old needles). Significant differences in Cu accumulation ability ($p<0.001$) in relation to the control site were exhibited at all the examined sites, except for 1-year-old-needles from Pančevo ($p<0.05$) (Table 3). The highest Cu concentrations for both years were measured at the control site (4.62 mg kg^{-1} for 1-year-old and

9.36 mg kg^{-1} for 2-year-old needles). All the obtained results are considerably below the optimum values for normal plant development suggested by Kabata-Pendias and Pendias (2001), which range between 5 and 30 mg kg^{-1}. Baker and Seneft (1995) suggested an average Cu content in plant tissues of around 10 mg kg^{-1}. As such, our study revealed that only 2-year-old needles from the control site contained sufficient levels of Cu for optimum plant development (9.36 mg kg^{-1}).

When it comes to Mn, the lowest levels were measured in 1-year-old (14.63 mg kg^{-1}) and 2-year-old needles (13.47 mg kg^{-1}) from Obrenovac. There were not found to be any statistically proven differences in Mn content between Pančevo and Smederevo and the control site, while significant differences ($p<0.001$) were recorded for Obrenovac and Belgrade for 1-year-old needles (Table 3). The highest Mn concentrations were measured in Belgrade for both needle types (1-year-old - 26.88 mg kg^{-1} and 2-year-old needles - 44.88 mg kg^{-1}). There were significant differences ($p<0.001$) in Mn accumulation ability by 2-year-old needles in relation to the control site at all the sampling sites, aside from Obrenovac ($p<0.05$). All the obtained results for 1-year-old needles, as well as for 2-year-old needles from Pančevo, Obrenovac, and the control site fell within the deficit range, i.e. not enough to cover the basic physiological needs of plants (Kabata-Pendias and Pendias 2001).

Concentrations of Zn in 1-year-old needles ranged from 22.66 mg kg^{-1} in Pančevo to 32.52 mg kg^{-1} at the control site, while in 2-year-old needles they varied from 18.13 mg kg^{-1} at the control site to 36.86 mg kg^{-1} in Belgrade (Table 3). A decline in Zn content in 2-year-old needles is evident from the obtained results, except in the case of Belgrade. The most marked decline in Zn concentrations (14.3 mg kg^{-1}) was observed between the two needle types at the control site. The results obtained from Pančevo and Obrenovac for 1-year old needles and for 2-year-old needles from all the sampling sites, apart from from Belgrade, fell within the deficit range for plant tissues (Kabata-Pendias and Pendias 2001). In 1-year-old pine needles from Belgrade and 2-year-old needles from Pančevo and Obrenovac, there were no statistically proven differences (ns) in terms of Zn concentrations in relation to the control site. Significant differences ($p<0.001$) were recorded in 1-year-old needles from Pančevo and Obrenovac, as well as 2-year-old needles from Belgrade.

3.5 Element concentrations in bark of *Pinus nigra*

Boron content in bark was considerably lower than in needles and ranged from 6.49 mg kg^{-1} at the control site to 12.66 mg kg^{-1} in Smederevo. There were significant differences ($p<0.001$) for all the samples in relation to the control site (Table 3).

The lowest Cr concentrations in bark were measured at the control site (1.16 mg kg^{-1}) and the highest were recorded in Smederevo (7.57 mg kg^{-1}). The minimum and maximum Cr levels for bark correspond to those sampling sites where the highest and lowest Cr content in needles was found. Bark samples from Smederevo, Obrenovac and Belgrade showed significantly ($p<0.001$) higher contamination than at the control site (Table 3).

Copper content in bark remained negligibly higher than in needles. The lowest Cu concentrations in bark were measured in Obrenovac (3.30 mg kg^{-1}), while the highest were at the control site (10.48 mg kg^{-1}) (Table 3). The results obtained for the minimum and maximum Cu concentrations in bark coincide with those sampling sites where the highest and the lowest Cu levels in needles were recorded. There were significant differences ($p<0.001$) in bark samples from all the sites when compared to the control site.

Bark contained a lower amount of Mn in relation to needles, except in the case of Obrenovac. Mn content in bark ranged from 4.02 mg kg^{-1} at the control site up to 20.89 mg kg^{-1} in Smederevo. There were significant variations ($p<0.001$) at all the sites when compared to the control site (Table 3).

Concentrations of Zn in bark varied in a narrow range from 23.36 mg kg^{-1} in Obrenovac to 35.24 mg kg^{-1} measured in samples from Smederevo. The results obtained from Pančevo and Obrenovac did not show any statistically significant differences (ns) in relation to the control site, while bark samples from Smederevo and Belgrade exhibited significant differences ($p<0.001$) (Table 3).

Table 3. Comparison of B, Cr, Cu, Mn and Zn concentrations in *Pinus nigra* needles, bark and soil (mg kg^{-1} d.w.)

City	M (SD)	*P* value	City	M (SD)	*P* value
			Boron		
	1-year-old needles			2-year-old needles	
Pančevo	22.02 (0.35)	***	Pančevo	29.08 (0.46)	***
Smederevo	50.87 (0.56)	***	Smederevo	61.76 (0.70)	***
Obrenovac	38.51 (0.71)	***	Obrenovac	35.52 (0.50)	*
Belgrade	33.91 (0.45)	***	Belgrade	65.72 (0.60)	***

Control site	26.19 (0.28)		Control site	36.81 (0.39)	
	bark			soil	
Pančevo	9.56 (0.53)	***	Pančevo	155.01 (0.49)	ns
Smederevo	12.66 (0.25)	***	Smederevo	162.02 (3.08)	ns
Obrenovac	11.27 (0.31)	***	Obrenovac	175.35 (2.29)	***
Belgrade	11.67 (0.71)	***	Belgrade	148.85 (2.95)	***
Control site	6.49 (0.33)		Control site	158.33 (3.16)	
Chromium					
	1-year-old needles			2-year-old needles	
Pančevo	1.50 (0.11)	ns	Pančevo	2.02 (0.14)	ns
Smederevo	2.45 (0.21)	***	Smederevo	2.87 (0.17)	***
Obrenovac	0.89 (0.14)	ns	Obrenovac	2.22 (0.69)	*
Belgrade	2.37 (0.13)	***	Belgrade	2.77 (0.43)	***
Control site	1.19 (0.21)		Control site	1.53 (0.13)	
	bark			soil	
Pančevo	2.60 (0.24)	*	Pančevo	87.32 (15.52)	ns
Smederevo	7.57 (0.52)	***	Smederevo	126.01 (3.41)	***
Obrenovac	6.65 (0.42)	***	Obrenovac	93.33 (0.77)	*
Belgrade	5.59 (1.35)	***	Belgrade	72.08 (2.49)	ns
Control site	1.16 (0.11)		Control site	74.05 (11.68)	
Copper					
	1-year-old needles			2-year-old needles	
Pančevo	3.68 (0.16)	*	Pančevo	3.09 (0.12)	***
Smederevo	2.86 (0.37)	***	Smederevo	2.49 (0.14)	***
Obrenovac	2.08 (0.25)	***	Obrenovac	1.70 (0.18)	***
Belgrade	3.07 (0.13)	***	Belgrade	3.18 (0.14)	***
Control site	4.62 (0.41)		Control site	9.36 (0.96)	
	bark			soil	
Pančevo	4.79 (0.42)	***	Pančevo	20.87 (1.18)	***
Smederevo	5.74 (0.32)	***	Smederevo	64.13 (0.23)	***
Obrenovac	3.30 (0.20)	***	Obrenovac	20.93 (0.08)	***
Belgrade	4.63 (0.41)	***	Belgrade	19.55 (0.43)	***
Control site	10.48 (0.37)		Control site	36.98 (0.93)	
Manganese					
	1-year-old needles			2-year-old needles	
Pančevo	19.83 (0.76)	ns	Pančevo	25.13 (1.17)	***
Smederevo	22.50 (0.54)	ns	Smederevo	33.76 (1.48)	***
Obrenovac	14.63 (1.78)	***	Obrenovac	13.47 (1.08)	*
Belgrade	26.88 (1.12)	***	Belgrade	44.88 (2.93)	***
Control site	20.09 (0.53)		Control site	16.93 (1.44)	
	Bark			soil	
Pančevo	12.47 (0.23)	***	Pančevo	676.38 (4.79)	***
Smederevo	20.89 (0.69)	***	Smederevo	595.61 (9.57)	ns
Obrenovac	19.45 (0.41)	***	Obrenovac	691.87 (11.04)	***
Belgrade	9.31 (0.40)	***	Belgrade	523.94 (18.75)	***
Control site	4.02 (0.19)		Control site	593.11 (7.81)	
Zinc					
	1-year-old needles			2-year-old needles	
Pančevo	22.66 (1.51)	***	Pančevo	18.54 (1.30)	ns
Smederevo	28.95 (0.74)	**	Smederevo	21.78 (1.35)	**
Obrenovac	22.92 (0.47)	***	Obrenovac	20.40 (1.01)	ns
Belgrade	31.16 (1.66)	ns	Belgrade	36.86 (2.16)	***
Control site	32.52 (1.32)		Control site	18.13 (0.75)	
	bark			soil	
Pančevo	24.41 (1.59)	ns	Pančevo	54.73 (0.29)	***

Smederevo	35.24 (0.54)	***	Smederevo	151.26 (1.62)	***
Obrenovac	23.36 (0.74)	ns	Obrenovac	65.71 (0.36)	ns
Belgrade	28.42 (0.81)	***	Belgrade	72.41 (1.45)	***
Control site	25.57 (1.33)		Control site	65.99 (1.09)	

Values are mean with s.d. in parentheses, n=5, levels of significance: *p<0.05, **p<0.01, ***p<0.001, ns–not significant.

Reference values: Kabata-Pendias and Pendias 2001 (mg kg^{-1} d.w.):

Deficit for plant tissue: B 3-30; Cr /; Cu 2-5; Mn 10-30; Zn 10-20

Normal range for plant tissue: B 10-100; Cr 0.1-0.5; Cu 5-30; Mn 30-300; Zn 27-150

Toxic range for plant tissue: B 50-200; Cr 5-30; Cu 20-100; Mn 400-1000; Zn 100-400

3.6 Differences in metal content between sampling sites

Differences between the sampling sites in terms of the soil content of the selected metals, as well as their separation on the basis of factors, are given in Fig. 2.

Fig. 2 Multivariate factor analysis for selected elements in soil: a) loading plot, b) score plot

Principal component analysis (PCA) was carried out in order to identify possible similarities or differences in relation to the tested elements, as well as the factors that determine their origin. PCA applied to the element levels in soil resulted in a model with three principal components that explain 89.6 % of the total variance among the data. PC1 comprises 47.7 %, PC2 covers 21.3 %, while PC3 explains 20.6 %. There is an evident clustering when observing PC1 and PC2. The variables Cu, Zn and Cr have a positive impact on PC1. The corresponding graph reveals three groups of clusters comprising Smederevo, Obrenovac and the control site, which are clearly mutually separated, but are also separated from the fourth cluster, which includes Pančevo and Belgrade. Furthermore, it is evident that the high content of Cu, Cr and Zn in soil samples caused the segregation of Smederevo from all the other soil samples, while B, which has a negative impact on PC2, has a dominant role in Obrenovac, suggesting it has a different origin.

4. Discussion

4.1 Soil properties

Soil texture is a very important factor since a whole range of physical (structure, porosity, water-air, heat) and chemical (adsorption and buffering capacity) properties depend on it. Soils dominated by the sand fraction, such as those in Pančevo, Smederevo and Belgrade, are well aerated and have large water permeability. The process of soil formation with a high percentage of sand is very slow and these soils are commonly very poor in nutrients (Antić et al. 1982). Soils from Obrenovac and the control site contain a relatively uniform percentage of sand, clay and silt and generally have better characteristics, better drainage, and more nutrients and moisture than sandy soils. pH values in an aqueous solution showed that all the soil samples had an alkaline reaction. This occurrence is not unheard of in urban areas due to the process of deposition of alkaline dust of anthropogenic origin, which is usually a consequence of coal combustion. A positive effect of high alkalinity can be seen in the immobilization of potentially toxic, labile forms, which form durable complexes with organic matter in soil (Morel 1997; Parzych and Jonczak 2014).

Soil OC and soil N play a major role in pedogenic processes and contribute to soil fertility, which is why they are involved in many biogeochemical processes that have a key impact on soil-plant interactions (Saint-Laurent et al. 2014). Organic carbon in soil has dual origin. It can occur naturally as a product of plant and animal decomposition, or as a result of contamination through anthropogenic activities. In our study, the location of the parks largely influenced the content of OC and total N in the studied soils. The highest content of OC was observed in Pioneer Park, which is located near several major roads, and can be attributed to the inflow of anthropogenic carbon (Table 1). The content of OC in those mid-town parks located in smaller cities was significantly lower, which is in accordance with research by Bielińska et al. (2009, 2013). Nitrogen content in soil mainly results from the mineralization of organic matter and is based on the actual organic input, which is why soils with a higher percentage of organic matter have a higher content of nitrogen compounds (Brady and Weil 2008; Saint-Laurent et al. 2014). It is therefore reasonable to find the highest N content in Pioneer Park, where the highest OC input was also recorded. The C/N ratio is one of the most important parameters in monitoring the composting process and determining the degree of maturity of newly-formed organic materials (Iglesias Jimenez and Perez Garcia 1992), and it also shows variations in the assimilation efficiency of the microbial biomass. It is believed that a C/N ratio below 20 allows organic matter to decompose more quickly (4-8 weeks), while a ratio above 20 requires additional N and slows the process down (Esmaeilzadeh and Ahangar 2014). The results obtained for the urban soils tested showed a favourable and balanced C/N ratio.

4.2 Element concentration in topsoil

The high content of B in the examined soils when compared to the average content described for soils in Serbia (25-40 mg kg^{-1}, Aubert and Pinta 1977) may be the consequence of alkaline reaction of soil (Kabata-Pendias and Pendias 2001), as well as the low rainfall and drought conditions that marked the entire year of the study (2012), which results in the inability of B to be sufficiently leached, and eventually leads to its accumulation in topsoil (Camacho-Cristóbal et al. 2008). The results obtained for B can represent a threat to the environment, given the fact that all soil samples surpassed the maximum allowable concentrations (MAC<50 mg kg^{-1}) set by the National Regulations of the Republic of Serbia (RS) (Off. Gazette of the RS, No.23/94). The highest soil concentration of B in Obrenovac is to be expected since the sampling point is in the vicinity of the 'Nikola Tesla' thermal power plant. Boron originating from fly ash is highly mobile and is easily transported into the surrounding environment (Pavlović et al. 2004). This area is exposed to emissions of different types of pollutants from coal combustion processes as well as fly ash disposal, in the form of many toxic elements such as, Cd, Cr and Pb. This was also confirmed by the significant correlation between Cr and B (r=0.401*), indicating the likelihood of their being of similar origin.

Chromium in soil mainly originates from the lithosphere, i.e. parent rock and minerals that form the Earth's crust, which is why its natural content is mostly influenced by the parent matrix during the process of paedogenesis. However, the presence of chromate in soils is mainly a consequence of anthropogenic deposition (Cary 1982; Kimbrough et al. 1999). Chromium is widely used in various types of industry, such as plaiting and alloying, but also in the manufacture of steel and other alloys (Avudainayagam et al. 2003). The dumping of chromium-bearing liquids and solid waste as chromium by-products, ferrochromium slag or chromium-plating baths also greatly affects Cr content in the environment (Kimbrough et al. 1999). In this study, the urban sampling sites selected are close to factories and heavy industry which mostly use Cr in their manufacturing processes and is hence the probable cause for the elevated Cr concentrations in soil samples when compared to background values. This is particularly evident in Pančevo, where the calculated C_f was 1.83, and in Smederevo (C_f =1.82). These indices are indicative of moderate and minor human influence. However, the Cr content in all soil samples was within the MAC (<100 mg kg^{-1}), except in Smederevo where it was slightly above (Off. Gazette of the RS, No.23/94).

Concentrations of Cu in soil samples did not exceed background values at the selected sampling sites, except in the case of Smederevo (64.13 mg kg^{-1}) and the control site (36.98 mg kg^{-1}) (Tables 2 and 3). The results obtained do not constitute a threat to the environment since all the soil Cu concentrations were below the maximum allowable concentrations (MAC<100 mg kg^{-1}) set by the National Regulations of the Republic of Serbia (RS) (Off. Gazette of the RS, No.23/94). Research by Kabata-Pendias and Pendias (2001) showed that Cu has a tendency to accumulate in the top horizons of soil profiles, which can be linked to various factors, but predominantly to recent anthropogenic sources and activities. The higher Cu background values in Smederevo are likely to have a local character and probably originate from its heavy industry, presumably the steelworks, whereby a significant correlation was established between Cu and Cr (r=0.711**)

Manganese is one of the most abundant trace elements in the lithosphere and varies in wide range. All the results obtained for Mn in the urban samples exceeded the global average value of 437 mg kg^{-1} for soils (Kabata-Pendias and Pendias 2001). Anthropogenic sources of Mn include mining, smelting, engineering, traffic, and agriculture. Manufacturing processes in the production of steel, glass, dry batteries and chemicals are also known to increase Mn content (World Health Organization 2004). Given the nature of the industry in Obrenovac (the thermoelectric power plant) and Pančevo (chemical manufacturing, the oil refinery, etc.), the high concentrations of Mn (691.87 mg kg^{-1} and 676.38 mg kg^{-1}) in the examined topsoil are to be expected.

The zinc content in soil was within acceptable limits for municipal areas and well below the MAC (<300 mg kg^{-1}) set by the National Regulations of the RS (Off. Gazette of the RS, No.23/94). The largest quantities of Zn were found at those sampling sites located in the vicinity of busy roads, such as in Smederevo and Belgrade. Similarly, a study by Parzych and Jonczak (2014) showed that the highest Zn accumulation occurred at the surface, at a depth of 0-20 cm, while the findings of Ottesen et al. (1999) suggest that this could be a consequence of traffic and the abrasion of car tyres and the possible impact of concrete surfaces, given the fact that zinc and its compounds are used as hardeners in cement and concrete (Adriano 2001). However, the Zn concentrations in Smederevo (151.26 mg kg^{-1}), which were more than twice as high, are most probably the result of iron smelter by-products, which is supported by the significant correlation between Zn-Cr (r=0.802**) and Zn-Cu (r=0.918**).

4.3 Indices of soil pollution

Due to the fact that the C_f for B was worked out on the basis of the upper average values, which is a limitation of the calculation, the results for B in soil samples indicating considerable contamination may not be reliable. In this study, all the sampling sites exhibited a moderate C_f for Cr. A moderate C_f was also calculated in Smederevo and at the control site for Cu, in Belgrade and at the control site for Mn, and in Smederevo and Belgrade for Zn. There was a low C_f for the selected elements at all the other sampling sites. The estimated values of C_f for the trace elements tested generally indicate low or moderate soil contamination. Selecting a control site for any studies in urban areas represents a serious challenge due to the fact that many parameters can affect environmental conditions. Due to the transportation of air pollutants, even large green areas on the city periphery can be unreliable as control sites, which proved to be the case with this research.

An assessment of the overall contamination of soil (C_{deg}) by the tested elements revealed a low degree of contamination ($C_{deg} \leq 8$) at all the sampling sites except Smederevo, which was on the border between the categories of a low and a considerable degree of contamination. Based on the results obtained for the sampled soils in terms of the C_f and C_{deg} indices, it can be concluded that the selected soils are not seriously contaminated by heavy metals.

4.4 Element concentrations in needles of *Pinus nigra*

Boron is relatively strongly sorbed by both inorganic and organic soil components and increases with soil pH (Goldberg et al. 2000). The pH is a guiding factor for the mobility and phytoavailability of B in soil where it is considered to be the most mobile element among the micronutrients, although its water-soluble fractions is relatively low and varies from about 3 to 5% of the total content (Kabata-Pendias and Kabata 2001). Its industrial sources include: mining operations, glass and ceramics industries, chemicals production, and coal fired power plants. It may occur in forms of aerosols or in particulate (<1–45 µm in size). Boron is unique among the essential plant nutrients in the sense that it has restricted mobility in many plant species, but is also freely mobile in others i.e there is a small window between deficiency and toxicity (Brown and Shelp 1997; Reid et al. 2004). Boron uptake by higher plants is highly dependent on its content as well as pH in nutrient solution, form of B, as well as transpiration rate of the plants, and is under control of membrane permeability and internal complex formation (Marschner 1995; Goldberg et al. 2000; Kabata-Pendias and Pendias 2001). Considerable genetic variation in response to high B has been identified in a wide range of plant species (Nable et al. 1997). Plant tolerance to B differs widely among plant species (Ferreya et al. 1997) and even between cultivars of the same species (Nable 1988; Marschner 1995). Therefore, Kabata-Pendias and Kabata (2001) stated that, depending on the plant species, normal B content varies between 10 and 100 mg kg^{-1}, but that toxicity symptoms can also occur between 50 and 200 mg kg^{-1}, so additional analyses are needed to establish whether the B content in 2-year-old needles from Smederevo and Belgrade is toxic. The higher B content in 2-year-old needles when compared to 1-year-old needles is a consequence of its translocation via xylem, which affects the higher accumulation in older leaves (Kabata-Pendias and Pendias 2001).

Given the fact that Cr is a toxic and nonessential element, plants do not possess any specific mechanism for its uptake, which is why it can assume the role of an essential element. The mechanism of absorption and translocation of Cr in the plant is similar to the mechanism of Fe absorption, which is why it can have serious consequences for plant metabolism (Kabata-Pendias and Pendias 2001; Shanker et al. 2005).The origin of Cr is mainly anthropogenic since it has heterogeneous industrial use, but also results from vehicular engine and body erosion (Al-Shayeb et al. 1995). Compared to research by Rossini Oliva and Mingorance (2006) and Sawidis et al. (2011), the results we obtained for Cr content in pine needles are considerably higher, although not in the toxic range. A significant correlation was found between Cr in soil and in 2-year-old needles (r=0.415*), probably due to prolonged accumulation in needle tissue.

Copper content varies significantly, depending on the plant part, the development stage, and the species (Parzych and Jonczak 2013). The deficiency of Cu in both pine needle samples, despite its sufficient levels in soil, can be accounted for in several ways. Primarily, root tissues clearly possess a great ability to prevent the transport of Cu to shoots and this is combined with Cu's low mobility in relation to other elements in plants (Kabata-Pendias and Pendias 2001). Moreover, the binding of Cu by soils is related to the formation of organic complexes and is highly dependent on soil pH. Furthermore, the overall solubility of both cationic and anionic forms decreases at about pH 7 to 8 (Kabata-Pendias and Pendias 2001).

It was found that 2-year-old needles accumulate more Mn than 1-year-old needles with 1-year-old needle samples containing insufficient amounts of Mn for optimal plant development. The amount of Mn available to plants is influenced by various soil parameters, predominantly pH, organic matter content, water content, and redox potential (Kabata-Pendias and Pendias 2001; Schmidt et al. 2016), but also by the soluble Mn pool in the soil. This is why plants grown on calcareous soils with elevated pH and on sandy soils with high porosity are prone to Mn deficiency, owing to the conditions that favour the oxidization of Mn to unavailable Mn oxides (Husted et al. 2005; Schmidt et al. 2016). Furthermore, the low phloem mobility of Mn prevents its remobilization from older to younger leaves (Loneragan 1988; Schmidt et al. 2016), which is linked to the deficit and lower content in 1-year-old needles, where, due to the existing soil conditions, a strong negative correlation between both needle types is found (r=-873** for 1-year-old needles and r=-750** for 2-year-old needles).

Our study revealed that only 1-year-old needles from Smederevo, Belgrade and the control site contained a sufficient amount of Zn to cover the physiological needs of plants. Since Zn represents an essential microelement (Mattiello et al. 2015), the part that a plant absorbs from soil is used for basic physiological processes, which can result in its lower content in 2-year-old needles. Only the 2-year-old needle samples from Belgrade contained a sufficient amount of Zn for optimal plant development, which is quite likely a consequence of traffic, not absorption from soil. The mobility of Zn highly depends on the soil content of clay and organic matter, which are capable of detaining Zn. It is also known that when plants grow in Zn-rich soils, roots often contain more Zn than plant tops (Kabata-Pendias and Pendias 2001). Furthermore, research by Marschner (1993) showed that in alkaline soils, the content of Zn in solution is very low due to the increased adsorptive capacity and it has limited mobility and transfer potential. All of these reasons are the most probable main causes of the Zn deficit in pine needles, despite its sufficient levels in soil.

4.5 Element concentrations in the bark of *Pinus nigra*

Elements in bark may originate from different sources, such as atmospheric deposition (wet and dry), soil, and through precipitation, but mainly from the atmosphere (El-Hasan et al. 2002). Many different factors have an effect on elements collecting on bark surface, such as heavy metal quantities in the air, physiological and chemical properties of the bark, precipitation, soil factors, climatic factors, and anthropogenic factors (Rykowska and Wasiak 2009).

Boron content in the bark of *Pinus nigra* was several times lower than in needles. The results of this study showed that there is a difference in the accumulation ability for B between bark and needles depending on the sampling site. Several studies displayed a similar pattern for B behaviour between leaves/bark, where B content in bark was significantly lower than in leaves (Reimann et al. 2007; Pavlović et al. 2017a: Pavlović et al. 2017b). Somewhat lower B concentrations (4.5 mg kg^{-1}) were found in the bark of pine trees in Ukraine (Dolobovskaya 1975). Chromium content in bark was slightly higher than in needles. Concentrations of Cr in bark samples of *P. nigra* from Salzburg, Belgrade and Thessaloniki obtained in a study by Sawidis et al. (2011) were mostly lower than the values found in this research. A significant correlation between Cr in soil and bark (0.563**) was found, which could explain the existence of notable differences between the sampling sites. Copper content in bark was relatively evenly distributed between the sampling sites. Bark contained slightly higher Cu concentrations than needles. Parzych et al. (2017) monitored elemental concentrations in the bark of several pine species, where they demonstrated that the accumulation of elements directly depends on the structure and porosity of bark. The Cu content in bark samples of *P. nigra* and *P. mugo* in their research varied from 6.9 mg kg^{-1} to 10.1 mg kg^{-1}, which coincides with the results from our study. However, Cu content in bark samples of *P. nigra* sampled in urban areas from the study by Sawidis et al. (2011) showed significantly higher values (18.35 mg kg^{-1} in Salzburg – 37.90 mg kg^{-1} in Belgrade) in relation to this research. Kosiorek at al. (2016) analyzed the tissue of three woody species (*Pinus sylvestris, Betula pendula* and *Acer platanoides*) and showed that Cu and Cr is better accumulated in bark, while leaves better accumulate Mn and Zn. A positive correlation between copper in soil and copper in bark samples (r=0.363*) was found. Manganese content in bark was slightly lower than in needles. Research by Kosiorek et al. (2016) for *Pinus sylvestris* (4.75 mg kg^{-1}- 6.50 mg kg^{-1}) and Parzych et al. (2017) for *Pinus nigra* (13. 0 mg kg^{-1}) showed similar results for the Mn content in pine tree bark. All the obtained values revealed a shortage of this essential element in plant tissue. Zinc content in bark varied in a narrow range and was relatively evenly distributed between sampling sites. However, a very strong correlation between Zn in soil samples and Zn content in bark samples was obtained (0.893**). The results obtained from this research showed sustainably lower quantities of Zn in bark compared to research by Parzych et al. (2017) (76.0 mg kg^{-1}) for *Pinus nigra*, but also a significantly higher Zn content in relation to the research by Kosiorek at al. (2016) (0.44 mg kg^{-1}-6.22 mg kg^{-1}).

Metal species deposited in the outer bark are physically separated from trace elements taken up by the inner bark, which originate from xylem or soluble metal ions (Kuang 2007). The metal concentrations in different plant parts are dependent on the amount of metals both in the air and soil, and are different within and between plant species (Satpathy and Reddy 2013).

4.6 Differences in metal content between the sampling sites

The close correlation between the pairs of metals Cr-Zn and Cu-Zn in soil samples indicates that they probably have the same origin. This is further explained by PCA, wherein, on the basis of the first factor, separation of Cr, Cu and Zn occurred. The score plot unequivocally confirmed the clear separation of Smederevo from all the other sampling sites, which supports the idea that these three elements are quite likely the result of anthropogenic pollution, i.e. are of industrial origin. PCA analysis undoubtedly indicates the different origin of B, which is associated with its content in Obrenovac, where it is probably influenced in part by the thermal power plant. The correspondence of manganese with the control site suggests it is of geological origin. However, the correlation coefficient between the total content of Mn and B in soil samples (r=0.671**) indicates their common origin and similar behaviour in such soil conditions.

5. Conclusions

An analysis of urban topsoil, supported by indices of soil pollution, has shown that there is no significant soil contamination originating from industrial sources or traffic. Although some metal concentrations exceeded the background values at the selected sampling sites, they remained within the acceptable limits for municipal areas. Sources of trace element pollution were assessed through PCA, which classified elements into two main groups according to their sources: geological origin and anthropogenic pollution.

Element content in plant material, both 1-year and 2-year-old needles, also indicates low pollution. Along with existing urban environmental conditions, the results obtained for essential elements often revealed a deficit in both types of pine needles, further contributing to stress factors.

It is indicative that the highest accumulation of trace elements was found at those sites with heavy industry and heavy traffic, such as Smederevo and Belgrade, which were the two most polluted sites according to the results obtained in this study. However, although results obtained in this study suggest low contamination from anthropogenic sources of pollution, it does not necessarily mean that contamination is not present. Namely, industrial pollution causes the alkalization of soils in the parks of the examined cities in Serbia, which leads to the immobilization of metal pollutants in soil, making them unavailable for plants at pH>8. Furthermore, due to extreme drought and low precipitation, as well as soil alkalization, the absorption of trace elements by *Pinus nigra* needles is limited. Special attention should be paid to possible threats to humans and the environment that are the consequence of atmospheric particulate pollution emitted from traffic and industry.

Conflict of Interest: The authors declare that they have no conflict of interest.

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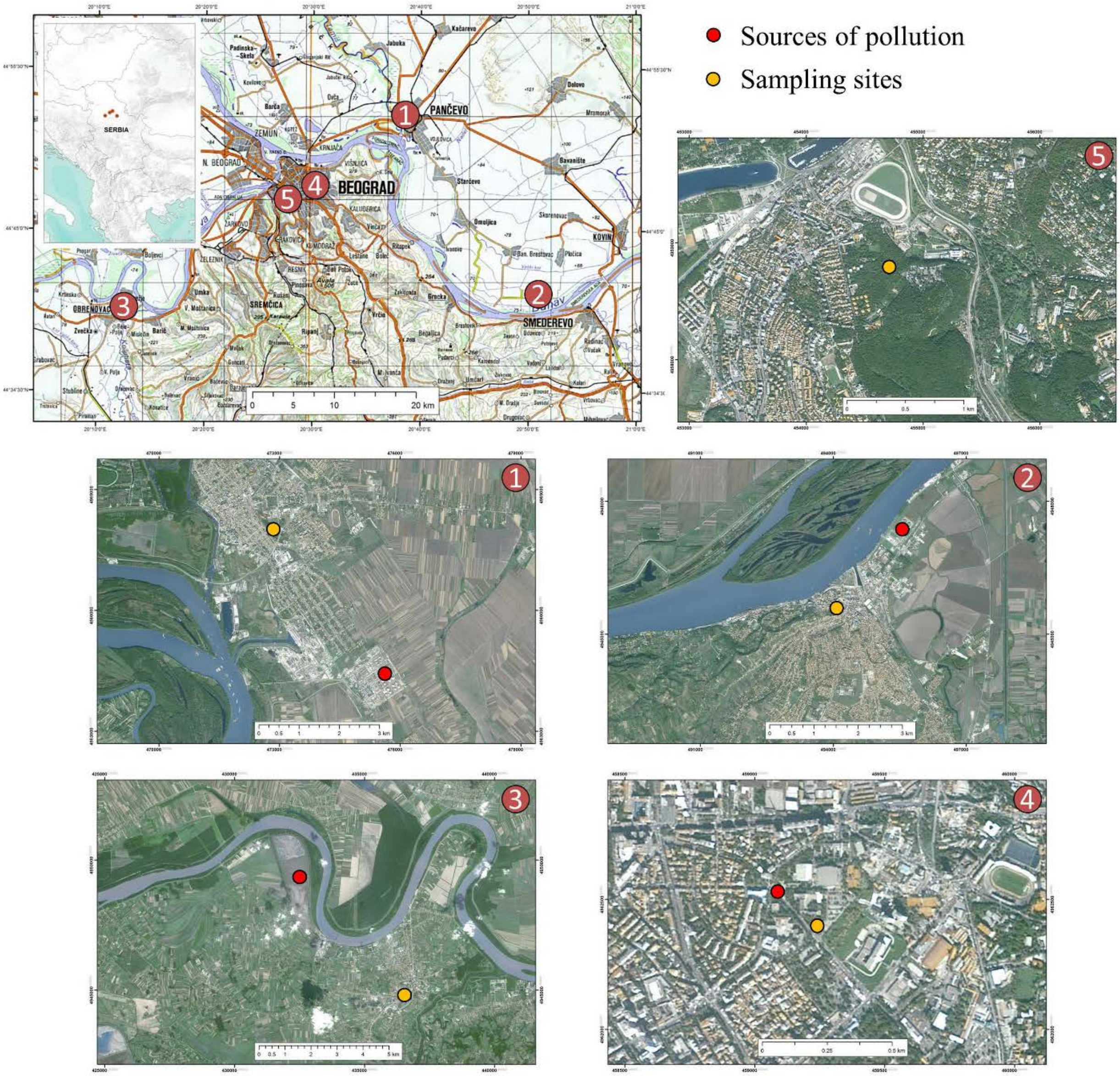

Fig. 1

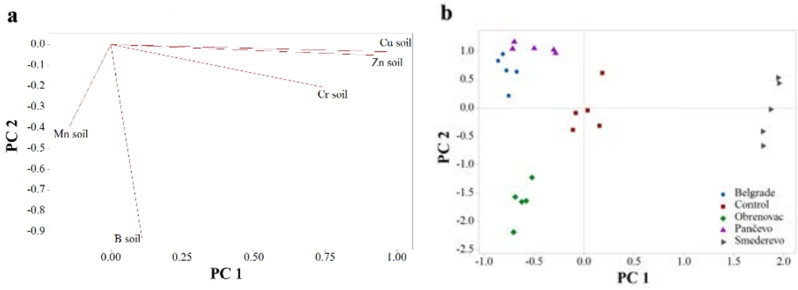

Fig 2a 2b