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Article

Using Fractionation Profile of Potentially Toxic Elements in Soils to Investigate Their Accumulation in *Tilia* sp. Leaves in Urban Areas with Different Pollution Levels

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Abstract: Optimal uptake of micronutrients (B, Cu, Fe, Mn, and Zn) and managing the potentially toxic elements (PTEs) (Co, Cr, Ni, Pb, and Sr) in the ranges not detrimental to plant function may be linked to improving plants' healthy growth and the ability to provide ecosystem services. We investigated concentrations, mobility, and potential availability of potentially toxic elements (PTEs) in soil samples from polluted and non-polluted municipal parks in Reading (UK) and Belgrade (Serbia) and their impact on elemental concentrations in *Tilia* leaves. We aimed to identify common limiting factors potentially affecting the growth/healthy function of this widely-used tree species. Levels of all elements in soil were below limits established by the directive of European Communities, except for Ni at Belgrade sites. Content of Co, Cr, Cu, Fe, Ni, Pb, and Zn in soluble fraction at all locations was <10%, indicating low mobility; B showed moderate mobility (11.1–20.7%), Mn (6.5–55.6%), and Sr—high (44–76.3%). Principal Component Analysis of *Tilia* leaf tissues showed a different capacity for uptake/accumulation of PTEs in different locations. Findings indicate the complexity of local edaphic influences on plants' elemental uptake and the risk of those leading to deficiency of important micronutrients, which may impede trees' function and thus the ability to optimally provide ecosystem services.

Keywords: lime trees; potentially toxic elements (PTEs); optimized BCR sequential procedure; PTEs fractionation profile; urban parks; urban soils



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1. Introduction

Urban areas are experiencing rapid population growth worldwide, with >80% of Europeans expected to live in urban areas by 2030 and 68% globally by 2050 [1,2]. This, coupled with negative environmental impacts of anthropogenic activities in urban areas (industrial activity, traffic, and energy use), causes densely populated urban areas in Europe to face environmental health challenges, including air pollution and contamination of water and soils. Pollution in urban soils has been recognized as one of the major concerns at local, regional, and global levels due to the impacts of the soil contaminants on human health as well as their disruption to the geochemical cycling of the urban ecosystems [3,4]. Contamination by the potentially toxic elements (PTEs) also causes environmental issues related to the toxicity, abundance, persistence, and bio-accumulative character of these compounds [5,6].

Cities are becoming regional sinks for resource consumption and sources of chemical emissions which results in elevated concentrations of PTEs but also the deficiency of certain essential elements due to the changed balance of the biochemical and geochemical cycles

of chemical elements in urban soils [7,8]. Particularly, urban soil plays a role of a scavenger agent and adsorption sink for PTEs because once introduced in the urban environment; they persist in soils over long periods [9–12]. Additionally, soils in urban areas often have a changed structure, physical and chemical characteristics, and low concentrations of essential elements [13]. PTEs in urban soils originate from multiple sources, lithogenic (i.e., natural) and anthropogenic [7,14]. They tend to accumulate at, or close to, the soil surface, and their mobility and bioavailability are dependent on their nature as well as on the physical and chemical properties of the soil. Therefore the determination of total concentrations can over- or under-estimate the risk to the urban environment, including its impact on the urban vegetation [15–18]. The analysis of bioavailable fractions provides a more realistic estimate of the pollutants' potential impact on urban vegetation. One of the main sequential extraction methods is the Bureau Community of Reference (BCR) protocol, which entails four fractions [12,19]. However, from an environmental and ecological point of view, the most important fractions of PTEs are the mobile ones, as they are easily adsorbed and can be readily released if the environmental conditions are suitable (e.g., pH or redox potential) [20]. Therefore, analysis of urban soils is important since the chemical composition of soil reflects both the soil lithogenic and the anthropogenic inputs of pollutants from industrial facilities and traffic. So far, most research has focused on the influence of the labile fraction of heavy metals in soil on bioavailability [8,17,21–23], with only a small number of studies discussing the effects of the fractionation of PTEs in soils (especially acid-soluble, oxide-bound, organic matter-bound fractions) as a factor of the bioaccumulation of elements by plants in urban sites. It is recognized that the labile fraction determined by sequential extraction can enter plants easily; thus, the ecological effect of potentially toxic elements is closely related to mobility and speciation of these chemical elements [8,24–26]. The most easily exchangeable fraction for each element associated with soil poses the highest risk because it may accumulate in plants in toxic concentrations. Distribution and geochemical speciation of PTEs in soil could help predict the transfer of PTEs from soil to plants and to assess the risks associated with the accumulation of these elements in plants; therefore, the bioavailable concentrations rather than the total concentrations should be used [22,27]. The fractionation of chemical elements in soils as a factor of the bioaccumulation of elements by plants has recently attracted the attention of researchers by using BCR sequential extraction procedure for the study of metal availability to plants [28,29].

Vegetation in urban environments, including trees, provides multiple ecosystem services—not least localized cooling, storm water mitigation, noise abatement, and impacts air quality [30,31]. However, this is dependent on plants remaining healthy, physiologically active, and growing to their full capacity. In terms of air quality improvement by vegetation, much research focused on leaf and canopy traits that can be linked to efficient removal of particulate pollution [32,33] but also green infrastructure forms, which are most efficient in urban context [34]. More linear types of vegetation (green facades, hedges) have been suggested as preferential in narrow street canyons, but urban trees still remain important positive environmental contributors in parks and public open spaces where the creation of a canyon effect (and consequent trapping of pollutants) is unlikely to happen [35]. The extent of the role of vegetation in the reduction and removal of airborne particulate matter is debated, with recent studies suggesting that the key measures for pollutant reduction should include reduction of sources, with vegetation viewed as a smaller contributor [36]. However, even when canopy sequestration of airborne pollutants is relatively small—vegetative surfaces do attract particulates (including heavy metals and other PTEs) and transfer these compounds into litter and soil (e.g., by rainfall) [37]. This poses the question of how those compounds are redistributed and mobilized in the soil. Plants in urban ecosystems can reflect the PTEs' pollution both in soil and atmosphere, enabling the biomonitoring of pollution over long periods to quantify pollution parameters and identify the spatial and temporal distribution patterns of the pollutants [37–39]. In the case of trees, the PTEs uptake takes place in the leaves and roots and is controlled by the species

characteristics, the concentration of metal, as well as the solubility and bioavailability of the metals [40,41]. Therefore, the use of PTEs as indicators of soil pollution in polluted habitats is widespread due to the visible and measurable effects they have on plants [42]. The species of *Tilia* genus have been often used as biomonitors of trace elements in urban and industrial environments and for large-scale surveys [37,43–45]. Within the present study, we aimed to investigate concentrations, mobility, and the potential availability of a range of PTEs in soil samples from polluted and non-polluted municipal parks in Reading (UK) and Belgrade (Serbia) within and between the cities. Lime trees were selected as the target species since they were available in all investigated sites. The lime tree (*Tilia* sp.) is a popular tree for landscaping and urban environments in central and northwest European countries [46]. Soil samples were analyzed by using a sequential extracting procedure, thus allowing us to differentiate and characterize bioavailable fractions of PTEs and permitting us to evaluate their potential toxic effects on urban vegetation, especially long-living plants such as lime trees. Investigated soils belong to the same type of urban soils, which differ greatly from natural ones, given the fact that they are located in areas of intense human activity, which results in changes in the original physical, biological, and chemical properties of the soil [47]. Intensive soil management in cities worldwide often create man-made soil, sometimes with the soil of unknown origin; therefore, these urban soils are considered technogenic soils (Technosols, WRB), [48,49] in those cases where the human impact on their structure is greater than that of natural processes, particularly in topsoil layers (0–10 cm) [50–53].

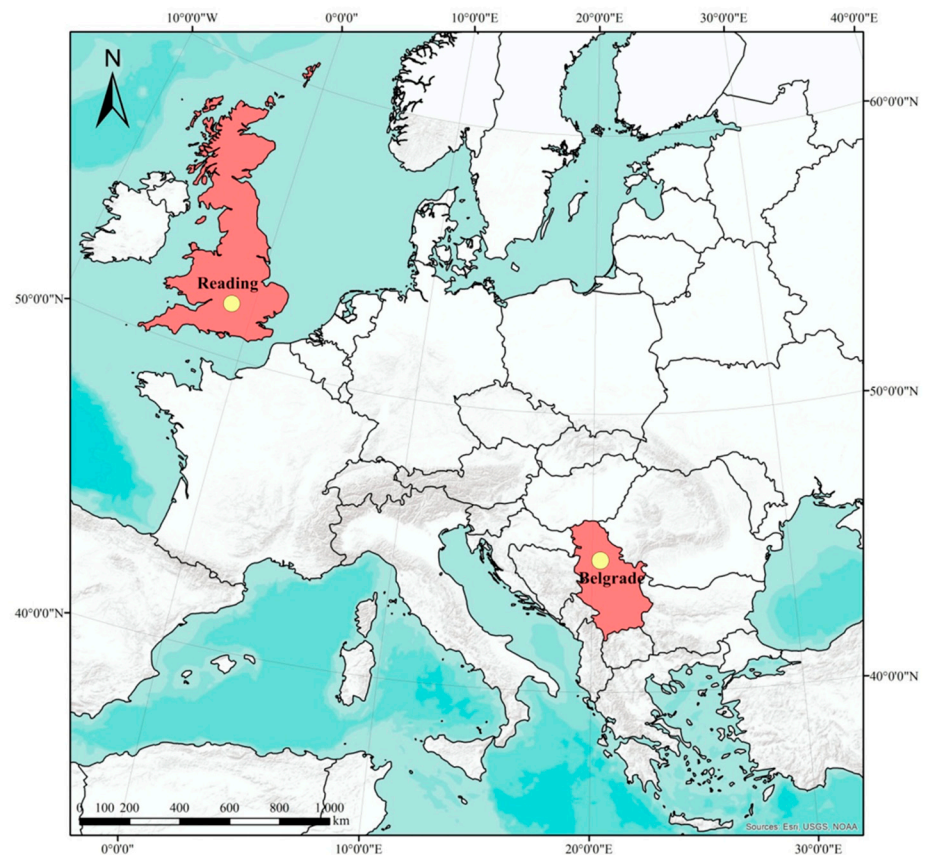
The fractionation of chemical elements in soils as a factor of the bioaccumulation of elements by plants has recently attracted the attention of researchers by using BCR sequential extraction procedure for the study of metal availability to plants [28,29]. In this regard, the presented research is the result of scientific collaboration showcasing two case studies from different cities aiming to promote BCR sequential extraction procedure for the study of PTEs availability to urban trees as a valuable approach in urban environmental pollution research and application.

2. Materials and Methods

2.1. Study Areas

Samples' collection was carried out in two European cities: Belgrade (Serbia) and Reading (United Kingdom) (Figure 1). In each city, two sampling sites were selected: municipal parks in the city centers under the influence of direct sources of traffic pollution (polluted) and municipal parks away from direct sources of pollution (unpolluted).

In Belgrade, Bristol Park (Belgrade polluted site-BP) (1.2 ha) was chosen as the polluted site because it is located in close vicinity to several major traffic roads, including two bus stations for national and international traffic as well as a railway station (data provided by City of Belgrade-City Secretariat for public transport), all under high traffic intensity, with 30,692 vehicles passing by per day, and 2140–2368 vehicles during rush hour. Arboretum Park (Belgrade unpolluted site-BU) of Faculty of Forestry (6.7 ha) is a protected natural area and important archive of native and non-native tree species [54], situated within the zone of mixed *Quercuetum frainetto cerris* Rudski. This forest park was selected as the unpolluted site due to the large distance from direct sources of pollution and from the city center. In Reading, for the polluted site (Reading polluted site-RP), a tree-lined street perimeter around the University of Reading (Pepper Lane entrance) in an area around the University's campus with high to moderate traffic intensity during the work hours (3000 vehicles per hour) was selected. The sampling area of the Reading polluted site was approximately 0.5 ha. The botanical garden of the University of Reading (Reading Park—Harris Garden, Reading unpolluted site-RU), which is located 3 km away from the town, was selected as an unpolluted site. The garden is an area of 4.9 ha, and includes several ponds and streams, meadows and gardens of different purposes, as well as woodland.



	Sampling site	GPS coordinates	Sources of pollution
Belgrade	Bristol Park (Belgrade polluted site-BP)	44°48'42" N 20°27'12" E	Traffic
	Arboretum Park (Belgrade unpolluted site-BU)	44°46'59" N 20°25'31" E	Without direct source of pollution
Reading	Reading Street (Reading polluted site-RP)	51°26'21" N 0°57'00" E	Traffic
	Harris Garden (Reading unpolluted site-RU)	51°26'19" N 0°56'19" E	Without direct source of pollution

Figure 1. Details of the study areas in Belgrade and Reading.

2.2. Sample Collection

At each of the four sampling sites, three sampling locations for plant material of *Tilia* sp. and associated soil sampling were selected (Belgrade polluted site-BP: BP-1, BP-2, and BP-3; Belgrade unpolluted site-BU: BU-1, BU-2, and BU-3; Reading polluted site-RP: RP-1, RP-2, and RP-3; Reading unpolluted site-RU: RU-1, RU-2, and RU-3). The sampling methodology was compatible with the methodology of empirical sciences, and when selecting the sampling sites, special care was taken to ensure that they were all approximately equidistant from the main sources of pollution and that the same baseline conditions applied to each of them. From each location, leaf samples of *Tilia* sp. were collected from five randomly chosen trees (50 g per tree) of the same age (20–30 years old) and at 1.5 m height from four quarters of the tree crowns. Soil sampling was carried out at the five points in the root zone of each tree (250 g under each tree), from a depth of 0–10 cm, with stainless-steel tools. Small stones, plants, and other foreign objects from soil samples were removed by hand. Leaf samples from *Tilia* sp. tree and their associated soil from each sampling location were then mixed, resulting in one composite sample of *Tilia* sp. leaves

and corresponding soil per sampling location [10,55–57]. Samples were collected in June 2017. In the laboratory, each representative plant and soil sample was air-dried at room temperature to constant mass, ground in a laboratory mill, and sieved through a 2 mm nylon sieve. The prepared samples were then used for analysis.

2.3. Soil and Plant Analysis

In the laboratory, the soil samples were air-dried and passed through a 0.25 mm stainless sieve, including blank sieving, prior to chemical analysis. Electrical conductivity (EC, dS m^{-1}) and pH in a 1:5 soil/water ratio was measured in composite soil samples representative of the areas being sampled [58]. For PTEs analysis, all the subsamples were homogenized to make composite samples. Soil samples (0.5 g) and plant samples (0.3 g) were air-dried prior to mineralization and transferred into Teflon (iPrep) vessels. Soil mineralization was conducted through wet digestion, using USEPA 3050B method [59], with plant samples digested using USEPA 3052 method [60] in the microwave oven. The final extracts were filtered and transferred into 50 mL volumetric flasks and then diluted to the mark with deionized water. To assess the mobility and availability of PTEs (B, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn) in soil, sequential extraction was performed using the optimized BCR procedure involving four steps [19,61]. The first step determined a fraction of metals that were exchangeable or associated with carbonates (acid-soluble/exchangeable fraction); the second was the fraction of metals associated with oxides of Fe and Mn (reducible fraction), the third was the fraction of metals associated with organic matter and sulfides (oxidizable fraction), and the fourth was the residual fraction or fraction of metals that strongly associated with the crystalline structure of minerals (residual fraction). The pseudo-total metal concentrations in soil samples were calculated as the sum of the metal concentrations in all four fractions.

2.4. Chemicals

All reagents used for plant digestion, as well as for BCR sequential extraction, were of analytical grade (Merck, Darmstadt, Germany). ICP-multi-element standard stock solutions (concentration of elements, 1000 mg L^{-1} in diluted nitric acid) used to prepare standard solutions for ICP-OES analysis were also obtained from Merck.

2.5. Instrumentation

A Chyo JK-200 analytical balance (Japan) was used for all weighing and a laboratory mill Cullatti Typ MFC (Kinematica AG, Switzerland) for samples' homogenization. An inoLab[®] 7110 pH meter (WTW, Germany) and Knick (Germany) Portamess 911 Conductometer were used to measure pH and electrical conductivity (EC). CEM MARS 6 Microwave Acceleration Reaction System (Matthews, NC, USA) was used for the digestion of plant samples. An end-over-end mechanical shaker and a centrifuge Sigma 2–16 KL (Sigma, UK) were used for extraction and separation of extractants from residues in the sequential extraction procedure. Concentrations of PTEs in plant and soil samples were determined by inductively coupled plasma optic emission spectrometry (ICP-OES, Spectro Genesis, Spectro-Analytical Instruments GmbH, Kleve, Germany).

2.6. Quality Control

Quality control and quality assurance of the analytical data was performed by using the standard reference material for leaves—Beech leaves—BCR—100, and certified reference material for soil—BCR-701 (Institute for Reference Materials and Measurements—IRMM, Geel, Belgium), as well as by analysis of both reagent blanks and replicates. The recovery values were within 95.0%–110.0% for leaves and within 84.1%–107.2% for soil, demonstrating a good agreement between the measured and certified values. The relative standard deviations of triplicate measurements were <10%. The detection limits for the analyzed elements in the soil samples were as follows (mg kg^{-1}): B-0.0003, Co-0.0006, Cr-0.0011, Cu-0.0007, Fe-0.0081, Mn-0.0006, Ni-0.0003, Pb-0.0042, Sr-0.0001, and Zn-0.0061.

2.7. Determination of the Mobility Factor (MF) and Bioaccumulation Factor (BAC)

In this study, the PTEs mobility (MF) has been calculated using Equation (1), as proposed by Kabala and Singh [62]:

$$MF = \frac{F1}{\sum F} \times 100 \quad (1)$$

where $F1$ is the concentration of a PTE extracted in the acid-soluble/exchangeable fractions, and $\sum F$ represents the sum of that PTEs concentration in all the fractions.

Bioaccumulation factor (BAC) as index of the ability of the plant to accumulate a particular element with respect to its concentration in the soil substrate was calculated as follows:

$$BAC = C_{leaf} / C_{soil} \quad (2)$$

where C_{leaf} —leaf PTE concentration (mg kg^{-1} , DW); C_{soil} —soil PTE concentration (mg kg^{-1} , DW), with $BAC > 1$ suggesting that a plant is a PTE accumulator.

2.8. Statistical Analysis

One-way analysis of variance (ANOVA) was performed to test the differences in PTEs accumulation in soil samples and *Tilia* sp. leaves, both from polluted and unpolluted sites (subsequent tests of normality by the Shapiro-Wilk W test and Levene's test of homogeneity of variances showed non-significant values for all the reported ANOVA breakdowns), and means were separated with Bonferroni test. Principal component analysis (PCA) was performed to detect differences between analyzed sites and *Tilia* sp. trees that grow at these sites based on the variations in the concentration of PTE in soil and leaves, as well as to establish the possible sources of toxic elements in the soil. This analysis included data on the concentration of all examined elements, and only main components with Eigen values > 1.0 were considered. To test the correlation between the variables, Varimax rotation with Kaiser's normalization was carried out. Correlation analysis was used to establish the inter-elemental relationship between soil and leaf samples. All statistical analyses were performed using the SPSS software package, Version 21, and program package Statistica [63].

3. Results and Discussion

3.1. Soil Properties

Soils have many ecological functions, including carbon absorption, water retention, and as an environment for microorganism growth. However, urban soils are routinely degraded, resulting in a negative impact on plants. Common issues associated with urban soils include compaction, water shortages (e.g., due to surface runoff), increased soil temperature, salinity, pollution, increased pH, and also the deficiency of organic matter and essential elements deficiency, depriving the service function of soil [64]. Soil pH has a great influence on soil chemical processes which determine the behavior of pollutants because the solubility of some elements tends to increase at lower pH and decrease at higher pH values [21,24,26,65,66]. Earlier work, including our own, showed reduced solubility of some PTEs in alkaline urban soils [8,10,67,68]. In this study, differences in pH and EC between sampling sites were evident; pH values in Belgrade ranged from 7.6 at BP-1 to 7.9 at BU-3, which classifies these soils as slightly alkaline (pH 7.4–7.8), while in Reading, it varied from 6.1 at RU-3 to 7.1 at RU-1, which classifies these soils as slightly acidic to neutral (pH 6.1–7.3, Table 1 and Table S1 provided in Supplementary Material) [69]. The concentration of total soluble salts (measured by EC) in the examined soils ranged from 0.111 at BP-2 to 0.246 dS m^{-1} at AP-2 in Belgrade City, while higher values were measured in Reading urban sites, in the range of 0.226 to 0.605 dS m^{-1} (at RU-2, RP-3, respectively, Table 1 and Table S1). These results indicate that the content of soluble salts in examined soils should not have a negative impact on the plants' growth due to EC values of $< 4 \text{ dS m}^{-1}$ [69,70]. Possible reasons for the $\text{pH} > 7$ in the examined soils include, in

particular, the release of alkaline leachates from calcareous materials and decomposing organic waste [71]. In addition, alkaline conditions in the soil, particularly in Belgrade, may be linked with widespread practice to add construction waste materials into soils during construction of urban parks, e.g., calcium carbonate or calcium-magnesium carbonate in gravel, tiles, cement, concrete, mortar, etc., or to the atmospheric deposition of alkaline material from industry such as coal combustion and waste incineration [8,72,73] while in terms of EC, it could be related to using of NaCl and CaCl₂ for de-icing in winter, as well as Ca-rich irrigation water during dry and hot summers which can also result in an increase of pH [74].

Table 1. Mean values and standard deviation in parenthesis of pH reaction and electrical conductivity (EC) in studied urban soils (i.e., polluted and unpolluted sites in Belgrade and Reading). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites.

	BP-1	BP-2	BP-3	BU-1	BU-2	BU-3	RP-1	RP-2	RP-3	RU-1	RU-2	RU-3
pH	7.6 (0.2)	7.7 (0.1)	7.6 (0.1)	7.8 (0.0)	7.8 (0.1)	7.8 (0.2)	7.1 (0.2)	6.8 (0.4)	6.8 (0.1)	6.5 (0.3)	6.30 (0.4)	6.1 (0.5)
average		7.6 (0.1) a			7.8 (0.1) a			6.9 (0.3) b			6.3 (0.4) c	
EC	0.186 (0.015)	0.111 (0.009)	0.208 (0.02)	0.168 (0.00)	0.246 (0.03)	0.183 (0.02)	0.579 (0.041)	0.541 (0.032)	0.605 (0.045)	0.265 (0.02)	0.226 (0.01)	0.230 (0.015)
average		0.168 (0.046) b			0.199 (0.040) b			0.575 (0.044) a			0.240 (0.023) b	

3.2. Concentration and Fractionation Profile of Selected Elements in Soil

Studies in different cities around the world routinely show that urban soils are subject to anthropogenic disturbance; however, these surveys are difficult to compare due to a lack of common sampling and analytical protocols. In this study, the urban soils of Reading and Belgrade were sampled and analyzed using the same sampling and analytical procedures. The pollution of urban soils with PTEs was estimated by determining the pseudo-total content of PTEs, including micronutrients (B, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn), which are listed as priority substances in the directive of European Communities and Background Values in European Soils [75,76]. Concentrations of all measured elements are provided in Table 2 and Table S2 (provided in Supplementary Material), and their partitioning into four BCR fractions are provided in Figure 2. Broadly, Belgrade sites (both polluted and unpolluted) had higher concentrations of B, Co, Cr, Mn, and Ni compared to Reading sites. Conversely, concentrations of Cu, Zn, and Sr were significantly higher in the Reading polluted site compared to all other sites in both cities.

The pseudo-total concentrations for B varied widely, from 19.5 mg kg⁻¹ at RU-3 location to 73.7 mg kg⁻¹ at BU-3, with levels above the average values for worldwide soils (22–40 mg kg⁻¹ [24]) measured at all sites, aside from locations RU-2 and RU-3. In Belgrade, B concentrations were somewhat higher in unpolluted soils, unlike in Reading, where polluted soils had several-fold higher concentrations. Gawlik and Bidoglio [76] do not propose limit values in soil for B, perhaps because high B content does not necessarily mean an environmental risk as the multiple factors influence the quantities, bioavailability, and the distribution of B in the soils. The highest content of B in samples from Belgrade was found in residual fraction (52.0–87.2%), while the rest was distributed mainly between the acid-soluble/exchangeable (3.1–20.7%), the reducible (6.3–15.7%), and the oxidizable fractions (3.27–17.93%). However, in soil samples from Reading, significant amounts of B were found in the first three fractions (approximately 50%), indicating its moderate mobility, implying potential availability to plant uptake [77].

Table 2. Mean values and standard deviation in parenthesis of pseudo-total element concentrations (mg kg^{-1} d.w.) in studied urban soils (i.e., polluted and unpolluted sites in Belgrade and Reading). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites.

	B	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
BP-1	62.7 (0.61)	8.1 (0.07)	23.3 (0.28)	21.0 (0.22)	27,832.1 (23.22)	511.50 (6.31)	29.2 (1.03)	8.7 (0.77)	10.2 (0.95)	49.3 (0.51)
BP-2	56.3 (0.48)	7.6 (0.06)	21.2 (0.22)	18.0 (0.22)	24,076.5 (16.95)	502.0 (5.47)	25.9 (0.52)	10.8 (0.84)	7.4 (0.63)	34.1 (0.34)
BP-3	65.0 (0.52)	8.3 (0.09)	23.3 (0.24)	21.0 (0.31)	28,062.4 (11.36)	530.8 (4.38)	28.6 (0.11)	7.9 (0.69)	9.5 (0.78)	40.2 (0.51)
BP average	61.3 (3.95) ab	8.0 (0.31) b	22.6 (1.04) b	20.0 (1.49) c	26,657.0 (1938.01) a	514.8 (13.53) a	27.9 (1.64) b	9.2 (1.43) d	9.0 (1.44) c	41.2 (6.60) b
BU-1	64.5 (0.64)	9.3 (0.07)	30.0 (0.19)	23.1 (0.33)	25,591.1 (13.01)	517.9 (3.89)	46.4 (0.56)	25.4 (0.21)	23.3 (0.12)	52.8 (0.48)
BU-2	69.1 (0.65)	9.8 (0.25)	34.0 (0.40)	23.3 (0.20)	26,823.3 (14.00)	532.1 (5.22)	62.1 (0.70)	27.6 (0.30)	31.1 (0.35)	51.5 (0.66)
BU-3	73.7 (0.69)	10.3 (0.14)	38.1 (0.32)	23.5 (0.19)	28,055.6 (14.13)	546.3 (4.01)	77.7 (0.67)	29.9 (0.17)	39.0 (0.41)	50.1 (0.49)
BU average	69.1 (4.01) a	9.8 (0.45) a	34.0 (3.53) a	23.3 (0.28) b	26,823.3 (1067.22) a	532.1 (12.91) a	62.1 (13.54) a	27.6 (1.95) b	31.1 (6.79) b	51.5 (1.25) b
RP-1	48.1 (0.45)	8.2 (0.07)	8.0 (0.67)	35.2 (0.33)	11,976.3 (5.63)	433.2 (3.28)	13.9 (0.14)	138.9 (1.44)	46.8 (0.52)	129.3 (0.33)
RP-2	53.5 (0.52)	8.5 (0.06)	9.1 (0.87)	39.6 (0.28)	14,738.8 (2.88)	426.7 (2.22)	16.6 (0.63)	137.1 (1.28)	44.7 (0.36)	147.5 (0.52)
RP-3	60.0 (0.63)	9.0 (0.09)	8.8 (0.91)	39.20.42)	14,813.8 (1.78)	462.8 (2.95)	15.6 (0.114)	147.0 (2.01)	50.2 (0.43)	134.1 (0.26)
RP average	53.9 (5.19) b	8.6 (0.35) b	8.7 (0.87) c	38.0 (2.11) a	13,843.0 (1400.36) b	440.9 (16.84) b	15.4 (1.26) c	141.0 (4.75) a	47.2 (2.43) a	137.0 (8.19) a
RU-1	22.8 (0.18)	1.7 (0.09)	5.2 (0.52)	5.8 (0.44)	5878.9 (3.56)	180.7 (1.88)	2.2 (0.23)	18.7 (0.96)	5.2 (0.47)	25.8 (0.17)
RU-2	20.0 (0.19)	1.6 (0.12)	5.1 (0.49)	7.6 (0.67)	5525.9 (14.52)	164.1 (1.56)	2.3 (0.32)	18.0 (0.89)	4.1 (0.33)	24.2 (0.17)
RU-3	19.5 (0.21)	1.7 (0.19)	5.1 (0.55)	6.8 (0.58)	5537.9 (10.78)	159.3 (1.84)	1.9 (0.96)	18.3 (0.85)	3.4 (0.29)	23.4 (0.18)
RU average	20.8 (1.57) c	1.7 (0.13) c	5.1 (0.46) c	6.7 (0.92) d	5647.6 (173.80) c	168.0 (9.87) c	2.2 (0.55) d	18.4 (0.83) c	4.2 (0.87) c	24.5 (1.09) c

(ANOVA—Bonferroni); Different letters in the same column indicate significant differences between sites at $p < 0.001$ level.

In the present study, the concentration of Co in the soil exhibited considerable variability, ranging from a minimum of 1.6 mg kg^{-1} RU-2 point to a maximum of 10.3 mg kg^{-1} at BU-3. Similar to B, in Belgrade, higher concentrations were recorded in an unpolluted site, while in Reading, it was the opposite. At Reading unpolluted site-RU, at all sampling points, all measured concentrations were below, while at Belgrade polluted site-BU, Reading polluted-RP and Belgrade unpolluted-BU sites except point BU-3 (10.3 mg kg^{-1}) were within the range of average values for worldwide soils ($5.5\text{--}10 \text{ mg kg}^{-1}$ [24]). As is the case with B, the European Council Directive does not propose limit values for Co content in soil [75,76]. Concentrations of Co were generally similar to those previously found in urban soils of Belgrade ($12.0\text{--}41.6 \text{ mg kg}^{-1}$, [78]), Palermo ($1.5\text{--}14.8 \text{ mg kg}^{-1}$ [79]), and Madrid ($5.3\text{--}12.1 \text{ mg kg}^{-1}$ [80]). Furthermore, the fractionation profile of Co varied between the samples. The dominating chemical form of Co at all the sampling points in Belgrade was associated with the reducible fraction (41.2–51.8%), followed by the residual fraction (40.4–45.3%). The oxidizable fraction also had a considerable presence of Co (4.8–8.5%). The relatively high percentage of Co in the reducible fraction is to be expected due to the very high absorption capacity of Co by Mn oxides [81,82]. However, in the soils from Reading, a different fractionation profile for Co was observed, especially in soil from Read-

ing unpolluted site-RU where its significant part was found in acid-soluble/exchangeable fraction (20.5–21.1%), indicating its bioavailability despite its very low level in the soil. The slightly acid reaction of the soil in Reading unpolluted site-RU could have been the reason for the higher content of Co found in the acid-soluble/exchangeable fraction, given the fact that the dominant form of Co in nature (Co II) becomes more available in acidic conditions [83].

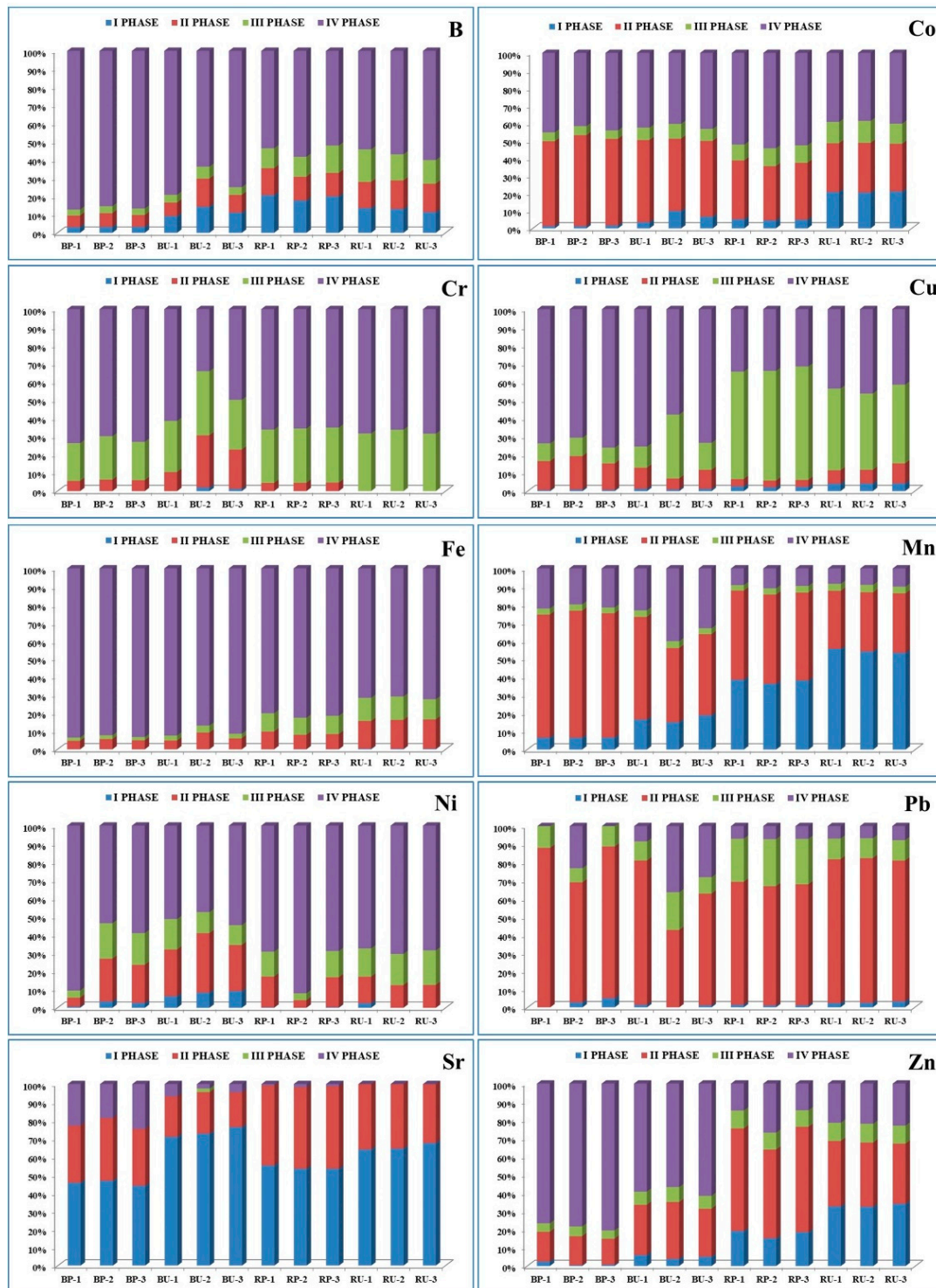


Figure 2. Partitioning of selected elements in studied urban soils (i.e., polluted-BP and RP, and unpolluted sites-BU and RU, in Belgrade and Reading). I: acid-soluble/exchangeable fraction; II: reducible fraction; III: oxidizable fraction; IV: residual fraction.

Pseudo-total Cr concentrations in Belgrade soils were also higher in unpolluted sites compared to polluted, unlike Reading which had a higher Cr concentration in the polluted site. Chromium concentrations varied from 5.1 mg kg⁻¹ (RU-2 and RU-3) to 38.1 mg kg⁻¹ (BU-3) and were below the mean values described for global as well as European soils (47–51 mg kg⁻¹ [24], 50–100 mg kg⁻¹ [75,76]), at all the sampling points. Earlier studies on urban soils in Belgrade [78], Madrid [80], and Palermo [79] also point to a variable Cr content. The fractionation characterization of Cr at Belgrade unpolluted site-BU showed that Cr is equally distributed between residual (34.1–61.5%), oxidizable (27.3–35.3%), and reducible (10.5–28.6%) fraction with the lowest content of Cr extracted in the acid-soluble/exchangeable fraction (0–2.0%). On the other side, all other sampling points showed that the major portion of Cr was bound to the silicate lattice and crystallized oxide minerals (65.1–73.6%), while the rest was associated with organic matter and sulfides (20.8–33.7%) and iron and manganese oxides (0–6.3%). The content of Cr in the acid-soluble/exchangeable fraction was very low—below the detection limit. These results were indicative that Cr had a strong association with the insoluble fraction and, thus, it was chemically stable and biologically unavailable for plants uptake [84]. Furthermore, high content of Cr in residual fraction together with slightly acid to slightly alkaline pH reaction indicate that in the studied soils, the dominant form of Cr is Cr (III), given the fact that Cr (III) is poorly water-soluble and almost completely precipitates at a pH above 5.5 [78,83,85]. These results are in broad agreement with earlier studies [8,86,87].

Copper showed considerable variation in concentration, from 5.8 mg kg⁻¹ at the RU-1 sampling point to 39.6 mg kg⁻¹ at RP-2. Total Cu concentrations in Belgrade soils were also higher in unpolluted sites compared to polluted, unlike Reading which had a higher Cu concentration in the polluted site. Copper content at all sampling points within Reading unpolluted site-RU was below-average values for worldwide soils as well as far below the normal background of urban contaminated soils in England (190 mg kg⁻¹ [88]), whereas its content in Belgrade unpolluted and Reading polluted sites was above it (13–23 mg kg⁻¹ [24]). Generally, the Cu content in soils is dependent on its content in ‘parent’ material but can also reflect anthropogenic pollution in surface soils since it represents one of the most serious environmental contaminants that is released from traffic and from processes in the metal industry [89,90]. However, results obtained from the current study suggest that Cu content in the soil does not constitute a threat to the environment since all were below the limit values established by the directive of European Communities (50–140 mg kg⁻¹ [75,76]). The distribution of Cu fractions in soil samples from Belgrade sampling sites indicate that the greatest proportion of Cu is associated with the residual fraction (57.9–76.1%), while the rest is distributed mainly in organic matter and sulfides (8.7–35.1%) and iron and manganese oxides (6.0–18.4%). A very small amount was associated with the acid-soluble/exchangeable fraction (0.6–1.3%), which is in good agreement with previously reported by Yutong et al. [91], Figure 2. In contrast, in soil from Reading, the highest portion of Cu was associated with organic matter and sulfides (41.9–62.4%), and the rest was distributed between residual (31.5–46.4%), reducible (3.6–11.0%), and acid-soluble/exchangeable (2.1–4.2%) fractions. It was previously reported that Cu in urban soils is mainly bound to the organic matter and sulfides followed by the residual fraction, and such modes of the occurrence of Cu may be due to the high affinity of Cu (II) to humic organic matter [92,93].

The Fe content in soil mostly depends on its content in parent material, but can also reflect anthropogenic pollution in surface soils, given the fact that dust produced in the industry process contains Fe, Zn, Ca, and Si in the form of oxides [90], which can be easily transferred to soil. The concentration of Fe in selected soil samples ranged from 5525.9 mg kg⁻¹ at RU-2 to 28,062.4 mg kg⁻¹ at BP-3. In Belgrade soils, Fe concentrations were similar between the unpolluted and polluted sites, unlike Reading which had a higher Fe concentration in the polluted sites. The highest concentration of Fe in studied soils was obtained in residual fraction (70.9–93.5%), suggesting that metals were strongly bound to the crystalline structures of the soil minerals and potentially unavailable to

plants [94]. The rest of Fe was associated with organic matter and sulfides (1.8–12.9%) and with iron and manganese oxides (4.7–16.1%). The lowest amount was extracted in the acid-soluble/exchangeable fraction (up to 0.4%), which confirms the results of previous studies [87,95–97]. In soil samples from Reading, somewhat higher Fe content was extracted in the first three phases of the sequential extraction in comparison with samples from Belgrade, but not in a quantity that may represent a risk to urban ecosystems.

According to Kabata-Pendias and Pendias [24], mean Mn values in worldwide soils range from 270 to 525 mg kg⁻¹, while there is no data for limit Mn values for European soils [75,76]. In this study, the lowest amount of Mn was found at the RU-3 point (159.3 mg kg⁻¹), while the highest was measured at BU-3 (546.3 mg kg⁻¹). In Belgrade, Mn concentrations were somewhat higher in unpolluted soils, unlike Reading, where polluted soils had several-fold higher concentrations. The highest Mn content in all soil samples was obtained in the reducible fraction (32.1–70.2%), which was expected, given the fact that manganese oxyhydroxides represent a principal target of the hydroxylammonium chloride reagent [98]. The exceptions were soil samples from Reading unpolluted site-RU where the highest portion of Mn had been extracted in the acid-soluble/exchangeable fraction (53.1–55.6%), moderate in reducible (32.1–33.2%), and the rest in the residual (8.5–10.0%) and oxidizable (3.6–4.1%) fraction. Fractionation profile for Mn showed that its content in the acid-soluble/exchangeable phase in soil samples from Reading (36.1–55.6%) was significantly higher compared to samples from Belgrade (6.5–18.9%), indicating that Mn can be remobilized if environmental conditions change, thus could represent a potential risk to the urban ecosystems [99]. The results obtained from soils both from Belgrade polluted and unpolluted sites, as well as Reading polluted sites, were in agreement with previous studies of urban environments [93,98,100], which also showed that reducible form is the most important fraction for Mn. However, Lu et al. [96] reported that Mn is uniformly distributed between the extractable, reducible, and residual fractions, while the lowest amounts are associated with the oxidizable fraction, which was in line with results from Reading unpolluted site-RU.

The Ni content in soil is highly dependent on its content in parent rock [24]. In the present study, in Belgrade, Ni concentrations were higher in unpolluted soils, unlike Reading, where polluted soils had several-fold higher concentrations. Nickel concentrations varied widely, with the lowest values measured at RU-3 point (1.9 mg kg⁻¹) and the highest at BU-3 (77.7 mg kg⁻¹). Nickel content, above the mean values for global soils (13–26 mg kg⁻¹ [24]) as well as the normal background Ni levels in urban contaminated soils in England (42 mg kg⁻¹ [88]), was measured at all points in Belgrade unpolluted site-BU and at BP-1 and BP-3 points and was above limit values proposed by directive of European Communities (30–75 mg kg⁻¹ [75,76]) at the BU-3 point. In general, Ni content in soil from Belgrade was significantly higher compared to Reading, which is the result of the specific geological substrate in central parts of Serbia, including Belgrade. Namely, the origin of Ni and Cr in the soil is determined by the geological substrate, showing an increased content of Ni and Cr in soils formed on serpentine rocks in western Serbia and in the valleys of large rivers, where they originate from pedogenetic processes of alluvium formation [101]. Sequential BCR extraction proved variable distribution of Ni among the fractions depending on the sampling site. The largest portion of Ni was bound to the silicate lattice and crystallized oxide minerals (47.5–92.1%), while the rest was mainly associated with iron and manganese oxides (4.1–32.6%) and organic matter and sulfides (3.8–19.5%). The lowest portion of Ni was distributed in the acid-soluble/exchangeable fraction (0–9.2%). However, Ni showed different distribution patterns at BP-1 and RP-2 points, where it was predominantly extracted in the residual fraction (90.5% and 92.1%, respectively), indicating that Ni is insoluble and relatively immobile in the selected soil samples. Furthermore, great amounts of this element in all samples from the Belgrade unpolluted site-BU sampling site were found in the first three fractions (approximately 50%), indicating that under suitable conditions (salinity, pH, and redox potential), it could potentially be released and represent a serious threat to the environment [99]. Irregular pat-

terns of Ni partitioning in soils are not unusual in literature. For instance, Ghrefat et al. [86] and Pavlović et al. [8] found that Ni was evenly distributed among residual, reducible, and carbonates fractions, while much lower content was extracted in exchangeable and organic matter fractions. Conversely, results obtained from other urban soil studies showed residual Ni is the dominant fraction [86,96,98].

In this study, pseudo-total Pb soil content ranged from 7.9 mg kg⁻¹ at BP-3 to 147.0 mg kg⁻¹ at RP-3, and was significantly lower compared to results obtained for London (approximately 294 mg kg⁻¹ [102]), Glasgow (approximately 389 mg kg⁻¹ [98]), Palermo (approximately 202 mg kg⁻¹ [79]) and Belgrade (approximately 252.9 mg kg⁻¹ [78]), and also within the proposed limit values for European soils (50–300 mg kg⁻¹ [75,76]) and normal background for Pb in urban contaminated soils in England (820 mg kg⁻¹ [88]) at all the examined sites. In Belgrade, Pb concentrations were somewhat higher in unpolluted soils, unlike Reading, where polluted soils had several-fold higher concentrations. Lead content above the mean values described for worldwide soils (22–27 mg kg⁻¹ [24]) was measured at points BU-2, BU-3, and at all sampling locations in Reading polluted site-RP, probably due to motor vehicle emissions and particulate matter deposition [93,103]. The fractionation profile of Pb was quite different from the above elements given the fact that the highest proportion of Pb was bound to Fe and Mn oxides (42.7–88.0%), while both oxidizable (7.8–26.0%) and residual (0.0–36.5%) fractions were equally represented in profile. Furthermore, the smallest part of Pb was extracted in the acid-soluble/exchangeable (0.0–5.1%) fraction. Such a result indicates that lead was mainly associated with the inorganic soil fraction and could become available if weakly acidic conditions are established [56]. These results coincide with the findings of Ramos et al. [104] that most of Pb was associated with the reducible fraction in polluted soils in Spain, with very low amounts in the exchangeable fraction. The tendency of Pb to be associated with Fe and Mn oxides has also been widely reported in other studies in urban regions [98,100].

Strontium content in selected soil samples varied across a wide range from 3.4 mg kg⁻¹ at RU-3 to 50.2 mg kg⁻¹ at the RP-3 sampling point; however, they were below the mean values described for global soils (87–210 mg kg⁻¹ [24]), while directive of European commission does not propose referent values for Sr in soils [75,76]. Similar to other elements in Belgrade, Sr concentrations were higher in unpolluted soils, unlike Reading, where polluted soils had several-fold higher concentrations. Due to the lack of relevant literature data, it was not possible to compare the content of Sr in tested soils with the same in urban soils of Europe and worldwide; however, our previous studies in urban areas indicate that the content of Sr in the soil is within the average values described for worldwide soils [10,57]. The highest difference, however, in relation to other studied elements is a very high portion of Sr in the first two fractions of BCR sequential extraction. The portion of Sr in acid-soluble/exchangeable and reducible fractions exceeds 90% in all soil samples, except samples from soils in Belgrade polluted site-BP (75.3–81.3%). Furthermore, the smallest part of Sr was associated with organic matter and sulfides (0.0–2.0%) and with the silicate lattice and crystallized oxide minerals (0.0–24.7%). Such a fractionation profile of Sr indicates its high mobility and potential bioavailability.

The pseudo-total Zn content ranged from 23.4 mg kg⁻¹ at RU-3 point to 147.5 mg kg⁻¹ at RP-2. In Belgrade, Zn concentrations were higher in unpolluted soils, unlike Reading, where polluted soils had higher concentrations. A significantly higher Zn content was found in Reading polluted site-RP, above the mean values described for worldwide soils (45–60 mg kg⁻¹ [24]) and below the proposed limit values for European soils (150–300 mg kg⁻¹ [75,76]). The higher content of Zn in soils at Reading polluted site-RP sampling site was quite likely the result of motor vehicle emissions and other waste products from traffic given the fact that this site is the closest to the road in relation to other sampling sites. Concentrations of Zn at this site was similar to previously determined in urban soils in Belgrade (118 mg kg⁻¹ [105]; 188 mg kg⁻¹ [10]), Glasgow (177 mg kg⁻¹ [98]) Madrid (210 mg kg⁻¹ [80]), Naples (180 mg kg⁻¹ [92]), and Torino (183 mg kg⁻¹ [106]). Fractionation profile for Zn varied with sampling site; in Belgrade, the dominant chem-

ical form of Zn was associated with the silicate lattice, and crystallized oxide minerals (56.7–80.5%), followed by the fraction of Zn bound to Fe and Mn oxides (14.2–31.1%) and organic matter and sulfides (4.6–8.3%). The lowest portion of Zn at these sampling sites was found in an acid-soluble/exchangeable (0.5–5.2%) fraction. This distribution was consistent with those previously published by Lu et al. [96] and Yutong et al. [91]. In contrast, in soil samples from Reading, the greatest proportion of Zn was found in the first two fractions (63.8–76.3%). In percentage terms, this is followed by the acid-soluble/exchangeable (15.2–34.2%) and residual (14.6–26.9%) fraction. These results indicate that in case of any change in the environmental conditions such as pH, redox potential, etc., Zn can be easily remobilized and become available for plant uptake [99].

3.3. Mobility Factor (MF) and Bioaccumulation Factor (BAC) of PTE

The mobility and bioavailability of elements in the soil are affected by physico-chemical and biological properties of the soil, such as pH, organic matter content, cation exchange capacity, soil texture, oxidation/reduction potential, plant and microbial activity, and the distribution of metals among various soil fractions [21,28]. Elements that are strongly bound to residual fraction have low mobility, and consequently, their availability to the plants is low, while elements found in the oxidizable and reducible fractions are more mobile and, under suitable environmental conditions, may become bioavailable. Elements extracted in acid-soluble/exchangeable fractions are weakly bound to the soil and are most mobile and easily bioavailable [93,107]. For estimation of element mobility in soils, relative index or mobility factor (MF) representing a share of an element expressed in percentage present in water/soluble, exchangeable, and carbonate fractions are often used [62,96,108], which in the case of BCR sequential extraction represents a share of the element released after the first step of extraction with 0.11 mol L^{-1} acetic acid [8,96,109].

The results for mobility factor values for B, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn in soil samples are presented in Figure 3. mobility factor for all elements, except for Ni, was higher in soil samples from Reading compared to Belgrade, indicating that they are more readily available for plant uptake in Reading soils. Low mobility (<10%) and high stability characterized the following elements: Co (except at Reading unpolluted sites-RU sampling site 20.5–21.1%), Cr, Cu, Fe, Ni, Pb, and Zn (except in Reading) since they were strongly connected to resistant minerals of the solid matrix with mobility factor less than 10% [107]. Moderate mobility characterized B (11.1–20.7%) in soil samples from Belgrade unpolluted sites-BU, Reading polluted sites-RP and Reading unpolluted sites-RU, as well as Zn (15.2–34.2%) in Reading. Among the studied elements, the highest mobility factors were determined for Sr (44.0–76.3%) and Mn (6.5–55.6%). Such results can be interpreted as the symptom of their high mobility and biological availability and can potentially affect the healthy function of plants growing in that soil and, more broadly, the ecosystem health in that location [93].

Results of BAC analyses/calculations suggest weak accumulation for most studied PTEs, apart from B and Sr where $BAC > 1$ (Table S3, Supplementary Material). This suggests that *Tilia* leaves are good accumulators of these two elements. Although great progress has been made in the studies of phytoremediation of soils polluted with potentially toxic elements, including heavy metals, its application is still very limited due to the unavailability of suitable plant species, i.e., absence of hyperaccumulator trees in urban habitats, and long growing seasons required. However, even if the trees cannot be considered as hyperaccumulators, the trees grown on the highly polluted soils are valuable phytoextractors able to extract toxic elements effectively or phytostabilizers to retain these elements in roots [6,42,56].

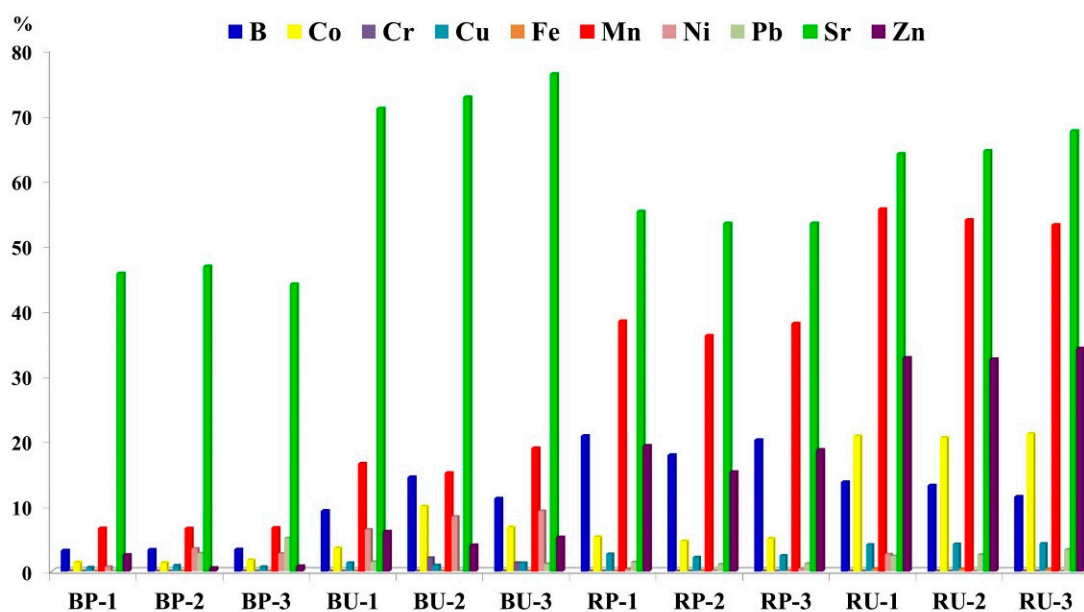


Figure 3. Mobility factor (%) for selected elements after modified BCR in studied urban soils (i.e., polluted- BP and RP, and unpolluted sites-BU and RU, in Belgrade and Reading).

3.4. Elemental Concentration in Plant Leaves

Concentrations of B, Cu, Fe, Mn, Ni, Sr, and Zn from each sampling site are presented in Table 3 and Table S2 (provided in Supplementary Material). Cobalt, Cr, Ni, and Pb were not detected in *Tilia sp.* leaves, while Ni was measured only in leaf samples from Reading. Of the tested elements Mn and Zn had the highest levels measured in leaves at Reading unpolluted site-RU sampling site, followed by B and Sr in leaves in Belgrade polluted site-BP and Cu and Fe in leaves in Belgrade unpolluted site-BU.

Boron content in *Tilia sp.* leaves varied widely from 36.9 mg kg⁻¹ at RU-2 point to 231.5 mg kg⁻¹ at BP-2 and was higher than its content in the soil. The results of one-way ANOVA showed significant differences between both polluted and unpolluted sites. In general, higher content of B was measured in *Tilia sp.* leaves in sites from Belgrade, indicating its close relation to the external B levels [110]. Boron uptake by plants mostly depends on the soil pH, parent material, form of B, the content of organic matter, aluminum (Al) and manganese (Mn) oxides, carbonates, transpiration rate, as well as climate and management practices [24,77,111]. In addition, B is considered to be one of the most mobile elements, where soil pH values above 6.5 increase its bioavailability for plants [24,112], therefore elevated content of leaf B in *Tilia sp.* from Belgrade polluted site-BP (224.6–231 mg kg⁻¹) and Belgrade unpolluted site-BU (87.8–95.3 mg kg⁻¹), as well as Reading polluted site-RP (78.6–82.3 mg kg⁻¹) was measured in comparison to the Reading unpolluted site-RU (36.4–36.9 mg kg⁻¹) with slightly acidic soil (pH 6.1–6.5). Boron is involved in a number of metabolic pathways [113]. Some plant species, and to some extent, some cultivars within species' differ in the B tolerance [114]. Normal B content in plants varies between 10 and 100 mg kg⁻¹, whereas symptoms of toxicity occur at levels over 100 mg kg⁻¹ [24], indicating that all the results obtained from Belgrade polluted site-BP were found to be in the toxic range as a result of pollution caused by fuels coal combustion. Namely, three coal thermoelectric power plants are located on the territory of Belgrade, within a radius of 50 km [115].

Table 3. Mean values and standard deviation in parenthesis of element concentration (mg kg^{-1} d.w.) in *Tilia* sp. leaves at polluted and unpolluted sites in Belgrade and Reading. BP and RP represent polluted, while BU and RU represent unpolluted sampling sites.

Sampling Point	B	Cu	Fe	Mn	Ni	Sr	Zn
BP-1	224.6 (0.19)	4.1 (0.22)	188.0 (0.90)	15.2 (0.16)	<DL	165.8 (3.88)	5.5 (0.37)
BP-2	231.5 (0.18)	4.2 (0.12)	200.3 (0.19)	15.7 (0.14)	<DL	170.0 (1.66)	3.2 (0.22)
BP-3	229.1 (0.17)	4.9 (0.71)	183.5 (0.16)	15.2 (0.13)	<DL	163.3 (2.03)	3.2 (0.26)
BP average	228.4 (3.04) a	4.34 (0.52) c	190.6 (7.52) b	15.4 (0.25) d	<DL	166.34 (3.76) a	4.0 (1.20) b
BU-1	93.4 (0.76)	6.9 (0.68)	233.3 (0.31)	27.5 (0.28)	<DL	66.4 (0.92)	2.6 (0.16)
BU-2	95.3 (0.69)	7.0 (0.22)	191.5 (0.98)	27.9 (0.35)	<DL	70.2 (0.58)	1.6 (0.49)
BU-3	87.8 (0.62)	6.4 (0.11)	234.4 (0.88)	27.0 (0.32)	<DL	67.7 (0.81)	1.5 (0.07)
BU average	92.2 (3.45) b	6.8 (0.44) a	219.8 (21.21) a	27.5 (0.48) c	<DL	68.1 (1.81) c	1.9 (0.59) c
RP-1	80.8 (0.55)	4.9 (0.23)	39.0 (0.42)	305.2 (2.89)	1.2 (0.01)	85.2 (0.75)	5.8 (0.62)
RP-2	82.3 (0.74)	4.5 (0.51)	37.6 (0.29)	307.8 (3.29)	1.1 (0.02)	87.3 (0.59)	5.8 (0.49)
RP-3	78.6 (0.68)	4.0 (0.33)	35.8 (0.41)	297.3 (1.31)	1.1 (0.21)	83.2 (0.91)	5.3 (0.61)
RP average	80.6 (1.73) c	4.5 (0.51) c	37.4 (1.41) c	303.4 (5.23) b	1.2 (0.11) a	85.2 (1.91) b	5.6 (0.55) b
RU-1	36.7 (0.45)	5.6 (0.32)	34.5 (0.27)	367.8 (2.41)	0.5 (0.05)	65.7 (0.32)	6.8 (0.71)
RU-2	36.9 (0.21)	6.2 (0.09)	42.6 (0.36)	368.8 (3.01)	0.6 (0.04)	68.2 (0.55)	7.2 (0.88)
RU-3	36.4 (0.12)	4.8 (0.10)	34.0 (0.28)	371.8 (2.87)	0.6 (0.44)	64.3 (0.27)	8.6 (0.77)
RU average	36.7 (0.34) d	5.6 (0.58) b	37.0 (4.17) c	369.5 (3.01) a	0.6 (0.22) b	66.1 (1.74) c	7.5 (1.05) a

(ANOVA–Bonferroni); Different letters in the same column indicate significant differences between sites at $p < 0.001$ level.

Although Co was present in an acid-soluble/exchangeable fraction at all sampling sites, its content in leaves was below the detection limit. This is probably due to limited uptake and translocation of Co from roots to shoots and its strong bonding in roots [116,117]. In soils with neutral and alkaline pH, Co is poorly mobile due to the low solubility of its hydroxides and carbonates, which represents a limiting factor for Co accumulation in plants [24].

Chromium in *Tilia* sp. leaves was also below the detection limit at all sampling sites due to its absence in acid-soluble/exchangeable fractions. Namely, Cr is predominantly present in the inaccessible form to plants, its translocation is very low, and most often, it is retained in roots [24]. In addition, soil pH also greatly affects Cr availability to plants, since in neutral and alkaline conditions (such as found in our study soils), it becomes unavailable for uptake [118].

The copper content in leaves of *Tilia* sp. varied in a narrow range from 4.0 mg kg^{-1} at RP-3 point to 7.0 mg kg^{-1} at BU-2. There were no statistically significant differences in Cu content between polluted sites; however, differences were observed between unpolluted sites (Table 3). Results obtained in leaves from polluted sites in both Belgrade and Reading were below the optimum values for normal plant development ($5\text{--}30 \text{ mg kg}^{-1}$ [24,65]).

Copper content can vary significantly depending on the plant part and development stage [118]; however, Cu deficiency often occurs in soils with low available Cu [119], which was the case at selected sampling sites (0.6–4.2% Cu extracted in acid-soluble/exchangeable fraction). Furthermore, Cu is known to have low mobility in relation to other elements in plants, and its overall solubility of both cationic and anionic forms decreases at pH 7–8 [24].

The results for Fe content in leaves of *Tilia* sp. revealed that samples from Belgrade show higher accumulation compared to samples from Reading. Samples from Belgrade unpolluted site-BU stood out with the highest Fe accumulation (191.5–234.4 mg kg⁻¹), followed by Belgrade polluted site-BP (183.5–200.3 mg kg⁻¹), with very similar results obtained from both sampling sites in Reading (34.0–42.6 mg kg⁻¹). Significant differences were observed between both polluted and unpolluted sites. Despite the wide range in the Fe content in plant species, some authors consider values of 200–500 mg kg⁻¹ Fe in leaves of woody species as elevated [120], while values over 300 mg kg⁻¹ could be considered toxic [121]. Interestingly, results of BCR sequential extraction showed that at Belgrade sampling sites, Fe was not present in acid-soluble/exchangeable fraction (0.00–0.02%), while it was also low in Reading (0.00–0.44%). Due to the low bioavailability of Fe, plants have probably developed different mechanisms to provide a sufficient amount of this essential element (e.g., activation of the enzyme Fe(III) reductase or increase in the secretion of non-protein amino acids [122]).

In contrast to Fe, Mn content in leaves samples from Reading (297.3–371.8 mg kg⁻¹) was several times higher compared to Belgrade (15.2–27.9 mg kg⁻¹), which can be attributed to Mn bioavailability in the acid-soluble/exchangeable fraction in soils from Reading (36.1–55.6%). Manganese presence in the acid-soluble/exchangeable fraction in Belgrade polluted site-BP amounted only (6.5–6.6%) and Belgrade unpolluted site-BU (15.1–18.9 %), respectively. Significant differences were found between both polluted and unpolluted sites. Despite more than sufficient amount of Mn in Belgrade soil (502.0–546.3 mg kg⁻¹) and its potential availability, the alkaline reaction of soil (pH 7.6–7.9) caused the plants to accumulate Mn in an insufficient amount for normal functioning in leaf samples from Belgrade (30–300 mg kg⁻¹ [24]). Furthermore, high Fe content in examined soil can cause a lower accumulation of Mn due to Mn-Fe antagonism [24]. In contrast to the narrow range of critical deficiency concentrations of Mn (10–27 mg kg⁻¹), the critical toxicity concentration varies widely among plant species, as well as environmental conditions [110,123]. Most plants can be affected by an Mn content over 400 mg kg⁻¹ [24]. A high share of Mn in the acid-soluble fraction in Reading unpolluted site-RU soil, as well as its slightly acid reaction (pH 6.1–6.8), resulted in increased Mn uptake by *Tilia* sp. trees from Reading sampling sites in concentrations which are considered as toxic [82]. Generally, Mn is easily taken up by plants when it is present in soluble form in the soil, such as was the case with trees from Reading. Here, a significant negative correlation (−0.829 **, Table S4, Supplementary Material) between the concentration of Mn in *Tilia* sp. leaves and soil was found, suggesting the presence of other sources of Mn (e.g., anthropogenic sources including atmospheric deposition).

Nickel content was below the detection limit in all the plant samples from Belgrade sites despite its presence and availability in acid-soluble/exchangeable fraction in soil from both Belgrade sampling sites (0.7–9.2%), which can be linked to alkaline soil reaction [124], but also to species-specific characteristics. Interaction with other elements, e.g., Fe, Cu, and Zn, can also affect Ni uptake by plants [24]. Unlike Belgrade samples, Ni content in the acid-soluble/exchangeable fraction in samples from Reading was significantly lower (0.0–2.6%); however, plants in Reading accumulated Ni in leaves (0.5–1.2 mg kg⁻¹), in an amount within the normal range for plants (3.7 mg kg⁻¹ [24]). The average content of Ni in lime leaves from Reading polluted site-RP was 1.2 mg kg⁻¹ and was higher in relation to the Reading unpolluted site-RU where only 0.6 mg kg⁻¹ was measured, which may be a result of higher Ni in soil from Reading polluted site-RP.

Lead was below the detection limit in all plant samples from all sites, although it was extracted in the acid-soluble/exchangeable fraction (0.0–5.1%) due to its low mobility both

in soils and plants. In plants, Pb can be accumulated either by uptake from soil or by foliar application [9]. The adsorption of Pb by roots is a passive process, and usually, the rate of its uptake from the soil is very low [82], which is why it predominantly accumulates in roots [9]. Additionally, Pb translocates poorly to other plant parts, thus rarely eliciting toxicity symptoms [83]. Furthermore, at $\text{pH} > 7$, Pb is most probably retained in the soil due to either co-precipitation with metal oxides or adsorption at metal oxide surfaces [95].

With Sr, significant differences were found between polluted while no significant differences were recorded between unpolluted sites, with higher Sr concentrations measured at polluted sites (Table 3). The lowest Sr content was measured in *Tilia* sp. leaves at RU-3 (64.3 mg kg^{-1}), while the highest in leaves at BP-2 ($170.03 \text{ mg kg}^{-1}$). Unlike other examined elements, the greatest proportion of Sr was bound to acid-soluble/exchangeable fraction (44.01–76.3%), indicating its high mobility and bioavailability, which is why the plants from all sampling sites accumulated Sr in levels that could be regarded as phytotoxic ($>30 \text{ mg kg}^{-1}$ [125]). Strontium is moderately mobile in soils and is usually sorbed by clay minerals and Fe oxides and hydroxides [82]. Unusual behavior, as well as negative correlation (-0.864^{**} , Reading polluted site-RP, Table S4, Supplementary Material) point to anthropogenic sources of Sr, which can be linked to traffic, individual heating units, or artificial materials in urban soils. Although Sr was not present in high concentrations in examined soils, its poor sorption probably allowed plants to easily accumulate it in leaves. Considering that Sr concentrations were higher in lime leaves than in the soil, it can be assumed that its source comes mainly from urban deposition [126]. Earlier studies proved that prolonging exposure periods to high levels of airborne Sr lead to its accumulation in the aboveground parts of plants [10,127]. Easy Sr uptake by plants can also be related to its similar biogeochemical characteristics to Ca; thus, plants are transferring it into aboveground organs.

Zinc content in leaves of *Tilia* sp. varied between 1.50 mg kg^{-1} in BU-3 up to 8.6 mg kg^{-1} in RU-3. Generally, higher Zn content was measured in leaves samples from Reading compared to Belgrade, which can be linked to greater Zn availability in acid-soluble/exchangeable fraction in Reading (15.2–34.2%) in relation to Belgrade (0.5–6.1%), as well as lower pH (6.1–7.1). Significant differences were measured between unpolluted sites. The rate of Zn absorption differs greatly among both plant species and growing media but depends mostly on soil pH [9], given the fact that the bioavailability of Zn at $\text{pH} > 7$ is substantially reduced. Optimal Zn levels in plant tissues according to Kabata-Pendias and Pendias [24] are considered to be from $27\text{--}150 \text{ mg kg}^{-1}$, while the critical deficiency concentrations are below $15\text{--}20 \text{ mg kg}^{-1}$ [128]. It is evident that Zn content in leaves was in the critical deficiency range, especially in samples from Belgrade. Severe Zn deficiency is often associated with alkaline soil conditions, where due to increased adsorptive capacity for soil particulates, Zn becomes immobile [128]. Furthermore, high Fe content in examined soils could affect Zn uptake due to Zn-Fe antagonism that depresses the effects of other elements [24].

3.5. Inter-Elemental Relationships in Plant and Soil Samples

Multivariate statistics revealed different associations between soil and plant PTEs in the two cities. Soil samples were clustered according to sampling site and were primarily differentiated according to their origin, with B, Co, Cr, Fe, Mn, and Ni in PC1 component (60.3% of the total variance), and Cu, Pb, Sr, and Zn in another (35.4% of the total variance, (Table S5, Supplementary Material), suggesting a natural (lithogenic) origin for the former group an anthropogenic one for the latter which could be linked to airborne emissions from the traffic [97,129]. The relationships between examined metals in the soil, based on the first two principal components (loading plot), are illustrated in Figure 4a. The score plot (Figure 4b) displays four different groups of samples. The first group contains the soil samples from Reading polluted site-RP, which are characterized by high Cu, Pb, Sr, and Zn content. The second group contained soil samples from Reading unpolluted site-RU site, which was characterized by the lowest content of all tested elements. The third group

contains soil samples from Belgrade polluted site-BP, where the elements are mostly of natural origin, whereas the fourth group contains soil samples from Belgrade unpolluted site-BU, where the content of all tested elements was higher compared to Belgrade polluted site-BP, especially Pb and Sr.

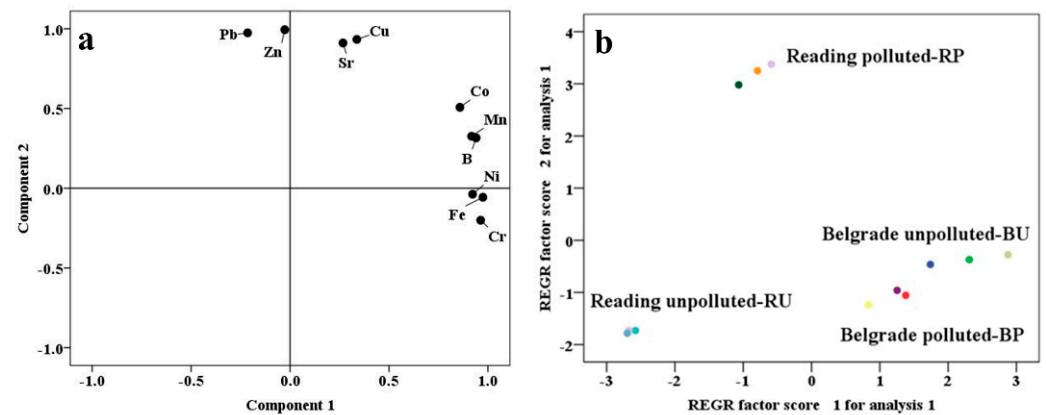


Figure 4. PCA for selected elements in soil ((a)-loading plot and (b)-score plot). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites.

Plant samples were clustered according to sampling sites. The PCA of PTEs in *Tilia* sp. leaves resulted in a two-component model, which explains 92.3% of the total variance (Table S5, Supplementary Material). The PC1 explains approximately 62.1% of the total variance and is significantly positively correlated with Mn, Ni, and Zn and negatively with Fe, while PC2 explains 30.3% of the total variance and is significantly positively correlated with B and Sr and negatively with Cu (Table S5, Supplementary Material). The relationships between the metals based on the first two principal components (loading plot) are illustrated in Figure 5a. The score plot (Figure 5b) displays three distinctive groups of samples belonging to different sampling sites. Namely, samples from Belgrade polluted site-BP formed the first cluster, where the dominant impact on distinction was contributed by high concentrations of B and Sr. Samples from Belgrade unpolluted site-BU created the second compact cluster due to the higher Cu concentration, while all samples from Reading formed the third cluster, which points to the similarity of uptake and accumulation pattern for Mn, Ni, and Zn, but also to significantly lower Fe concentrations compared to Belgrade sampling sites.

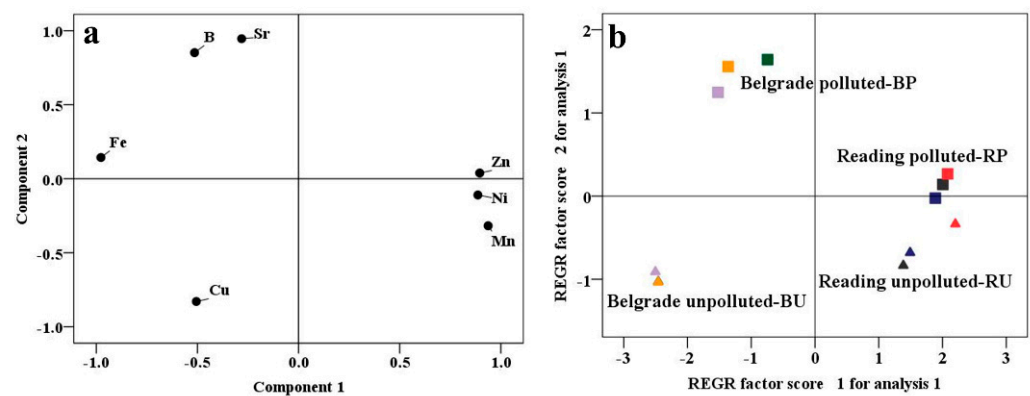


Figure 5. PCA for selected elements in *Tilia* sp. leaves ((a)-loading plot and (b)-score plot). BP and RP represent polluted sampling sites, while BU and RU represent unpolluted sampling sites.

4. Conclusions

This study investigated pseudo-total content, mobility, and potential bioavailability of B, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn in soils, as well as the accumulation ability of *Tilia* sp. leaves sampled from urban parks in Reading and Belgrade. The research revealed that concentrations of all examined elements were within limit values proposed by the directive of European Communities [75,76]. The distribution of soil PTEs showed site-dependent characteristics, with the highest concentrations of Co, Cr, and Ni measured in Belgrade (BP-1, BU-2, and BU-3), which is related to the nature of geological substrate in certain parts of Serbia, including the Belgrade area. Higher concentrations of Cu, Pb, Sr, and Zn were measured in soils of Reading polluted site-RP. Content of Fe and Mn was similar in both polluted and unpolluted sampling sites in Belgrade and higher in relation to the same at both Reading sampling sites. The lowest concentration of all measured elements was found in Reading unpolluted site-RU. A similar relation for all elements was established between unpolluted sites in both cities, with higher concentrations of all analyzed elements in samples from Belgrade compared to Reading.

Mobility factor for all elements, except for Ni, was higher in soil samples from Reading compared to Belgrade, indicating that they are more readily available for plant uptake in Reading urban soils. In general, low mobility (MF < 10%) characterized Co, Cr, Cu, Fe, Ni, and Pb, while moderate mobility was found for B and Mn, which could represent a threat to urban vegetation due to their increased mobility and bioavailability.

Multivariate statistics revealed different associations between soil and plant PTEs in the two cities. Soil samples were clustered according to sampling sites and were primarily differentiated according to their origin. The results of PCA showed that soil B, Co, Cr, Fe, Mn, and particularly Ni have a geogenic origin, unlike Cu, Pb, Sr, and Zn. In the absence of major industrial facilities with substantial metal emissions in the vicinity of our study locations, our data are consistent with traffic-derived sources of these elements.

PCA of elemental concentration in leaf samples showed the different capacities for uptake and accumulation of PTEs in different locations. Trees growing at urban sites in Belgrade readily accumulated B, Fe, and Sr, while those in Reading accumulated more Mn, Ni, and Zn. At all the sites, Cu concentrations were similar, mostly in the deficiency range. The results also revealed deficiency for essential elements Mn and Zn in samples from Belgrade due to the alkaline reaction of soils. Excessive uptake of Sr concentrations, in the toxic range in all the sampling sites regardless of its total content, was likely due to its high content in bioavailable fractions in soils.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su13179784/s1>: Table S1: Individual pH and EC values in studied urban soils; Table S2: Individual values of element concentrations (mg kg⁻¹ d.w.) in *Tilia* sp. leaves and urban soils (i.e., polluted and unpolluted sites in Belgrade and Reading). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites; Table S3: Bioaccumulation factor (BAC) for PTEs in *Tilia* sp. at selected sampling sites (i.e., polluted and unpolluted sites in Belgrade and Reading). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites. Levels > 1 are denoted in bold; Table S4: Correlation matrix for selected PTEs concentrations in leaves and corresponding soil samples at selected sampling sites (i.e., polluted and unpolluted sites in Belgrade and Reading). BP and RP represent polluted, while BU and RU represent unpolluted sampling sites; Table S5: The results of PCA (Varimax normalized) for selected soil samples and *Tilia* sp.

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