



## Content and cycling of main biogenic and toxic elements in fragmented ecosystems of the Sofia city, Bulgaria

Venera Tsolova, Ivona Nikova and Plamen Tomov\*

ISSAPP "Nikola Poushkarov", Sofia 1331, Bulgaria, Shosse Bankya 7

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### Abstract

*This article deals with the content and cycling of main biogenic and toxic elements within six fragmented ecosystems of the Sofia city. All of them are part of recreational areas and have been modified to varying degree by urbanization. Depending on the degree of profile sequence disorder, studied soils can be divided into four groups: 1. Buried soils; 2. New soils; 3. Soils with undisturbed profile and 4. Cultivated soils. Presented classification follows the principles of the Bulgarian and WBR classification schemes. The results indicate that urbanization activities do not lead to soil pollution with Cr, Zn, Pb, Cu, Ni, and Co, but significantly increase the spatial variability of Pb, Co and Mn content. Therefore, these elements could be considered as an indicator of geochemical remodelling of urban soils. All studied elements prevail in background total and bioavailable concentrations in soils except for available phosphorus which occurs in extremely low amount ( $< 7 \text{ g } 100^{-1} \text{ g soil}$ ) independently on the degree of soils reformations, and Pb. occurs in toxic available concentrations in four soil types, but plant communities slightly accumulate it. No aberrant concentrations of trace elements were found in the aboveground biomass of vascular plants in studied urban habitats.*

**Keywords:** Bioavailability, ferromagnesian trace elements, geochemistry, lead toxicity, urban soils

### Introduction

Living conditions in an urban environment are extremely important because most of the population, industry and economy are concentrated in cities. Recently, many studies have focused on urban soils because of environmental pollution (Thornton, 1991; Li *et al.*, 2004; Wong *et al.*, 2006; Doichinova *et al.*, 2014). Heavy metals are typical contaminants of urban soils (McBride *et al.*, 2014; Seleznev and Yarmoshenko, 2014; Tom *et al.*, 2014) and can easily enter the human body through ingestion, inhalation, and skin contact. As a key component of urban ecosystems, urban soils accumulate metals and retain them through the soil adsorbent for a long period of time. Therefore, soil acidity, organic matter content, chemical and geochemical properties are important factors managing the cycling of contaminants in urban ecosystems. The nutrition of plants is also directly dependent on them.

Lead is the most common urban soil pollutant of all the heavy metals since its compounds had been used as detonating agents to increase the octane number in gasoline until 1989. It is estimated that 4.5 to 5.5 million tons of lead used in gasoline have been deposited in soils, which is why soils next to heavily congested roads are usually

contaminated (Rodríguez-Flores and Rodríguez-Castellón, 1982). Another main source of lead in residential areas is paints. Lead paints were used in 75% of houses built before 1978, at which time it was banned.

It is already known that in order to get a better understanding of biological, metabolic and toxicological effects of heavy metals, it is necessary to determine not only their total content but also the content of various metals chemical forms. Currently, the analysis of chemical state of elements has become an effective and reliable tool for assessing the environmental risks caused by the presence of heavy metals (Guillén *et al.*, 2012; Chai *et al.*, 2014; Paramasivam *et al.*, 2015). This analysis has been preferred in determining their potential bioavailability and remobilization in plant, human, sediment, microbiotic and aquatic systems (Vig *et al.* 2003; Giller *et al.*, 2009; El-Sadaawy *et al.*, 2013; Hou *et al.*, 2013).

Exchangeable forms of metals are thought to be the most bioavailable to plants (Cajuste *et al.*, 2000; Zhang *et al.*, 2006, 2010). The soil extraction with ammonium acetate and the subsequent determination of content of extracted exchangeable metal cations is the most common method for determining the metal's bioavailability in soils (Xing-chu *et*

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\*Email: ptomoff@gmail.com

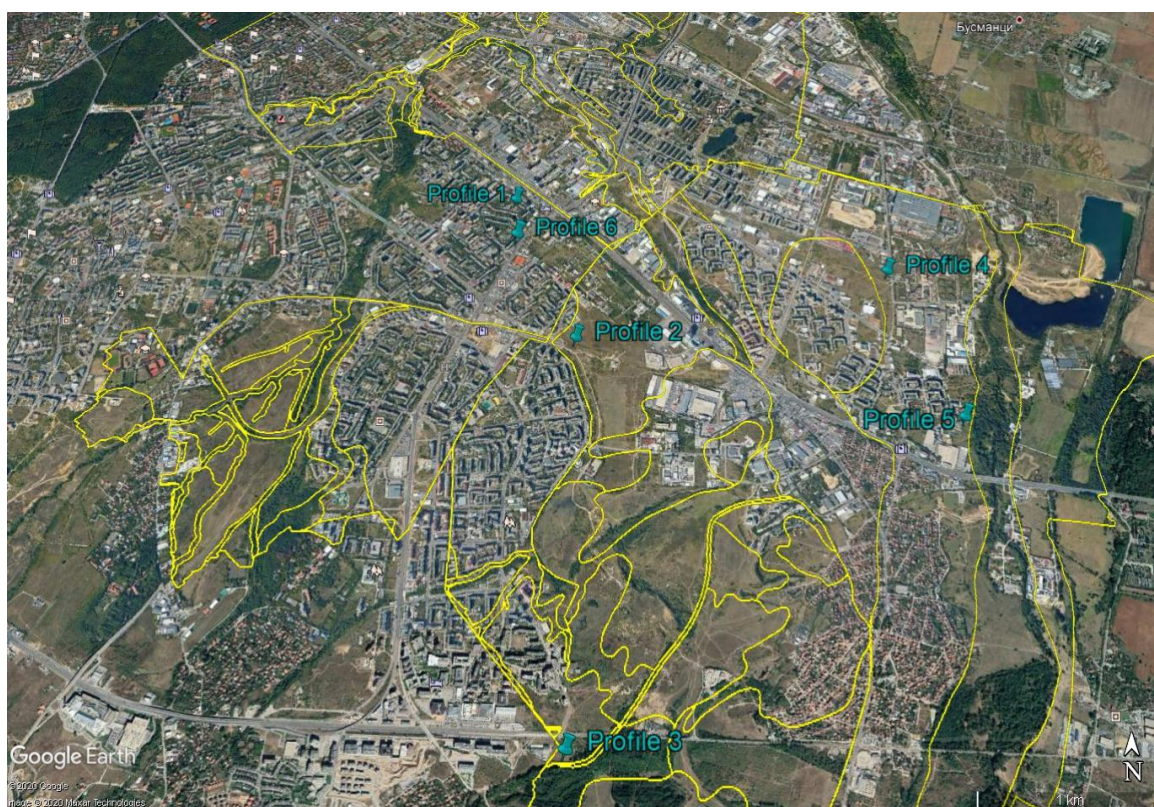
*al.*, 1985; Anjos *et al.*, 2012; Tsoleva *et al.*, 2014). This method was also used in the present study to determine the contents of bioavailable trace elements in soils in order to assess their toxicity and translocation in plants inhabiting urban areas with varying degrees of urbanization. The content of essential nutrition elements was also measured with a purpose to reveal the competition mechanisms controlling absorption of trace elements by plants.

## Materials and Methods

Six soil varieties located in the south-eastern part of Sofia city were investigated (Figure 1). All soils are located in green areas of recreational importance and are modified to various degrees as a result of urbanization.

elements was determined after sample mineralization with aqua regia (ISO 11466:1995) via EAAS (ISO 11047:1998) on a Perkin-Elmer 2100. Readily soluble and plant available trace element contents were determined in 1 M  $\text{NH}_4\text{OAc}$  (pH 7) extracts (Sheldrick, 1984; Borge, 1997; Pansu and Gautheyrou, 2006). Soil: extractant ratio was modified in order to increase the measurement sensibility and was fixed to 10 g soil: 200 mL – 1 M  $\text{NH}_4\text{OAc}$ .

Main mineral nitrogen forms were quantified via Bremner and Keeney procedure (1965), and available potassium and phosphorus – by the method of Ivanov (1984). In brief last includes: extraction of 2 g soil with 50 mL mixed solution (of 0.15 M calcium lactate, 0.2 M ammonium acetate, 10 mL 10 N hydrochloric acid and 12 mL glacial



**Figure 1: Soil map of the Sofia city and location of sampled pedons**

The soil survey was consistent with BDS ISO 18400-205 protocol (2019). The points, where soils were probed were localized with GPS Trimble (Juno SB) and georeferenced with ArcPad 10.2 software. The classification of soils was done according to the principles of the Bulgarian (Koinov *et al.*, 1968) and WRB (2015) classification schemes.

Soil samples were pre-treated according to the BDS ISO method (11464:2012). The content of ferromagnesian trace

acetic acid to reach pH 4.2) for 1 hour on shaker. Potassium was determined directly in extracts via flame photometer. Phosphorus was measured calorimetrically after dilution of extracts with deionized water 1: 2 and addition of 8 mL colouring reagent (1.056 g of ascorbic acid was dissolved in 200 mL of Murphy-Riley reagent).

The content of trace elements in plant samples were also determined by the method of atomic absorption



spectrophotometry after dry incineration at 500° C and dissolving the residue with 20% HCl upon heating (Milcheva and Brashnarova, 1975).

The content of ferromagnesian trace elements was estimated by two coefficients widely used in geochemistry and statistics:

- Coefficient of concentration (Kc) – reflects the ratio between the element content in studied soils and in Bulgarian soils based on the mean values provided by Atanasov *et al.* (2009).

- Coefficient of variation (V) to evaluate the degree of homogeneity of an element distribution according to equation 1:

$$V = \frac{s}{x} \cdot 100 \quad (1)$$

where

S is a standard deviation; x - the mean element content in studied soils.

The V values in the range of 10-12% show homogeneous distribution of the element, 12-30% slight heterogeneity and > 30% strong heterogeneity. If it is assumed that the slight inhomogeneity is due to natural geological and geochemical processes, then only values above 30% can be interpreted because of modern processes of redistribution.

## Results and Discussion

### 1. Distribution of main biogenic and toxic elements in soils

Considering morphogenesis, the studied soils can be divided into four groups.

#### 1.1. Buried soils (profile sequence disorder)

- Profile 1: Urbic Technosol (Humic, Transportic, Eutric, Loamic) over Pellic Vertisol (Chernic, Endocalcaric), corresponding to the Bulgarian unit anthropogenically overlapped moderately leached Smolnitsa, deep, heavy sandy clayey.

#### 1.2. New soils

- Profile 2: Urbic Technosol (Mollic, Transportic, Calcaric, Amphyskeletal) or Anthropogenic soil, moderately deep, sandy loam, moderately stony.

#### 1.3. Soils with an undisturbed profile organization

- Profile 3: Chromic Endocalcaric Luvisol (Differentic, Profondic, Humic, Clayic) or moderately leached Cinnamonic forest soil, sandy loam, slightly eroded.

- Profile 4: Hypereutric Fluvisol (Somerimollic, Loamic) - Alluvial soil, moderately deep, slightly stony.

- Profile 6: Pellic Vertisol (Mollic, Hypereutric, Profundifumic) - strongly leached Smolnitsa, super deep, heavy sandy clayey.

### 1.4. Cultivated soils (grassed areas by citizens)

- Profile 5: Hypereutric Fluvisol (Pachic, Epiclayic, Endoloamic) - Alluvial meadow soil, very deep.

Despite the reported anthropogenic impacts, studied soils are not contaminated with heavy metals (Cr, Zn, Pb, Cu, Ni and Co) according to maximum permissible concentrations (MPC) introduced by Ordinance No. 3 (Table 1). Content of studied trace elements is close to their background values in Bulgarian soils and decreases in the following order according to the average values: Mn (561.0 mg kg<sup>-1</sup>) > Cu (37.7) > Zn (37.9) > Cr (20.9) > Pb (20.4) > Ni (15.4) > Co (15.3 mg kg<sup>-1</sup>). The content of Mn, Cu, Zn and Pb is much lower than those obtained from Uzunov *et al.* (1996) during the study of Sofia soils, located to the north and east of studied area: Mn 2659,0 mg kg<sup>-1</sup>, Zn 303,0 mg kg<sup>-1</sup>, Cu 168,0 mg kg<sup>-1</sup> and Pb 137.0 mg kg<sup>-1</sup>. Still, the only one element found in concentrations above background value (24 mg kg<sup>-1</sup>) in all studied soils is copper. It is also the element with the lowest coefficient of variation (21.7%), which suggests that copper was not distributed through the anthropogenic activity in studied region.

The lack of accumulation of Mn, Zn, Cr and Ni is confirmed by the concentration coefficients (Kc) which are < 1.0. Keeping in mind that some authors accept Kc values up to 2 because of natural fluctuations (Müller, 1969; Uzunov *et al.*, 1996) all elements can be considered naturally present in soils. Soil genesis and registered reorganizations also reveal a natural pattern of distribution linked to geochemical features of parent materials rather than contamination. Some of these soil-forming materials are richer in cobalt, such as materials covering leached Smolnitsa (average 1.5-fold) and in manganese - materials constructing Anthropogenic soil (2-fold). The extremely heterogeneous distribution of these elements (V > 60%) on relatively small size of studied area can be used as an indicator of geochemical remodelling of soils in the south-eastern part of Sofia city.

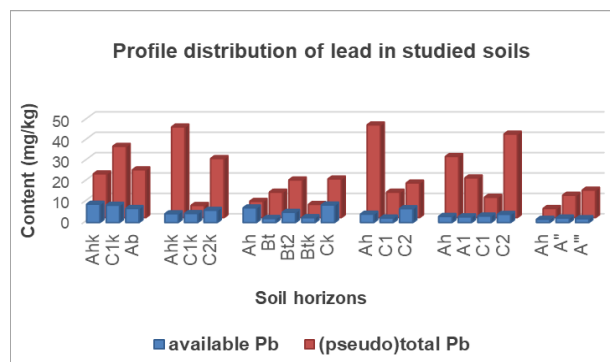
Lead is also strongly fluctuating element (V = 60.7%) and shows several distributional trends (Table 1, Figure 2). Its total content unevenly varies across all profiles, indicating that soil formation processes do not affect Pb distribution and again emphasizing the role of geochemical features inherited from parent materials.





**Table 1: Total content of trace elements in studied soils (mg kg<sup>-1</sup>)**

	Mn	Kc	Zn	Kc	Cu	Kc	Fe
min	50.0	0.1	16.5	0.2	24.0	1.0	2125.0
max	1450.0	2.0	69.0	1.0	52.5	2.2	29350.0
mean	561.0	0.8	37.9	0.5	37.7	1.6	16344.0
SD	385.8	-	15.5	-	8.2	-	8818.6
V, %	68.8	-	40.8	-	21.7	-	54.0
Backg.	740.0	-	69.0	-	24.0	-	n.d.
MPC	n.d.	-	400	-	300	-	
	Cr	Kc	Pb	Kc	Ni	Kc	
min	4.5	0.1	4.5	0.3	6.0	0.2	
max	36.0	0.8	45.5	2.5	26.0	0.9	
mean	20.9	0.5	20.4	1.1	15.4	0.5	
SD	6.2	-	12.4	-	5.5	-	
V, %	29.7	-	60.7	-	35.6	-	
Backg.	43.0	-	18.0	-	30.0	-	
MPC	200		200	--	100	-	

**Figure 2: Lead content by depth of studied soils (from left to right profiles 1, 2, 3, 4, 5 and 6)**

Both total and mobile lead (Table 1, 2) are related to the sand fractions ( $r = 0.4$  and  $0.6$ , respectively) considering the data on particle size distribution provided by Tsoleva and Tomov (2018). An equally significant negative correlation with clay fractions indicates that sorption is not the leading mechanism for Pb accumulation in urban soils, and hence the mineral forms are of major importance. This trend explains why Smolnitsa is the soil with the lowest content of total and mobile lead, which seems quite unexpected in view of soil proximity to a congested highway.

Significant correlation of available Pb and nitrogen ( $r = 0.56$ ) simultaneously with correlation between available Pb and pH ( $r = 0.45$ ) suggests that lead can occur in the form of lead dinitrate. The correlation with available nitrogen is most pronounced in profile 3 ( $r = 0.70$ ) and in profile 6 ( $r = 0.50$ ) where probably Cr provides the coupling with nitrogen: Pb - Cr ( $r = 0.87$ ), Cr -  $\text{NH}_4\text{NO}_3$  ( $r = 0.87$ ).

Having in mind the link  $\text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$  ( $r = 0.87$ ), the presence of coordination complex of Cr with Pb and ammonia ligands (as Cr (III) nitrate is very soluble in water) may be expected in profile 6.

Another form of lead is phosphate. Pb- $\text{P}_2\text{O}_5$  bond in profile 1 ( $r = 0.72$ ), profile 2 ( $r = 0.59$ ) and profile 3 ( $r = 0.56$ ) is not always accompanied with  $\text{P}_2\text{O}_5\text{-H}_2\text{O}$  link (profile 1 is exception) so lead phosphate  $\text{Pb}_3(\text{PO}_4)_2$  could also be present. It has been identified as a carcinogen (Wright, 2003) and could be extremely dangerous. In profile 1 Pb- $\text{K}_2\text{O}$  link ( $r = 0.62$ ) can be realized by potassium plumbate, but in fact this correlation is observed only here.

In Alluvial soils (profiles 4 and 5) available Pb mainly correlated with available Cu and Ni content or Cu, Ni and Zn content revealing possible substitution reactions and competitive mechanism of Pb retention in soils.

In surface horizons which have the greatest biological importance, content of mobile lead does not exceed the content in soil-forming materials, indicating that, for the time being, there is a balance between the processes of accumulation and migration of lead. Considering the toxicity threshold value of  $4 \text{ mg kg}^{-1}$ , determined by Chapman (1971) for Pb extracted with  $\text{NH}_4\text{OAc}$ , lead toxicity can be expected in two soils (Urbic Technosol and Anthropogenic soil) and in surface horizons of other two soils - moderately leached Cinnamonic forest soil and Alluvial soil (profile 4).

The other biogenic trace elements (Fe, Zn, Mn and Cu) are found in low bioavailable amounts (Table 2), which



**Table 2: Content of bioavailable nutritious and pedogenic elements in studied soils**

Horizons	pH H <sub>2</sub> O	$\Sigma\text{NH}_4+\text{NO}_3$ Mg kg <sup>-1</sup>	P <sub>2</sub> O <sub>5</sub> Mg 100 <sup>-1</sup> g	K <sub>2</sub> O Mg 100 <sup>-1</sup> g	Mn Mg kg <sup>-1</sup>	Zn	Cu	Fe	Cr	Pb	Ni	Co
<b>Profile 1. Urbic technosol over pellic vertisol</b>												
A <sub>hk</sub>	7.1	23.6	28.5	62.3	3.7	6.0	0.2	1.2	1.3	9.0	0.1	0.1
C <sub>k</sub>	7.3	31.7	2.0	12.1	3.6	6.6	0.3	2.0	0.9	8.5	0.3	0.1
A <sub>b</sub>	7.0	42.0	0.2	17.1	1.8	4.3	0.1	1.1	1.1	6.9	0.8	0.1
mean	7.1	32.4	10.2	30.5	3.0	5.6	0.2	1.4	1.1	8.1	0.4	0.1
SD	0.2	9.2	15.8	27.7	1.1	1.2	0.1	0.5	0.2	1.1	0.4	0.0
<b>Profile 2. Urbic Technosol</b>												
A <sub>hk</sub>	7.3	34.0	1.2	28.8	8.9	4.7	0.4	1.2	1.0	4.3	0.1	0.1
C <sub>1k</sub>	7.5	25.9	4.5	8.8	8.4	4.6	0.3	3.0	1.5	4.4	0.1	0.3
C <sub>2k</sub>	7.5	30.5	4.7	9.8	7.6	4.8	0.6	3.2	1.0	6.0	0.9	0.3
mean	7.4	30.1	3.5	15.8	8.3	4.7	0.4	2.5	1.2	4.9	0.4	0.2
SD	0.1	0.4	2.0	11.3	0.7	0.1	0.2	1.1	0.3	1.0	0.5	0.1
<b>Profile 3. Chromic endocalcic luvisol</b>												
A <sub>h</sub>	5.9	35.1	1.1	29.5	4.3	5.7	0.1	2.6	0.8	7.2	0.5	0.1
B <sub>t</sub>	6.1	25.9	0.2	20.8	2.4	5.0	0.1	2.9	1.7	2.0	0.1	0.4
B <sub>t2</sub>	7.1	29.4	0.2	22.2	3.8	5.6	0.2	2.0	1.5	5.0	0.4	0.3
B <sub>tk</sub>	7.3	29.4	4.0	25.1	6.5	4.1	0.2	1.6	0.9	2.4	0.1	0.1
C <sub>k</sub>	8.0	30.5	10.5	19.5	20.8	4.3	0.4	2.8	0.8	8.6	0.8	0.1
mean	6.9	30.1	3.2	23.4	7.6	4.9	0.2	2.4	1.1	5.0	0.4	0.2
SD	0.9	0.3	4.4	4.0	7.5	0.7	0.1	0.6	0.4	2.9	0.3	0.1
<b>Profile 4. Hypereutric fluvisol (somerimollic, loamic)</b>												
A <sub>h</sub>	6.3	20.2	5.3	18.9	2.6	6.4	1.1	1.7	1.9	4.1	0.1	0.1
C <sub>1</sub>	6.5	10.4	1.7	10.2	3.0	4.7	1.3	1.5	0.8	2.2	0.1	0.2
C <sub>2</sub>	6.7	8.6	0.3	13.3	1.0	6.9	2.8	1.1	1.4	6.8	0.3	0.1
mean	6.5	13.1	2.4	14.1	2.2	6.0	1.7	1.4	1.4	4.4	0.2	0.1
SD	0.2	0.6	2.6	4.4	1.1	1.2	0.9	0.3	0.6	2.3	0.1	0.1
<b>Profile 5. Hypereutric fluvisol (pachic, epiclagic, endoloamic)</b>												
A <sub>h</sub>	6.1	9.8	16.0	44.3	1.5	5.0	0.2	1.8	0.8	3.0	0.3	0.1
A <sub>1</sub>	6.0	10.9	5.5	46.0	1.3	5.2	0.3	1.9	1.0	2.8	0.1	0.1
C <sub>1</sub>	6.0	8.6	4.8	29.4	1.4	5.1	0.3	2.0	0.9	3.2	0.1	0.1
C <sub>2</sub>	6.0	10.9	4.3	10.5	1.2	5.1	0.7	1.2	1.0	4.0	0.5	0.1
mean	6.0	10.1	7.7	32.6	1.4	5.1	0.4	1.7	0.9	3.3	0.3	0.1
SD	0.0	0.1	5.6	16.5	0.1	0.1	0.2	0.4	0.1	0.5	0.2	0.0
<b>Profile 6. Pellic vertisol</b>												
A <sub>h</sub>	6.7	9.2	20.7	33.5	2.8	5.6	0.4	2.0	0.9	1.6	0.3	0.1
A <sub>''</sub>	6.7	11.5	2.3	33.6	2.9	4.7	0.3	1.8	1.0	2.2	0.3	0.1
A <sub>'''</sub>	6.8	13.8	1.9	32.9	2.4	4.6	0.5	1.5	1.0	1.9	0.2	0.1
mean	6.7	11.5	8.3	33.3	2.7	5.0	0.4	1.8	1.0	1.9	0.3	0.1
SD	0.1	0.2	10.7	0.4	0.3	0.6	0.1	0.3	0.1	0.3	0.1	0.0

could lead to their deficiency. Depending on the mean values of acetate extractable concentrations studied elements can be arranged in the following groups:

- Concentrations below 0.5 mg kg<sup>-1</sup> (average for all soils): nickel (0.31 mg kg<sup>-1</sup>) and cobalt (0.15 mg kg<sup>-1</sup>).

Nickel and Co are similar in both chemical and physiological properties and usually occur in small bioavailable amounts in soils - 1 mg kg<sup>-1</sup> Ni and 0.05 - 2 mg kg<sup>-1</sup> Co but levels < 0.1 mg kg<sup>-1</sup> Co are considered deficient (Mengel *et al.*, 2001), so Co content is at the brink of shortage in profiles 1, 5 and 6.



- Concentrations between 0.5 - 1.0 mg kg<sup>-1</sup>: copper (0.51 mg kg<sup>-1</sup>). The critical level of 0.2 mg Cu kg<sup>-1</sup> soil for the adequate growth of cereal crops is suggested by Follett and Lindsay (1970) and the toxic level of 8 mg.kg<sup>-1</sup> for Cu extracted with NH<sub>4</sub>OAc by Davidescu *et al.* (1988). Except for Cinnamonic soils studied urban soils are able to provide proper Cu cycling within soil-plant system. Although the low amounts are largely due to the chemical form of Cu and its presence in organic complexes that cannot be completely extracted with ammonium acetate (Tsolova *et al.*, 2014), there is substantial evidence for the decreased Cu extractability with time (Oorts, 2012).

- Concentrations between 1.0 - 2.0 mg kg<sup>-1</sup>: iron (1.91 mg kg<sup>-1</sup>) and chromium (1.1 mg.kg<sup>-1</sup>). According to Lindsay (1974) most agricultural crops require less than 0.5 µg g<sup>-1</sup> available Fe in the soil and studied soils ensure these amounts. Although soil Cr is largely unavailable to plants because it occurs in relatively insoluble compounds, the levels found in urban soils of Sofia cannot be considered insufficient for normal plant growth (Mengel *et al.*, 2001).

- Concentrations between 4.2 - 5.2 mg kg<sup>-1</sup>: manganese (4.38 mg kg<sup>-1</sup>), lead (4.58 mg kg<sup>-1</sup>) and zinc

(5.19 mg kg<sup>-1</sup>). The critical deficiency level of Mn for most plant species vary between 10 and 20 mg Mn kg<sup>-1</sup> in dry matter of mature leaves. Having in mind that ammonium acetate extractable Mn correlated best with Mn deficiency, plant Mn, and response to treatment these levels could be observe when available Mn is < 1.2 mg kg<sup>-1</sup> (Mengel *et al.*, 2001). Such low values are not typical of studied urban soils but still occur in deep horizons of Alluvial soils (profile 4 and 5). The critical levels for available Zn are toxicity level 43 mg kg<sup>-1</sup> (Davidescu *et al.*, 1988) and deficiency level for most crops between 0.5-2.0 to 3.0 mg kg<sup>-1</sup> (Sims and Johnson, 1991). Since none of these values are established, studied soils should be considered well supplied with available Zn.

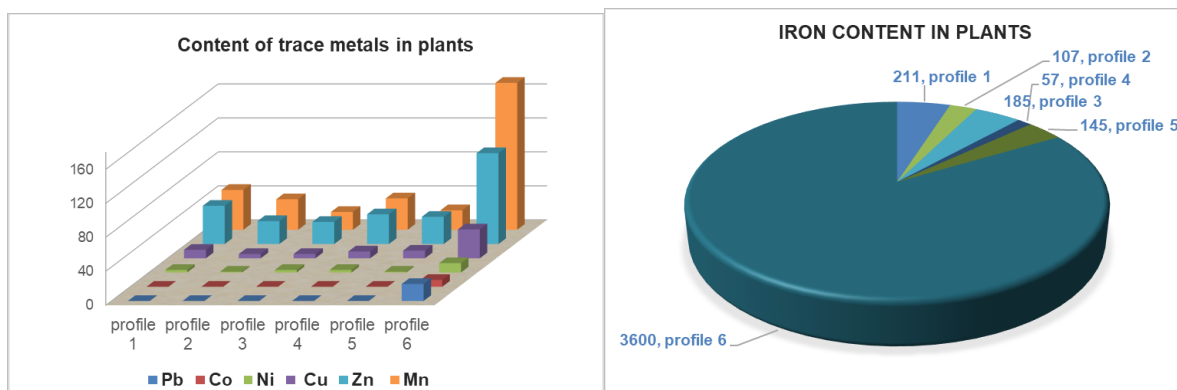
## 2. Translocation of studied trace elements in plants

Plant samples consist of dominant species which were analysed separately or as aggregate sample when plant communities are very diverse (Table 3).

According to plant analysis and mean values, content of elements decreases in the following order: Fe (717.5 mg kg<sup>-1</sup>) < Mn (56.2 mg kg<sup>-1</sup>) < Zn (45.3 mg kg<sup>-1</sup>) < Cu (11.8 mg kg<sup>-1</sup>) < Ni (3.7 mg kg<sup>-1</sup>). Pb and Co prevail in concentrations

**Table 3: Dominant plant species in studied urban ecosystems**

Soil type	Plant species
Technosol over Vertisol - profile 1	<i>Poa pratensis</i>
Technosol – profile 2	Aggregate sample of <i>Dactylis glomerata</i> , <i>Lotus corniculatus</i> L., <i>Leontodon</i> and forbs
Luvisol – profile 3	Aggregate sample of <i>Sesleria</i> , <i>Agrimonia eupatoria</i> and forbs
Hypereutric Fluvisol – profile 4	Aggregate sample of <i>Apera spica-venti</i> , <i>Vicia tetrasperma</i> , <i>Poa pratensis</i> and forbs
Hypereutric Fluvisol – profile 5	Aggregate sample of <i>Trifolium campestre</i> , <i>Medicago lupulina</i> , <i>Trifolium pratense</i> , <i>Vicia lutea</i> , <i>Achillea millefolium</i> agg., <i>Dactylis glomerata</i> and <i>Poa pratensis</i>
Vertisol – profile 6	moss



**Figure 3: Content of trace elements in plant samples (mg kg<sup>-1</sup>)**



$< 1 \text{ mg kg}^{-1}$  and only in moss sample are found in detectable amounts (Figure 3). Considering available Pb toxic content in profiles 1 - 4 and low amount in plants it might be accepted that plant communities developed there slightly accumulate Pb (Table 3; Figure 3) - its content in pasture grasses is normally about 2 to 3  $\text{mg kg}^{-1}$  dry matter (Mengel *et al.*, 2001). The bioavailable cobalt content is also low ( $0.15 \text{ mg kg}^{-1}$  average), although studied soils contain more than 4  $\text{mg kg}^{-1}$  Co and cannot be considered as cobalt-deficient (Boikat *et al.*, 1985). Many authors find that pasture grasses are a poor source of cobalt and accumulate insignificant amounts, averaging to  $0.15 \text{ mg kg}^{-1}$  (Minson, 1990).

The typical copper content in plants growing in uncontaminated soils varies from 4 to 20  $\text{mg kg}^{-1}$  (Kabata-Pendias and Pendias, 2001) but normally is less than 10  $\text{mg Cu kg}^{-1}$  dry matter (Mengel *et al.*, 2001). The values, obtained for higher plants ( $5\text{-}10 \text{ mg kg}^{-1}$ ), are close to those of Beeson *et al.* (1947), who found that copper content in 17 grass species from one habitat ranged from 4.5 to 21  $\text{mg kg}^{-1}$  without any signs of copper deficiency.

Nickel is extracted relatively fast and easy from the soil, and the absorption process by plants depends on its content in soil solution, especially in acidic soils (Berrow and Buridge, 1979). In the neutral to slightly alkaline reaction of studied soils, its accumulation in biomass seems not affected by pH and the values obtained are not low ( $1 - 3 \text{ mg kg}^{-1}$  in vascular plants). Normally the Ni concentration of plant material is about 0.1 to 5  $\text{mg Ni kg}^{-1}$  dry matter.

Iron plays an important role in soil chemistry, participating in a number of reactions that are reflected in soil morphology. As a result of interaction with other elements, it can significantly affect the availability of micro- and macro elements. The absorption of Fe by plants is also influenced by different properties of the soil. Several authors report anomalies in Fe uptake caused by high levels of heavy metals in soils such as Mn and Cu (Lutz *et al.* 1972; Kohno and Foy, 1983; Foy, 1984). There is a clear antagonism between Fe and Mn that can affect the mineral composition of plants to a great extent. For example, extensive research of Somers and Shive (1942) on soybeans found that plant growth was normal when Fe/Mn ratio in plant leaves was in the range of 1.5 to 2.6. When the ratio was outside this range, pathological symptoms had developed. A ratio over 2.6 prevails in urban soils, indicating an excess of Fe, while only in plant communities on Alluvial soil it is in the optimal range. Keeping this in mind, it can be assumed that Mn disorders will be manifested most strongly in plant communities grown on Cinnamonic forest soils (Fe/Mn 8.8). Many authors believe

that Mn deficiency is usually observed in alkaline or neutral soils and its toxicity - in acidic soils (Ganev, 1990; Mengel *et al.*, 2001; Nikova, 2009). Our study reveals that the highest content of available Mn is found in the most calcareous horizon of Cinnamonic soil. The strong nexus between Mn (total and available) and carbonates ( $r\ 0.85$  for total Mn and  $r\ 0.99$  for available) in this soil suggests that increasing of acidity will increase the solubility of  $\text{MnCO}_3$  and thus Mn availability although there are many other factors that affect Mn availability for plants (El-Jaoual and Cox, 1998). Thomas (1970) reviewed the literature and found out that most cereals contain 15 to 50  $\text{mg kg}^{-1}$  manganese. This is also the optimal range of concentrations beyond which the deficiency or toxicity symptoms might be observed.

The content of Zn in plants generally varies between 20 and 100  $\text{mg kg}^{-1}$  dry weight, depending on the species, the degree of plant maturity, the soil nature and, of course, the climate conditions. The level of Zn in Zn-deficient plants is low and usually in the range  $0\text{-}15 \text{ mg Zn kg}^{-1}$  dry matter although in some deficiency areas (i.e., British Guiana) Zn content varies from 18 to 42  $\text{mg kg}^{-1}$  in cattle grazing pasture (Legg and Sears, 1960). Values established in our studies fall in the range of concentrations considered typical ( $20$  to  $80 \text{ mg kg}^{-1}$ ) for various plants (Mengel *et al.*, 2001).

The biological absorption coefficient arranges the elements in the following order:  $\text{Zn } (1.20) \ll \text{Cu } (0.31) < \text{Ni } (0.24) < \text{Mn } (0.10) < \text{Fe } (0.04)$ . Due to low concentrations of cobalt and lead in vascular plants, these elements are not included in the order. Calculated coefficients generally symbolize the biomigration process and the ability of plants to extract different elements from soils. This process, as noted above, is multifactorial and complex, which is why the derived coefficient can only be considered the final and most general result of elements translocation and cycling.

## Conclusions

Anthropogenic activities accompanying the urbanization in studied areas do not provoke contamination of soils with Cr, Zn, Pb, Cu, Ni and Co but increase the spatial variability in Pb, Co and Mn content. Therefore, these elements can be used as an indicator of geochemical remodelling of urban soils in the south-eastern part of Sofia city. All studied elements prevail in background total and bioavailable concentrations in soils except available phosphorus which occurs in extremely low amount ( $< 7 \text{ g } 100^{-1} \text{ g soil}$ ) independently on the degree of soils alterations and lead. Geochemical features of soils are inherited from parent materials and soil genesis does not affect the distribution of studied ferromagnesian trace elements.



Biogenic elements expectedly predominated in surface horizons of soils.

Pb is found in toxic available concentrations in all four soil types but urban ecosystems (mainly consisting of *Dactylis glomerata*, *Lotus corniculatus* L., *Leontodon*, *Sesleria*, *Agrimonia eupatoria*, *Apera spica-venti*, *Vicia tetrasperma*, *Poa pratensis*, *Trifolium campestre*, *Medicago lupulina*, *Trifolium pratense*, *Vicia lutea*, *Achillea millefolium* agg., *Dactylis glomerata* and *Poa pratensis*) slightly accumulate lead and reduce its phytopathological effect.

Calculated statistical correlations reveal possible substitution reactions and competitive mechanism of Pb retention in soils (with ammonia, Cu, Ni and Zn). Nitrates and phosphates are the most common compounds of Pb, and therefore the presence of carcinogen lead phosphate  $/\text{Pb}_3(\text{PO}_4)_2/$  and soluble lead dinitrate  $/\text{Pb}(\text{NO}_3)_2/$  could be suspected.

Content of studied elements in the aerial parts of plants fall in the normal ranges cited in the literature for plurality of species. In fact, disorder of manganese uptake by plants rarely occurs within the normal range of concentrations of biogenic and pedogenic elements.

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