Environ Earth Sci (2016) 75:1211
DOI 10.1007/s12665-016-6012-8

ORIGINAL ARTICLE

Changes in soil and sediment properties due the impact of the urban environment

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Received: 24 March 2016 / Accepted: 20 August 2016

Abstract During our investigation, we analyzed the urban soils from stream banks and sediment of Rák Creek in the area of Sopron, Hungary. The aim of this work was the determination of the anthropogenic influence on a given stream that flows through an urban area (in this case through the city). The assumption was that the streamflow becomes increasingly polluted with toxic elements as it passes through Sopron; we tried to determine the extent to which the stream is polluted. We had 72 urban soil samples at 36 points at 0–10 and 10–20 cm depths on 6 sub-catchments for analyzing the background pollution of Rák Creek. In addition, 6 soil samples from the bank and 12 sediment average samples were taken from the dead region and from the thalweg as well. We analyzed the physical and chemical parameters as well as the heavy metals (e.g., Cd, Co, Cu, Pb, Zn and Ni) in all of the samples. Two element fractions, the total (HNO_3+H_2O_2-extractable) and the available (NH_4-acetate+EDTA-extractable) were used for element determination. Toxic elements were measured by ICP-OES in the urban soils and the sediments as well. Urban soils of sub-catchments confirmed the following tendency. On the investigated creek points, the Co and Ni values were below the natural background limits (Co_{total} 4.90–14.53 mg kg^{-1}, $Co_{available}$ 0.64–3.12 mg kg^{-1}; Ni_{total} 10.77–24.61 mg kg^{-1}, $Ni_{available}$ 0.75–3.21 mg kg^{-1}). Cu_{total} content was low except in the case of GYORI point. Pb_{total} were under the pollution limit, but $Pb_{available}$ were higher than the suggested pollution limit (>25 mg kg^{-1}) in the sediment of thalweg and in the soil of the creek bank at the GYORI site. Summarized, GYORI point was the most polluted; this is also confirmed by the enrichment factor (EF). EF for Pb and Zn increased as we moved toward the city. Based on the investigated properties, there were significant differences in heavy metals between the urbanized and non-urbanized areas. The concentrations of heavy metals were higher in the dead region than in the thalweg except for the GYORI samples. According to our results, the city affects the stream and its influence appears in the values: as soon as the stream reaches the city, most of results increase. Therefore, the degree of heavy metal contamination depends mainly on land use.

Keywords Heavy metals · Sediment contamination · Soils of creek banks · Water quality

Introduction

Populated areas have become increasingly important in ecosystems; soils play several roles in these urban areas (Morel and Heinrich 2008). The activity of the working group (WG) on soils of urban, industrial, traffic, mining and military areas (SUITMAs) proves that urban systems differ greatly and are more impaired than the natural system from which they originate (Morel et al. 2015). In Hungary, soil pollution was determined in soils of the capital city in the middle of the 80s by Kovács and Nyári (1984). Because of the increase in environmental sustainability, some of the larger universities have started to investigate the heavy metal content of soils of their seats

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(Sándor and Szabó 2014; Puskás and Farsang 2009; Szolnoki et al. 2013; Horváth et al. 2015).

In the case of Sopron, topsoil (0–5 cm) next to urban trees was analyzed several years ago (Varga et al. 1999) and there exists a city-wide investigation that covers the whole settlement by Horváth et al. (2015).

Heavy metals in soil and sediment may exist as result of the chemical leaching of bed rocks, runoff and water drainage from the surroundings of the stream (banks, subcatchments), and emission of industrial and urban wastewaters. Investigation of sediments has been widely used to find contamination sources and to monitor contaminants in case of streams (Soares et al. 1999; Müller et al. 1994). Heavy metals present in watercourses appear in different chemical forms or ways of binding (Rauret 1998; Pickering 1986). The sediments show a high capacity to accumulate and integrate the low concentrations of trace elements in water through time. The presence of heavy metals in sediments allows for the determination of metals even when the levels in water are extremely low (Soares et al. 1999; Luoma and Davis 1983; Horowitz 1985). Heavy metals in soil and sediments cause potentially adverse health effects to the ecosystem through the various routes by which sediment metals reach the biota (Bryan and Langston 1992; Dickinson et al. 1996; Poulton et al. 1996; Fatoki and Mathabatha 2001; McCready et al. 2006; Chen et al. 2007).

Toxic elements (e.g., Cu, Pb and Zn) are especially detrimental to human health. Abundant literature exists about pollution of complete ecosystems (Zöttl 1987; Szabó et al. 2008; Cuypers et al. 2012). The behavior of toxic elements is influenced mostly by the geochemical background in case of total element fraction, besides the physical–chemical properties have much more impact on available or mobile soil element fractions (Rékási and Filep 2012). Several studies have been carried out on the amount of toxic elements in soils close to public roads in Hungary, where the deposition of pollution was influenced by distance and time (Kovács and Nyári 1984; Zs et al. 2013). Heavy metals are mostly released by traffic. First, they spread in the air and then they reach the surface (Fiedler 1990) where they leach into the soil. Fuels contained lot of toxic heavy metals (e.g., Pb) in the past, and the Pb levels are still high in the soils of the city (Horváth et al. 2015). Nowadays heavy metals still can enter the environment through the corrosion of vehicle chassis and tire wear (Zn, Cu, Cd). Low amounts of elements are essential for living organisms (e.g., Cu, Co, Zn and Ni), but toxicity increases at high levels. Toxic element accumulation happens in the form of complexes (Zöttl 1987). Complex stability usually decreases with the acidification of the soil and making these pollutants available to urban plants (Horváth et al. 2015).

In 2011, our university engaged in a complex urban ecology project that focused on the impacts of urbanization as well as the impacts of industrial, agricultural and forest technologies on the natural environment. By the criteria of urban ecology, three Hungarian cities and their surroundings were chosen for the city-wide investigations; chemical, hydrological, pedological and GIS surveys were completed (Albert and Jancsó 2012). The aim of the project was to identify the changes in different processes (geology, location, history, abiotic factors) against—mostly—the same human impacts.

This study focused on the content of heavy metals in soil and sediment along the Rák Stream system in the city of Sopron. To demonstrate different degrees of contamination, samples were taken along the stream from undisturbed natural part and from urbanized sections. The basic hypothesis of our work was that differences in the accumulation of heavy metals in natural and urbanized areas exist.

Materials and methods

Sopron is located near the northwestern border of Hungary and has been inhabited since the prehistoric age. The studied area was the catchment of Rák Creek which flows through the Township of Sopron. Half of the catchment is located in the Sopron Hills, where the source of creek is located. The other part is situated in the Sopron Basin, where the majority of the city is located. The studied creek is nearly 19 km long, and it flows through Sopron for cc. 5 km (Gribovszki et al. 2012). The elevations of the catchment range are between 191 and 568 m above Baltic Sea level. The Sopron Hills (gneiss and mica schist) were formed during the Cambrian period. The city is covered by Neogene deposits (e.g., Badenian clay), but there are also gravel cover, glacial loam, loess sediment with recent (Holocene) alluvium (Dövényi 2010). The characteristic soil types are luvisols in the Sopron Hills and fluvisols in the basin, but in the town technosols (calcic) evolved along the creek (Charzyński et al. 2013; IUSS Working Group 2007).

Sample collection was carried out during the summer of 2015. From the catchment of the Rák Creek, 72 soil samples were collected from 36 points in depths of 0–10 and 10–20 cm (blue dots on Fig. 1). In addition, we collected 2 sediment samples (from thalweg and dead region) and 1 soil sample from the bank of the creek at 6 sampling points. Dead region is the part of the cross section which is located on both side of the stream, where the flow path is noticeable and the velocity is low. The thalweg is the path of deepest flow at the middle part of the cross section where the velocity is high (Gordon et al. 2004). Figure 1 shows

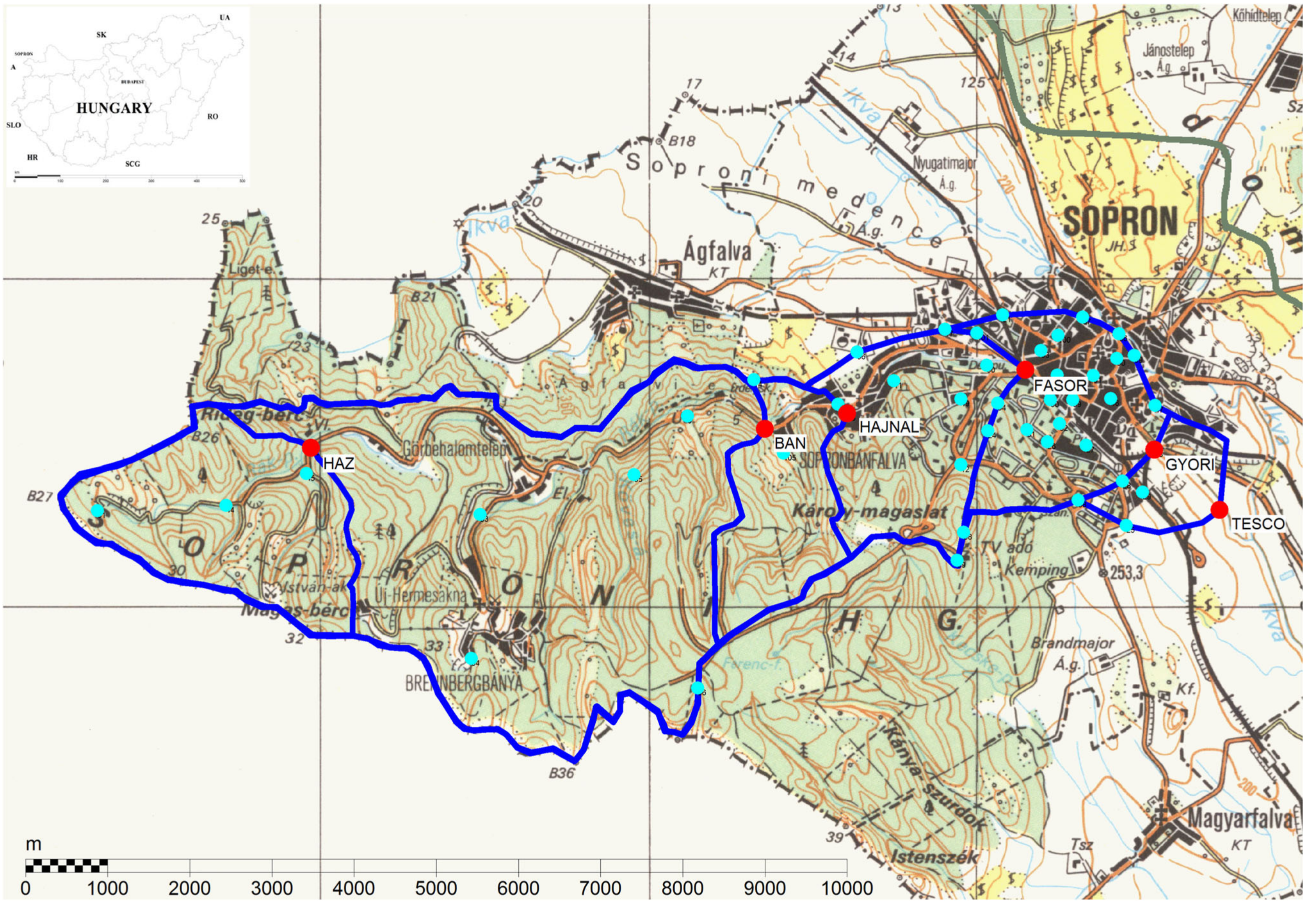

Fig. 1 Distribution of samples on the study area. (The *red points* are the sampling points next to the creek, the *blue points* are the soil samples from the sub-catchments)

the catchment of Rák Creek and the area of Sopron, where the sub-catchments classified into natural (*HAZ, BAN*), seminatural (*HAJNAL*) and urbanized (*FASOR, GYORI, TESCO*) areas.

Firstly, we made local descriptions about every sampling site, which were useful for evaluation of results. In case of urban soils (which gave a base about the background pollution of Sopron), we determined the following analysis in soil laboratory: soil pH, $CaCO_3$ content, texture/particle size distribution (MSZ-08-0205 1978; Stefanovits et al. 1999). Besides of acidity, we determined the fractions of the sediments by Van Reeuwijk (2002) as well.

For pollution designation, two element fractions had been measured. Twenty-four heavy metals were measured following the method of bioavailable (MSZ 21470-50 2006—NH_4-acetate+$EDTA_{soluble}$) element content, and pseudo-total element fraction was determined (MSZ 21470-50 2006—cc. 5 cm^3 HNO_3+2 cm^3 H_2O_2) in microwave Teflon bombs (MSZ 21470-50 2006) using ICP-OES. Altogether, 24 elements were measured (e.g., Hg, Cr, Fe, Mn and Sr), but we focused on the most common urban pollutants: Co, Cu, Ni, Pb and Zn. The statistical process was made by the R program and the DIGITERRA GIS system. Pearson multiple correlation analysis was applied to measure relationship between all observed and counted variables. Hmisc R package was used to calculate the connections of parameters.

The coordinates of the measurement points and the percentage of urbanized area of the sub-catchment are shown in Table 1. The first point, *HAZ,* is an outlet point of an undisturbed, totally forested catchment. The point, *BAN*, is on the border of the natural environment and urbanized area. Two small villages and some farm houses are on the watershed. The sampling point *HAJNAL* is inside the suburban area. Private houses with gardens are on the sub-catchment only. The *FASOR* point is at the end of the Erzsébet Public Garden. The creek flows in a 0.6-km-long artificial tunnel in one part of the sub-catchment. The sub-catchment is covered by mainly suburban areas with some sport grounds. The next point, *GYORI* is after the long tunnel (1.6 km) under the city. The creek flows in a tunnel all along the sub-catchment. The sub-catchment is the totally built-in downtown area. The last point *TESCO* is located in an industrial area. The whole sub-catchment of

Table 1 Coordinates of the measurement points

	TESCO	GYORI	FASOR	HAJNAL	BAN	HAZ
Catchment (km^2)	37.38	35.96	31.69	27.04	23.67	5.76
	TESCO-GYORI	GYORI-FASOR	FASORH-AJNAL	HAJNAL-BAN	BAN-HAZ	HAZ
Sub-catchment (km^2)	1.42	4.27	4.65	3.37	17.91	5.76
Urban (artificially modified) area	1.16	3.76	1.69	0.07	0.29	0.00
Agricultural land	0.26	0.15	0.91	0.50	1.23	0.00
Grassland	0.00	0.00	0.00	0.00	0.92	0.21
Forest and bushy area	0.00	0.36	2.05	2.80	15.47	5.55

A_w total watershed belongs to the sampling points, A_{sb} sub-catchment between the actual and upper sampling point (Gribovszki et al. 2012)

TESCO point is covered by an industrial area as well (Gribovszki et al. 2012). Regarding to all sampling points, the definition of sub-catchment in our study is differenced of sub-catchment which is associated with one sampling point.

In each sampling point, the geometry of 5 cross-sectional profiles (which are representative of the channel) and the velocity distribution were measured. The streambed materials were collected in all sampling points as well.

The velocity profiles were observed close to the stagnation (dead region) and at the thalweg in every cross-sectional profiles. In each verticals, the velocity profile was measured with NIVUS PVM PD (based on Doppler principle). The number of the measurement points in a given vertical depended on the water depth (60, 20 and 80 %; 15, 55 and 85 % of the depth).

Shear stress was calculated from the slope of the velocity profiles using the following equations.

$$\tau_o = \rho * (V_*)^2$$

$$V_* = \frac{b}{5.75}$$

where τ_o is the shear stress [N m^{-2}], ρ is a density of the water [kg m^{-3}], V_* is the shear velocity [m s^{-1}], and b is the slope of the logarithmic velocity profile (Gordon et al. 2004).

The bed material samples were collected by hand at the stagnation and at the thalweg within Rák Creek at 29 July 2015. We have collected 5–5 individual sediment samples from the thalweg and also from the dead region at each measuring section. From the 5–5 samples, 1–1 average thalweg and dead region sediment samples have been made on each measuring point. Furthermore, 1 soil sample from the bank of the creek was taken in each sampling point. Parallel water samples were also taken from every sampling point.

Metal contamination was detected using the calculation of EF (enrichment factor), which shows and differentiates between human-made and naturally occurring metal source concentrations (Chen et al. 2007). We choose Al as a reference element to normalize the measurements, because Al is a predominant content of sediments.

The definition of EF was determinate by:

$$\mathrm{EF} = \frac{\frac{X}{Al}\,\mathrm{sediment}}{\frac{X}{Al}\,\mathrm{crust}}$$

where crust is the abundant of elements in the continental crust.

Evaluation categories:

- EF < 1 indicates no enrichment
- EF < 3 minor enrichment
- EF = 3–5 moderate enrichment
- EF = 5–10 moderately severe enrichment
- EF = 10–25 severe enrichment
- EF = 25–50 very severe enrichment
- EF > 50 extremely severe enrichment.

The crust averages for the investigated metals studied by Taylor (1964).

Results and discussion

Urban soil samples were grouped regard naturalness of sub-catchments. The forest soils of the Sopron Hills mainly have low soil pH; therefore, the soils of *HAZ* and *BAN* sub-catchments were acidic (pH 4.8–5.5 on average). The soil pH is slightly acidic (pH 5.9 on average) in the *HAJNAL* region located in the suburban area of the city, but a sample with neutral pH also occurred. Calcium carbonate appears in samples. The soil pH of the 3 sub-watersheds in the city shows an increase toward the stream mouth. Most of the Sopron Basin is still covered with Badenian clay, but the predecessor of the Ikva Creek overlaid calcareous gravel and loess sediment in Holocene (Scönlaub 2000; Dövényi 2012). Nowadays, the high $CaCO_3$ content originates from building waste and artifacts (Horváth et al. 2015) in generally. So the geological processes and human activities resulted calcareous deposition in Sopron Basin, which influenced the soil pH (pH 6.2–7.8 on average) and $CaCO_3$ content (6–14 % $CaCO_3$). Artifact content was not typical in urban soil samples. The alkaline soil pH is favorable for heavy metal accumulation; therefore, we supposed the results of sediment samples from the township will confirm the same hypothesis. Texture was predominantly clayey (silt fraction 0.05–0.002 mm), which is made easier the binding of toxic metals to clay minerals also (Horváth et al. 2015).

The average water pH (see below on Fig. 4) ranged between 8.0 and 8.2. The values of pH increased from the upper part to the lower part of the stream. The sediments' pH increased toward the stream mouth as well. The sediments' pH was always higher in the thalweg than in the dead region. The conductivity of the water significantly increased from *HAZ* point (426.37 $\mu S\ cm^{-1}$) to *TESCO* point (966.79 $\mu S\ cm^{-1}$).

Along the stream system, the shear stress (Fig. 2a) and the velocity (Fig. 2b) were always higher in the thalweg than in the dead region (Fig. 2a, b). The velocity of the thalweg was significantly different from the dead region in the undisturbed, natural regions, while the velocity profiles of the two regions are more balanced in the urbanized areas.

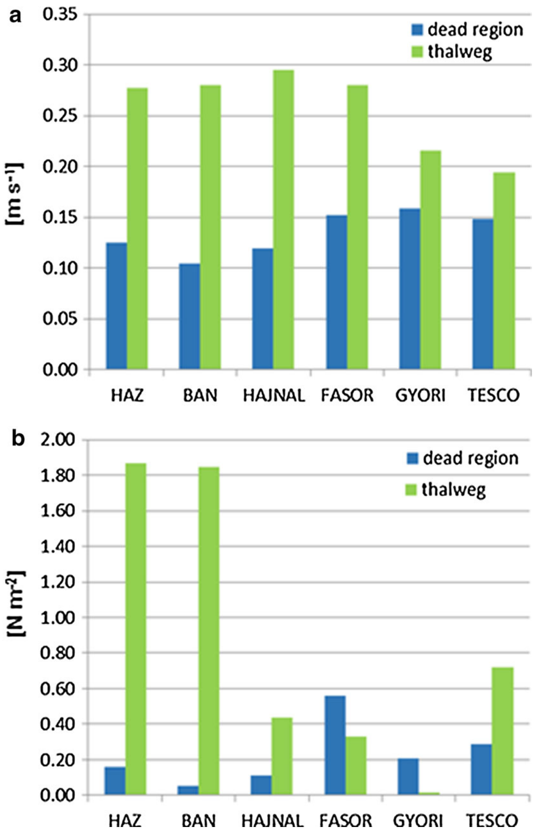

Fig. 2 Velocity (v [m s^{-1}]) of Rák Creek (**a**) and the shear stress [N m^{-2}] of Rák Creek (**b**)

The concentrations of heavy metals were smaller in the thalweg than in the dead region except for the *GYORI* samples. The larger heavy metals value of the thalweg in the case of point *GYORI* was caused by the relatively wide stream bed. The streambed possesses a braided characteristic; the horizontally velocity distribution in the cross section is uniform; typical dead region cannot be found here.

The concentrations of heavy metals of the sediments were lower in the sampling points of natural regions than in the sampling points of urbanized regions.

The changing of concentrations of zinc (Fig. 3a), copper (Fig. 3b) and lead clearly showed the effects of urbanization. The zinc and the copper contents of sediment were three times higher in the urbanized region than in the natural region. The lead concentration of sediment was five times higher in the disturbed part of the catchment than in undisturbed conditions.

The concentrations of toxic elements in the water were negligible for each studied sites even through higher heavy metals contents of the sediments inside the town. Consequently, the sediments showed a high capacity to accumulate and integrate the metals transported by the water. In the next part of the evaluation, the focus was on the impact of human activities along the river. There is a regressive tendency in the amount of heavy metals from natural to urbanized regions. The mean amounts of heavy metals in soil samples are always higher in the case of sub-catchment *GYORI* because of the land cover. The concentration of heavy metals is above the maximum allowable concentration or near that concentration in the case of the means of the *GYORI* soil samples (Fig. 3c, d). The mean of the soil samples was calculated from different data points (*TESCO* = 2; *GYORI* = 12; *FASOR* = 11; *HAJNAL* = 3; *BAN* = 5; *HAZ* = 3). There were more samples from the urbanized regions than the natural regions. The maximum allowable concentration was settled by Joint Decrees 6/2009. (IV. 14) KvVM-EüM-FVM and 10/2000. (VI. 2) KöM-EüM-FVM-KHVM) to specify the pollution limits for heavy metals in soils and water (Table 2). The Environmental Protection Agency (EPA) has guidelines for classifying sediments (Baudo et al. 1990), but we used the Hungarian standard, which is stricter. In addition, we took into consideration the suggested temporary pollution limits by Kádár (1998) for the results of the method of Lakanen-Erviö.

Before the investigation of the streamwater, we used an urban soil database for Sopron as background pollution. We separated the urban soil samples into sub-watersheds, and we classified the urban soils into catchment areas in order to get a picture of the environmental background

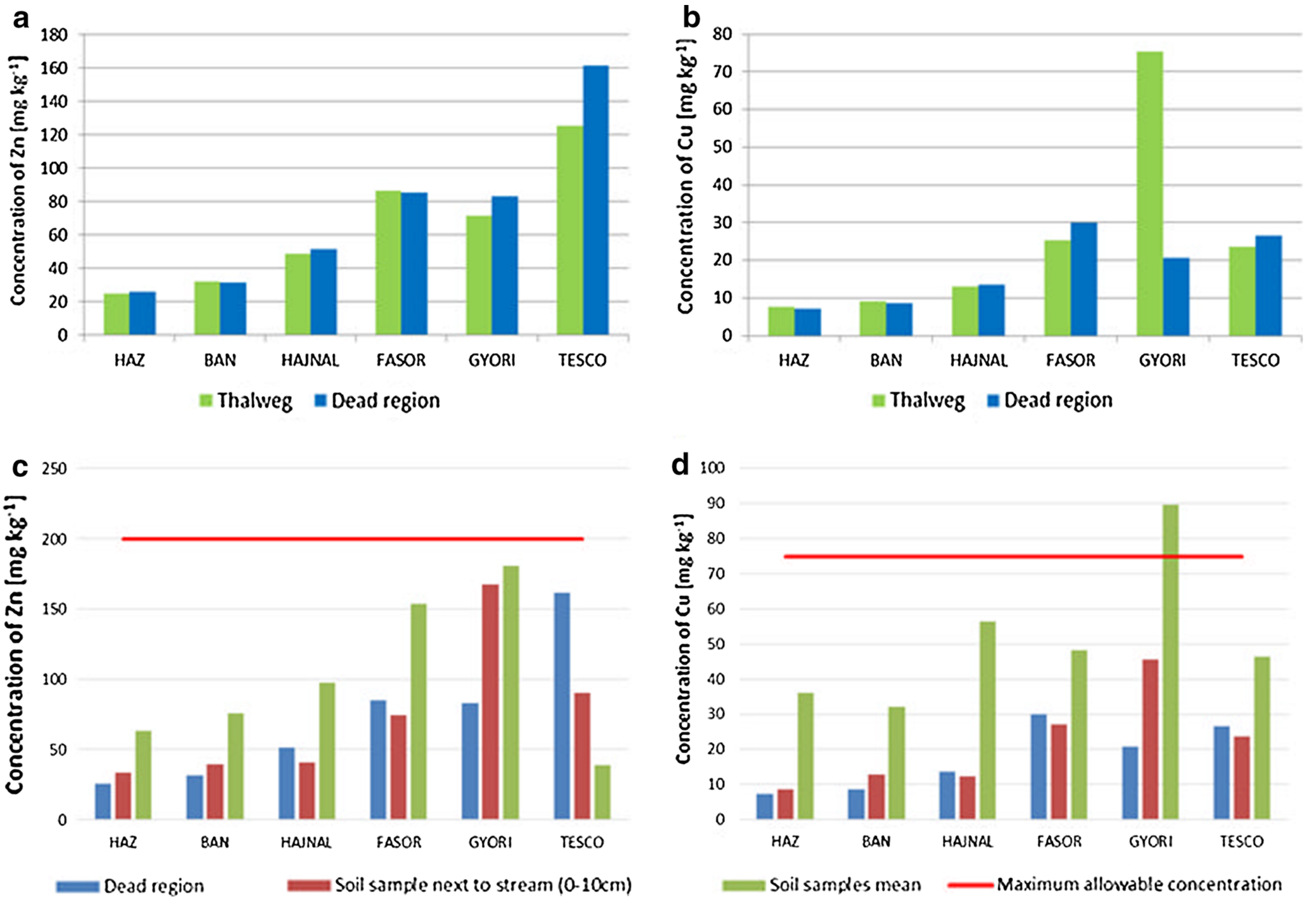

Fig. 3 Concentration of Zn_{total} (**a**) and Cu_{total} (**b**) in the sediment of dead region and thalweg. Comparison of Zn_{total} (**c**) and the Cu_{total} (**d**) content in dead region, in the soils of the creek bank and background pollution

Table 2 Pollution categories for available and for total content of heavy metals

		Available (mg kg^{-1})					Total (mg kg^{-1})				
		Co	Cu	Ni	Pb	Zn	Co	Cu	Ni	Pb	Zn
No pollution	Code	0–5	0–10	0–10	0–10	0–5	0–15	0–30	0–25	0–25	0–100
Maximum allowable concentration	A	5–10	10–40	10–20	10–25	5–20	15–30	30–75	25–40	25–100	100–200
Pollution limit	B	10–20	40–90	20–60	25–70	20–40	30–100	75–200	40–150	100–150	200–500
Intervention pollution limit (highly sensitive area)	C1	20–30	90–140	60–90	70–150	40–80	100–200	200–300	150–200	150–500	500–1000
Intervention pollution limit (sensitive area)	C2	30–40	140–190	90–120	150–300	80–160	200–300	300–400	200–250	500–600	1000–2000
Intervention pollution limit (less sensitive area)	C3	40<	190<	120<	300<	160<	300<	400<	250<	600<	2000<

values. Thus, when examining the stream, those factors that affect urban soils (runoff, infiltration, etc.) had to be taken into consideration (Horváth et al. 2015).

Based on pH values of the mentioned sampling points, Fig. 4 shows definite differences between natural (*HAZ, BAN*), seminatural (*HAJNAL*) and urbanized (*FASOR, GYORI, TESCO*) areas.

There were significant differences in toxic elements between the urbanized and non-urbanized areas. Co and Ni contents showed uniform distribution because their presence is evident due to the natural bedrock. Clastic sediments contain much Ni, Cr and Co which is primarily attributable to the deterioration of the migmatite of the eastern Alps (Ódor and Horváth 2003; Barna 2008).

Fig. 4 Comparison of thalweg dead region and soil result on same sampling point. *Orange* slightly acidic (5.5–6.5), *yellow* neutral (6.5–7.5), *light blue* slightly alkaline (7.5–8.2) pH, *red line* pH of water samples

The Co and the Ni values were below the natural background limits ($\text{Co}_{\text{total}} < 15$ mg kg^{-1}, $\text{Co}_{\text{available}} < 1.5$ mg kg^{-1}; $\text{Ni}_{\text{total}} < 25$ mg kg^{-1}, $\text{Ni}_{\text{available}} < 10$ mg kg^{-1}).

Cu content was low except in the case of *GYORI* point. At that sampling point, total Cu content was higher than 75 mg kg^{-1} at *GYORI* thalweg, which is the first intervention pollution limit. The deposition process was more typical on undisturbed soil surfaces. Usually, the copper accumulate in 0–5 cm depth of topsoil (Szegedi 1999).

In the natural plots, lead contents were low. But in the area of the city, the concentrations were higher mainly at *FASOR* and *GYORI* point, where anthropogenic effects and traffic are heavy. Pb_{total} were under the pollution limit (<100 mg kg^{-1}), but $\text{Pb}_{\text{available}}$ were higher than the suggested pollution limit (>25 mg kg^{-1}) in the sediment of thalweg and in the soil of creek bank on *GYORI* site. The impact of the city appears in results (Fig. 5).

Zinc levels were also low on the upper part of the creek. Zn_{total} were below the pollution limit (<200 mg kg^{-1}). Higher concentrations appear at *FASOR*, *GYORI* and *TESCO*. $\text{Zn}_{\text{available}}$ were higher than the suggested intervention pollution limit (>40 mg kg^{-1}) and pollution limit (>20 mg kg^{-1}) in the sediments and also in the soil of the creek bank (Fig. 6).

The atmospheric zinc emanates mainly from traffic and from tire wear. Plants can absorb zinc in larger amounts than they can absorb other elements; therefore, zinc is more mobile in soil–plant systems than other micronutrients (e.g., Cu or Co) (Alloway 2012; Kabata-Pendias and Pendias 2001; Tack 2010; Szolnoki et al. 2013). Also, it has a strong correlation with lead, which can easily accumulate along the roads. Thus, these two elements accumulate together in heavy traffic zones (Manta et al. 2002; Bretzel and Calderisi 2006). Copper concentration depends mostly on parent material in natural areas. Copper is very mobile in acidic pH, and the decrease in pH enhances this mobility. The appearance of copper is caused by the corrosion of copper pipes in urban areas. Accumulation of copper is typical near the surface mainly in undisturbed sites (Szegedi 1999). Generally Pb levels are high in the soils or sediments of Hungary despite the disappearance of leaded fuels. The pH is mostly alkaline in settlements; therefore, Pb accumulates in and binds to the humus of green areas.

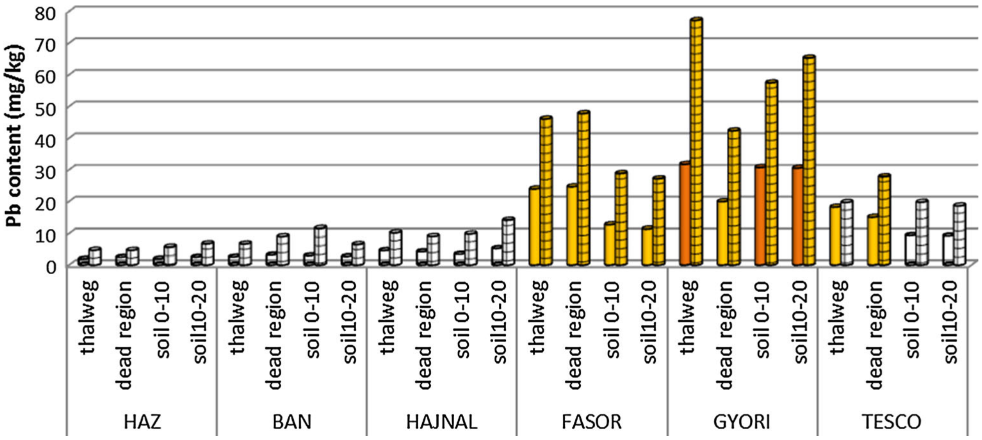

Fig. 5 Available (*empty column*) and total (*striped column*) lead content in the cross-sectional profiles. **a** Natural background limit: *yellow*. **b** Pollution limit: *orange*. **c** Intervention pollution limit: *red*

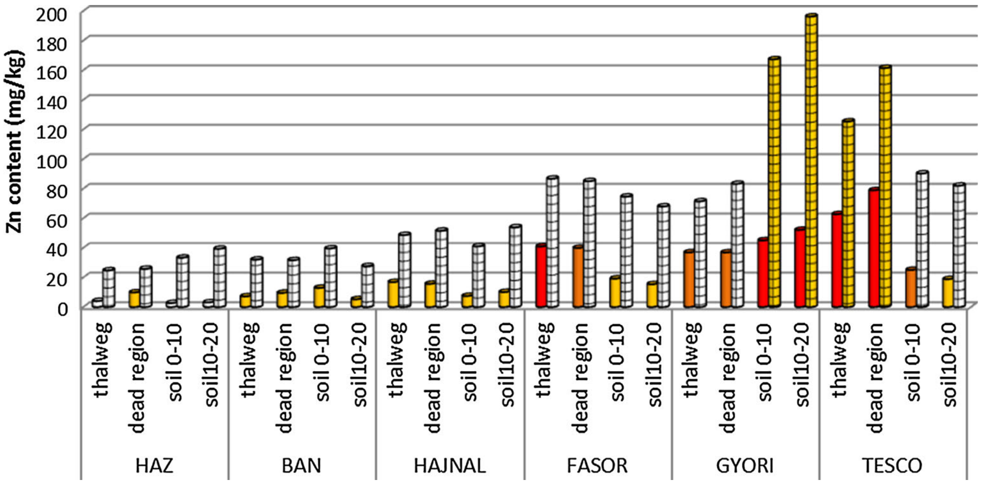

Fig. 6 Available (*empty column*) and total (*striped column*) zinc content in the cross-sectional profiles. **a** Natural background limit: *yellow*. **b** Pollution limit: *orange*. **c** Intervention pollution limit: *red*

Table 3 EF values of investigated metals for each cross-sectional profile at Rák Creek

		Co	Cu	Ni	Pb	Zn
HAZ	Dead region	0.3	0.2	0.2	0.6	0.6
	Thalweg	0.3	0.3	0.2	0.7	0.7
BAN	Dead region	0.4	0.3	0.3	1.5	0.9
	Thalweg	0.4	0.4	0.3	1.1	1.0
HAJNAL	Dead region	0.4	0.4	0.3	1.2	1.2
	Thalweg	0.4	0.4	0.3	1.3	1.1
FASOR	Dead region	0.4	1.1	0.4	7.8	2.5
	Thalweg	0.4	0.8	0.4	6.5	2.2
GYORI	Dead region	0.4	0.8	0.4	7.3	2.6
	Thalweg	0.4	3.2	0.5	14.5	2.4
TESCO	Dead region	0.4	0.9	0.3	4.1	4.2
	Thalweg	0.4	0.8	0.4	3.0	3.4

Table 3 presents the EF values of the metals studied in the thalweg and in the dead region. The content of Al was used to normalize the metals in sediments. The EF values were generally higher in dead region than in thalweg except of *GYORI* point. Lead had the highest EF values between the five metals investigated. The EF values for Pb were generally greater than five which indicates the moderate degree of Pb contamination inside the town. Zn had the second highest EF values among metals studied. Co, Cu and Ni exhibited the lowest in our EF values. The largest heavy metal values were in sampling point *GYORI*. The EF values for Pb and Zn increased as we moved toward city.

Chen et al. (2007), Kaushik et al. (2009) and Cevik et al. (2009) investigated the enrichment factor in their works as well. Chen et al. (2007) found a high degree of Hg and Cd contamination. The Cd, the Ni and the Cr enriched in the

Table 4 Values of Pearson's correlation coefficients and *p* values

	Cu_{total}	*p*	Pb_{total}	*p*	Zn_{total}	*p*	$Cu_{available}$	*p*	$Pb_{available}$	*p*	$Zn_{available}$	*p*
$Cu_{available}$	0.9064	0.0127	0.7815	0.0664	0.9498	0.0037	1.0000	NA	0.8063	0.0526	0.9430	0.0048
$Pb_{available}$	0.9234	0.0086	0.9948	0.0000	0.6192	0.1899	0.8063	0.0526	1.0000	NA	0.6395	0.1715
$Zn_{available}$	0.8167	0.0473	0.5908	0.2169	0.9950	0.0000	0.9430	0.0048	0.6395	0.1715	1.0000	NA
Cu_{total}	1.0000	NA	0.8888	0.0179	0.8111	0.0502						
Pb_{total}	0.8888	0.0179	1.0000	NA	0.5728	0.2347						
Zn_{total}	0.8111	0.0502	0.5728	0.2347	1.0000	NA						
$Cu_{available}$	0.7488	0.0867	0.8704	0.0241	0.7517	0.0848	1.0000	NA	0.9686	0.0015	0.8036	0.0541
$Pb_{available}$	0.8688	0.0247	0.9427	0.0048	0.6723	0.1435	0.9686	0.0015	1.0000	NA	0.7436	0.0902
$Zn_{available}$	0.4440	0.3777	0.4858	0.3286	0.9940	0.0001	0.8036	0.0541	0.7436	0.0902	1.0000	NA
Cu_{total}	1.0000	NA	0.9452	0.0044	0.3459	0.5019						
Pb_{total}	0.9452	0.0044	1.0000	NA	0.3940	0.4396						
Zn_{total}	0.3459	0.5019	0.3940	0.4396	1.0000	NA						

NA not available

sediments can be found in the work of Kaushik et al. (2009). Cd had the highest EF values among the five metals studied in the article of Cevik et al. (2009). Cd is the only element which has a high degree of contamination in the sediments in all studies, but our results for the Rák Creek cannot confirm this hypothesis because of the small amount of Cd. Therefore, the degree of heavy metal contamination depends mostly on land use.

Computed Pearson r values for dead region were compared with critical r values (0.707, $p < 0.05$) as suggested by Orbay (1990) (Table 4). We found tight correlation between the available and the total values of Cu, Pb and Zn ($r = 0.76$–0.99). The mentioned heavy metals cannot build into the mineral lattice very easily, although large amounts of these elements are available for plants.

In the case of urban soils of creek banks, the silt fraction showed positive significant correlation with Co_{total} ($r = 0.83$) and Ni_{total} ($r = 0.77$). This connection confirmed the presence of these elements in the parent material that bind to surface of clay minerals.

The available Cu, Pb, Zn moved together ($r = 0.92$–0.97), as well as the total Cu, Pb, Zn ($r = 0.96$–0.98). Therefore, we could suppose that the origin of these heavy metals was human activity. These correlations also confirmed the conclusion of the Pb/Zn ratio and the connection between Zn and Cu.

Conclusion

The present study concludes that Rák Creek, which flows through Sopron, has been significantly contaminated with Zn, Pb and Cu. The enrichment factor of Pb showed severe and moderately severe enrichment in the urban area. Zn showed moderate enrichment at the last sampling point. The anthropogenic contamination of Rák Creek by Co and Ni is negligible.

The difference between natural and urban areas seemed definite based on our results. The values of pH decreased in both the soil samples and the sediments samples along the creek, although the changes in pH levels are more robust in case of soil samples. Heavy metals generally bind to fine fractions in sediment like silt and clay, which is clearly shown in the significantly high concentration and enrichment of heavy metals that was discovered in the dead region. Even though the flow characteristic of the dead region and thalweg of the natural part of the stream was different, the heavy metals accumulated in the dead region mainly in the urbanized area.

Acknowledgments This research is supported by TÁMOP 4.2.1.B-09/1/KONV-2010-0006 and the "Agroclimate.2" (VKSZ_12-1-2013-0034) EU joint national funded research projects.

References

Joint Decree No. 10/2000. (VI. 2) KöM-EüM-FVM-KHVM of the Ministers of Environmental Protection, Public Health, Agriculture and Regional Development, and of Traffic, Communication and Water Management on the Limit Values Necessary to Protect the Quality of Groundwater and the Geological Medium (in Hungarian)

Joint Decree No. 6/2009. (IV. 14) KvVM-EüM-FVM of the Ministers of Environmental Protection and Water Management, Public Health, Agriculture and Regional Development on the Limit Values Necessary to Protect the Quality of Geological Medium and the Groundwater and on Measurement of Pollution (in Hungarian)

Albert L, Jancsó T (2012) Complex study of the urban eco-environment in the Western Transdanubia Region. In: Neményi M, Heil B (eds) The impact of urbanization, industrial, agricultural and forest technologies on the natural environment. Publishing House of National Textbook, Budapest, pp 119–128

Alloway BJ (2012) Soil processes and the behaviour of heavy metals. In: Alloway BJ (ed) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Glasgow, pp 11–37

Barna S (2008) Development of a rapid biotest adaptable to plants to characterize heavy metal contents of soils. Dissertation. Szent István University (**in Hungarian**)

Baudo R, Giesy JP, Muntau H (1990) Sediments: chemistry and toxicity of in-place pollutions. Lewis Publishers, Michigan

Bretzel F, Calderisi M (2006) Metal contamination in urban soils of Coastal Tuscany (Italy). Environ Monit Assess 118:319–335

Bryan GW, Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediment with special reference to United Kingdom estuaries: a review. Environ Pollut 76:89–131

Cevik F, Göksu M-Z, Derici O-B, Findik O (2009) An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. Environ Monit Assess 152:309–317

Charzyński P, Bednarek R, Greinert A, Hulisz P, Uzarowicz Ł (2013) Classification of technogenic soils according to WRB system in the light of Polish experiences. Soil Sci Ann 64:145–150

Chen C-W, Kao C-M, Chen C-F, Dong C-D (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 66(8):1431–1440

Cuypers A, Remans T, Weyers N, Colpaert J, Vangronsveld J (2012) Soil-plant relationships of heavy metals and metalloids. In: Alloway BJ (ed) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Glasgow, pp 161–194

Dickinson WW, Dunbar GB, McLeod H (1996) Heavy metal history from cores in Wellington Harbour, New Zealand. Environ Geol 27:59–69

Dövényi Z (ed) (2010) Hungarian microregions. Hungarian Academy of Sciences, Budapest **(in Hungarian)**

Dövényi Z (ed) (2012) Geography of the Carpathian-Basin. Publishing house of Academy, Budapest **(in Hungarian)**

Fatoki OS, Mathabatha S (2001) An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. Water SA 27:233–240

Fiedler HJ (1990) Bodennutzung und Bodenschutz. VEB Gustav Fischer Verlag, Jena

Gordon N, Mcmahon T, Finlayson P, Gippel C, Nathan N (2004) Stream hydrology: an introduction for ecologists, 2nd edn. Wiley, Chichester

Gribovszki Z, Kalicz P, Csáfordi P, Sermaul K, Szita R (2012) The water status change of a small stream system due to urbanization.

In: Neményi M, Heil B, Kovács AJ, Facskó F (eds) The impact of urbanization, industrial, agricultural and forest technologies on the natural environment. Publishing House of National Textbook, Budapest, pp 161–170

Horowitz AJ (1985) A primer on trace metal—sediment chemistry. United States Government Printing Office, Alexandria

Horváth A, Szűcs P, Bidló A (2015) Soil condition and pollution in urban soils: evaluation of the soil quality in a Hungarian town. J Soils Sediments 15(8):1825–1835

IUSS Working Group WRB (2007) World reference base for soil resources 2006. 1st update 2007. World Soil Resources Reports No. 103. FAO, Rome

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants, 3rd edn. CRC Press, Boca Raton

Kádár I (1998) Remediation handbook 2. Investigation of contaminated soils. Ministry of Environment, Budapest **(in Hungarian)**

Kaushik A, Kansal A, Santosh Meena, Kumari S, Kaushik C-P (2009) Heavy metal contamination of river Yamuna, Haryana, India: assessment by metal enrichment factor of the sediments. J Hazard Mater 164:265–270

Kovács M, Nyári I (1984) The heavy metal contents of the public places of Budapest. Agrochem Soil Sci 33(3–4):501–510 **(in Hungarian)**

Luoma SN, Davis JA (1983) Requirements for modeling trace metal partitioning in oxidized estuarine sediments. Marine Chem 12:159–181

Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci Total Environ 300:229–243

McCready S, Birch GF, Long ER (2006) Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity—a chemical dataset for evaluating sediment quality guidelines. Environ Int 32:455–465

Morel JL, Heinrich AB (2008) SUITMA—soils in urban, industrial, traffic, mining and military areas; an interdisciplinary working group of the 'International Union of Soil Science' (IUSS) dedicated J Soils Sediments to soils strongly modified by human activities. J Soils Sediments 8:206–207

Morel JL, Charzyński P, Shaw RK, Zhang G (2015) The seventh SUITMA conference held in Toruń, Poland. J Soils Sediments 15:1657–1658

MSZ 21470–50 (2006) Environmental testing of soils. Determination of total and soluble toxic element, heavy metal and chromium(VI) content, Hungarian Standard Association, Budapest **(in Hungarian)**

MSZ-08-0205 (1978) Determination of physical and hydrophysical properties of soils. Hungarian Standard Association, Budapest **(in Hungarian)**

Müller HW, Schwaighofer B, Kalman W (1994) Heavy metal contents in river sediments. Water Soil Air Pollut 72:191–203

Ódor L, Horváth I (2003) Element distribution and environmental conditions in geochemical mapping. In: Gy Pantó (ed) Material flows and their impact on nature. Hungarian Academy of Sciences, Budapest, pp 151–188 **(in Hungarian)**

Orbay L (1990) Multivariate regression funds and economic use of wood. Manuscript. University for Forestry and Wood Sciences, Sopron **(in Hungarian)**

Pickering WF (1986) Metal ion speciation—soils and sediments (a review). Ore Geol Rev 1:83–146

Poulton DJ, Morris WA, Coakley JP (1996) Zonation of contaminated bottom sediments in Hamilton Harbour as defined by statistical classification techniques. Water Qual Res J Canada 31:505–528

Puskás I, Farsang A (2009) Diagnostic indicators for characterizing urban soils of Szeged, Hungary. Geoderma 148(3–4):267–281

Rauret G (1998) Extraction procedures for the determination of heavy metals in contained soil and sediment. Talanta 46:449–455

Rékási M, Filep T (2012) Fractions and background concentrations of potentially toxic elements in Hungarian surface soils. Environ Monit Assess 184:7461–7471

Sándor G, Szabó G (2014) Influence of human activities on the soils of Debrecen, Hungary. Soil Sci Annu 65(1):2–9

Scönlaub HP (ed) (2000) Geology of Austrian provinces—Burgenland. Geologische Bundesanstalt, Wien **(in German)**

Soares HMVM, Boaventura RAR, Machado AASC, Esteves da Silva JCG (1999) Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. Environ Pollut 105:311–323

Stefanovits P, Gy Filep, Gy Füleky (1999) Soil Sciences. Publishing House of Agriculture, Budapest **(in Hungarian)**

Szabó G, Elek Z, Sz Szabó (2008) Study of heavy metals in the soil-plant system. Cereal Res Commun 36(1):403–406

Szegedi S (1999) The heavy metal pollution of the soil in Debrecen. Hung Sci 106/66(10):1192–1200 **(in Hungarian)**

Szolnoki Z, Farsang A, Puskás I (2013) Cumulative impacts of human activities on urban garden soils: origin and accumulation of metals. Environ Pollut 177:106–115

Tack FMG (2010) Trace elements: general soil chemistry, principles and processes. In: Hooda PS (ed) Trace elements in soils. Wiley, Chichester, pp 9–38

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Acta 28:1273–1285

Van Reeuwijk LP (ed) (2002) Procedures for soil analysis (6th ed.). Technical Paper 9. Wageningen

Varga G, Konkoly-Gyúró É, Kovács G, Schmidt G, Radó D, Baranyi K, Czimber K, Boros G, Héjj B, Krassay L, Rácz I, Szemerédy M, Varga T (1999) Information system describing the condition of urban trees and forests. Urban Green Landsc Archit Koppenhaga, 23–25 June 1999

Zöttl HW (1987) Responses of forest decline to experimental fertilization. In: Hutchinson TC, Meema KM (eds) Effects of atmospheric pollutants on forests, wetlands and agricultural ecosystems. Springer Series G: Ecol Sci 16:255–265