ISSN 1313 - 8820 (print)
ISSN 1314 - 412X (online)
Volume 9, Number 2
June 2017

AGRICULTURAL SCIENCE AND TECHNOLOGY

2017

An International Journal Published by Faculty of Agriculture,
Trakia University, Stara Zagora, Bulgaria

Scope and policy of the journal

Agricultural Science and Technology /AST/ – an International Scientific Journal of Agricultural and Technology Sciences is published in English in one volume of 4 issues per year, as a printed journal and in electronic form. The policy of the journal is to publish original papers, reviews and short communications covering the aspects of agriculture related with life sciences and modern technologies. It will offer opportunities to address the global needs relating to food and environment, health, exploit the technology to provide innovative products and sustainable development. Papers will be considered in aspects of both fundamental and applied science in the areas of Genetics and Breeding, Nutrition and Physiology, Production Systems, Agriculture and Environment and Product Quality and Safety. Other categories closely related to the above topics could be considered by the editors. The detailed information of the journal is available at the website. Proceedings of scientific meetings and conference reports will be considered for special issues.

Submission of Manuscripts

There are no submission / handling / publication charges.

All manuscripts written in English should be submitted as MS-Word file attachments via e-mail to editoffice@agriscitech.eu. Manuscripts must be prepared strictly in accordance with the detailed instructions for authors at the website www.agriscitech.eu and the instructions on the last page of the journal. For each manuscript the signatures of all authors are needed confirming their consent to publish it and to nominate on author for correspondence.

They have to be presented by a submission letter signed by all authors. The form of the submission letter is available upon from request from the Technical Assistance or could be downloaded from the website of the journal. Manuscripts submitted to this journal are considered if they have submitted only to it, they have not been published already, nor are they under consideration for publication in press elsewhere. All manuscripts are subject to editorial review and the editors reserve the right to improve style and return the paper for rewriting to the authors, if necessary. The editorial board reserves rights to reject manuscripts based on priorities and space availability in the journal.

The journal is committed to respect high standards of ethics in the editing and reviewing process and malpractice statement. Commitments of authors related to authorship are also very important for a high standard of ethics and publishing. We follow closely the Committee on Publication Ethics (COPE), http://publicationethics.org/resources/guidelines

The articles appearing in this journal are indexed and abstracted in: DOI, EBSCO Publishing Inc. and AGRIS (FAO).

The journal is accepted to be indexed with the support of a project № BG051PO001-3.3.05-0001 "Science and business" financed by Operational Programme "Human Resources Development" of EU.

The title has been suggested to be included in SCOPUS (Elsevier) and Electronic Journals Submission Form (Thomson Reuters).

The journal is freely available without charge to the user or his/her institution. Users can read, download, copy, distribute, print, search, or link to the full texts of the articles, or use them for any other lawful purpose, without asking prior permission from the publisher or the author.

This issue is printed with the financial support by Contract No DNP 05-21/20.12.2016, financed from Fund 'Scientific Research' grant Bulgarian scientific Periodicals.

Address of Editorial office:
Agricultural Science and Technology
Faculty of Agriculture, Trakia University
Student's campus, 6000 Stara Zagora
Bulgaria
Telephone: +359 42 699330
+359 42 699446
www.agriscitech.eu

Technical Assistance:
Nely Tsvetanova
Telephone: +359 42 699446
E-mail: editoffice@agriscitech.eu

ISSN 1313 - 8820 (print)
ISSN 1314 - 412X (online)

Volume 9, Number 2
June 2017

AGRICULTURAL SCIENCE AND TECHNOLOGY

2017

An International Journal Published by Faculty of Agriculture,
Trakia University, Stara Zagora, Bulgaria

AGRICULTURAL SCIENCE AND TECHNOLOGY, VOL. 9, No 2, pp 144 - 150, 2017
DOI: 10.15547/ast.2017.02.026

Heavy metal pools in urban soils from city parks of Sofia, Bulgaria

V. G. Kachova[1]*, I. D. Atanassova[2]

[1]Forest Research Institute, Kliment Ohridski Blvd. 132, 1756 Sofia, Bulgaria
[2]Nikola Poushkarov Institute of Soil Science, Agrotechnology and Plant Protection, 1080 Sofia, Bulgaria

(Manuscript received 4 April 2017; accepted for publication 30 May 2017)

Abstract. *With a population ~ 1 300 000 million and an area of 1344 km^2, Sofia, Bulgaria is one of the most densely populated cities in Europe with registered contamination of the air, water and soils of the city including heavy metals. The purpose of the study is to analyze the different pools under which heavy metals in urban soils exist. The chosen sites are the largest forest parks in Sofia. Cu, Zn, Pb and Cd in soil of samples were sequentially extracted and separated soluble F1 (70% ethyl alcohol solution), liable F2 (1N CH_3C00Na, pH = 7), carbonate bound F3 (1N CH_3C00Na + 1N CH_3C00H, pH = 3), soil organic matter bound F4 (30% H_2O_2), amorphous iron oxide bound F5 (0.5 M Na-citrate), total "aqua regia" content and residual fraction F6 (measured as a difference from total). These operationally defined fractions give estimates of available (F1, F2), potentially liable (F3, F4, F5) and pseudo-total contents in soils, respectively. Metals were manly concentrated in the "residual fraction" F6. Organic matter associated is manly Cu and Pb, while carbonates-bound and amorphous iron oxides-bound were Pb and Zn. The mobility of the studied metals decreased in the order: Cd > Zn > Cu ≥ Pb. The soils with high pH and Cation exchenge capacity measured at pH = 8.2 ($CEC_{8.2}$) show lower amounts of mobile (easily-available) forms of heavy metals.*

Keywords: urban soils, heavy metals, sequential extraction

Introduction

Distinctive feature of soils from urban areas is the presence of a surface layer enriched with heavy metals (Kabata-Pendias and Pendias, 1992; Stroganova and Agarkova, 1993; Stroganova et al., 1998; Manta et al., 2002; Seleznev and Yamoshenko, 2014; Alekseenko and Alekseenko, 2014). Elevated concentrations of heavy metals (HM) in the top-soil negatively affect soil biota and plant biodiversity (Kapusta and Sobczyk, 2015) and conditions are created for disturbances in mineral nutrition, changes of metabolic and physiological processes in green plants. The deteriorated status of green systems directly reflects on the quality of the city environment. Soil pollution with heavy metals can have significant toxic effects on human health by inhalation of dust or direct contact in public green places, parks and gardens (Dolotov and Ponomareva, 1982; Obukhov and Kutukova, 1990). This fact determines the need of research concerning the content of HM in soils from parks of many cities around the world (Shao-Lian et al., 1989; Hou et al, 2015). The study of large parks in Stara Zagora (Bulgaria) reveals technogenic loads on soils with heavy metals on the bases of technogenic coefficient and coefficient of abnormality but without risks for ecosystems (Petkov et al., 2010). Links between soil pollution with heavy metals and age of the park are determined also (Li et al., 2001; Hou et al., 2015). Increased concentrations of Cd, Cu, Zn and Pb and other heavy metals were observed in the soil of the old city parks located in commercial and industrial areas, and this is attributed to the automobile and industrial activities in the areas (Tchuldjian, 2008; Qingjie et al., 2008; Du et al., 2013; Hussain et al., 2015). Determination of total content of metals is used in the identification and general description of soils, but to study their toxicity and behavior, distribution of heavy metals among different soil compartments is useful (Ladonin and Karpukhin, 2011; Minkina et al., 2014). By the term "pools of heavy metals" are not considered separate heavy metal compounds, but rather forms of compounds distinguished by many common features and properties (Ladonin, 2002). It is widely considered that the chemical forms of heavy metals determine their mobility and bioavailability to living organisms, and hence the strength of their toxicity (Ladonin, 2002; Lu et al., 2003; Doichinova et al., 2014). For determination of the mobile (bioavailable) forms of heavy metals are used either non-selective: NH_4OAc at pH 7; 2M HCl; NH_4OAc / EDTA / HCl: NH4OAc / EDTA (Nowack et al., 2001; Mahava et al., 2003; Doichinova et al., 2014), or selective extractants for fractionating Cu in soils; for determination of non-silicate forms of Fe and Mn in soils (Mehra-Jackson, 1960; McLaren and Crawford, 1973). Over the years are used various successive sequential extraction treatments, where in the fractions are separated and defined as „pools of heavy metals in soils" (Lu et al., 2003; Janoš et al., 2010; Arenas-Lago et al., 2014).

The aim of the study is to analyze the different pools of heavy metals in urban soils from the largest city parks in Sofia.

Material and methods

Geographically, Sofia region is covering all Sofia valley with clearly differentiated kettle bottom, foothills and surrounding mountains with temperate climate. Frequent fogs are a characteristic feature. Temperature inversions, which determine the removal of ground air of polluting substances toward the higher levels, are also common phenomenon. Annual emissions of SO_2 and NO_2 are over 100 t / km^2 for 2010. These indicators determine the capital city as one of the most polluted towns in the country. Dust and metal aerosols are durable components in the air and meteorological conditions make it possible for their dissemination around the whole area.

In the soil surface (~ 20 cm) is located a large part of the fine

* e-mail: vaniakachova@gmail.com

roots of trees. We conducted our research in the surface soil layers (0 – 20cm). The measured heavy metals are Cu, Zn, Pb and Cd, which are prevalent pollutants in urban environment (Doichinova et al., 2006). The study was carried out in the spring time month of April, 2014, in four parks of the capital, located in four directions from the centre:

U1 - Boris Garden at a distance from the city center 3.3 km, average sea level 550 m, slope 4, exposure: east-southeast, the predominant tree species: summer oak (*Quercus pedunculiflora C. Koch*) and soils *Anthrosols* with Hortic horizon (WRB, 2014), and deeper with characteristics of anthropogenic Vertisols. The morphological disruption of soil profile till parent rocks is: A'h (0-10cm); A'' (10-30cm); A''' (30-53cm); AB (53-73cm); B (73-83cm); BC (83-110 ↓ cm). The total area of park is 3.02 km^2 from which was chosen an area of 0.05 ha for sample plot (SP) with homogenous vegetation.

U2 - Loven Park at a distance from the city center 3.7 km, average sea level 570 m, slope 4, exposure: south-southeast, predominant tree species: red oak (*Quercus rubra L.*) and soils *Anthrosols* with Hortic horizon (WRB, 2014), and deeper with characteristics of Haplic Luvisol. The morphological disruption of soil profile till parent rocks is: A'h (0-6cm); A'' (6-34cm); B_1 (34-60cm); B_2 (60-80cm); BC (80-110 ↓ cm). The total area of park is about 0.5 km^2 from which was chosen an area of 0.05 ha for SP with homogenous vegetation.

U3 - West Park at a distance from the city center 3.8 km, average sea level 525 m, slope 6, exposure: west-southwest, predominant tree species: red oak (*Quercus rubra L.)* and soils *Anthrosols* with Hortic horizon (WRB, 2014) and deeper with characteristics of anthropogenic Vertisols. The morphological disruption of soil profile till parent rocks is: A'h (0-10cm); A'' (10-30cm); A''' (30-73cm); AB (73-83cm); B (73-105cm); BC (105-110 ↓ cm). The total area of park is about 2.16 km^2 from which was chosen an area of 0.05 ha for SP with homogenous vegetation.

U4 - North Park at a distance from the city center 5.6 km, average sea level 575 m, slope 4, exposure: northeast predominant tree species red oak (*Quercus rubra L.*) and soils *Anthrosols* with Hortic horizon (WRB, 2014). They have characteristic of Haplic Anthrosols according to updated Bulgarian classification (Gencheva, 2000). The morphological disruption of soil profile till parent rocks is: I_{Ah} (0-3cm); II (3-19cm); III (19-53cm); B (53-64cm); BC (64-83 ↓ cm). The total area of park is about 0.78 km^2 from which was chosen an area of 0.05 ha for SP with homogenous vegetation.

Soil samples (0-20cm) were taken at fourth replicates in the center of the plots plus one from soil profile (5 samples per plot and 20 samples in total). Soil characteristics were determined according to standardized methods (Donov et al. 1974) i.e., texture according to the method of Kachinsky (full description of all fractions is given by Doichinova et al. (2006), organic carbon (C%) according to the method of Turin, phosphorus – colorimetric method by Kirsanov (Donov et al., 1974).

The total content of heavy metals, macro and micro-elements in soil were measured after treatment with HCl: HNO_3 (ISO 11466) and analyzed by atomic absorption spectroscopy (AAS) on Perkin Elmer 370 A. Cation exchange capacity was determined by the method of Ganev (Ganev and Arsova, 1980). In order to determine the "forms of heavy metals in soils" we used the method of sequential extraction of Kuznetsov and Schimko (1990). Consistently, the following factions were separated: F1 - "soluble pool" by 70% alcohol solution (to reduce the influence of ion exchange); F2 - "labile pool" by 1N CH_3COONa at pH 7; F3 "carbonates-bound pool" by a solution of 1N CH_3COONa + 1N CH_3COOH at pH 3,5; F4 "organic matter- bound pool" by 30% H_2O_2; F5 "amorphous hydroxides bound pool" by 0.5 M Na-citrate. The fraction F6 "residual" or "insoluble" was calculated as a difference from total contents of heavy metals in soils (Dąvkowska-Naskręt, 2000). The ratio between the solid phase (soils) and the extraction solution is 1: 5.

In order to determine the heavy metal composition of fine roots (⩽ 2 mm) wet combustion by concentrated HNO_3, thermal ashing in a muffle furnace at 450˚C, extraction with 20% HCl and analysis by AAS was used.

The data was present as mean and +/- SD; at significant level $p < 0.05$.

Results

General characteristic of soils (0-5; 5-10; 10-20 cm) and the average contents of heavy metals in fine roots of the tree species is given in Table 1.

Soils from the parks in the city of Sofia are slightly acidic to neutral with the exception of Loven Park where soils in depth are highly acidic. Textural composition varies from light sandy loam (Boris garden) to heavy sandy loam (Northern park). According to the values of $CEC_{8.2}$ (cation exchange capacity at pH=8.2) soils are moderately colloidal (Boris garden and Loven park) to highly colloidal (Western and Northern park) and are characterized by high soil organic matter contents (Northern park). The content of HM in fine roots tends to decrease in the deeper layers. The average contents of heavy metals in the separate fractions from the 0-20cm layers the soils and the average total content (OF) are presented in Table 2.

The fraction of "soluble pool" (F1) has the lowest contents. The fraction of easily mobile "labile pool" (F2) represents predominantly ionic chemical bonds or weak complexes to soil components and is easily removed into soil solution. This fraction together with the fraction of the "soluble pool" (F1) is the most easily assimilated by plants. The fraction of the "carbonates-bound pool" (F3) is extracted with acidified solution of the extractant (pH = 3.5), and is most sensitive to a change in the acid status of the soil. Upon acidification these forms become available to the plants (Lu et al., 2003), and such acidification *"in situ"* may be caused, as a result of root exudates. In acid medium, the fraction F5 „amorphous Fe, Mn hydroxides bound" is also unstable, which defines this fraction as "potentially available" to plants. The fraction F4 "organic matter-bound" is potentially available for root extraction in case of alteration in redox conditions in soils and/or pH 5 and above (Alloway, 1995), which corresponded to most of our samples. Therefore, the total sum of the content of heavy metals in all these fractions, without fraction F6 "insoluble residue", represents the sum of the active (potentially digestible) metals in the soil (Xu and Yang, 1995).

Heavy metals in park soils of the city of Sofia exist mainly as "insoluble residue-pool" (F6). Active heavy metals are associated mainly with organic matter, carbonates and hydroxides of Fe and Mn. "Easily mobile pool" and "soluble pool" are not in large quantities.

Figures 1a, 1b, 1c, 1d represents a distribution of the heavy metals in different pools. In these figures are discribed separately Cu, Zn, Pb и Cd in sequentially extracted fractions: F1 - soluble; F2 - labile; F3 - carbonate-bound; F4 - organic matter-bound; F5 - amorphous hydroxides-bound; F6 - residual. In U1, U2, U3 and U4 from top towards bottom are represented layers: 0-5; 5-10; 10-20 cm

Table 1. Soil characteristics and average contents of heavy metals in fine roots (mean ± 0.01)

Soil Classification Hortic Ahthrosols (FAO)	pH (H_20)	Silt + Clay %	$CEC_{8.2*}$ cmol/kg	SOM** g/kg	P (mg/kg)	Cu in fine root mg/kg	Zn in fine root mg/kg	Pb in fine root mg/kg	Cd in fine root mg/kg
U1 Boris garden									
0-5 cm	6.65	26.54	30.04	45.0	292	16.33	44.34	26.97	1.07
5-10 cm	6.50	28.57	26.06	36.8	312	12.40	33.25	24.19	0.96
10-20 cm	6.60	32.72	27.01	27.4	336	13.81	35.04	23.20	0.82
U2 Loven park									
0-5 cm	5.10	20.53	28.15	53.7	410	14.39	31.86	20.24	0.63
5-10 cm	4.90	29.30	24.31	31.2	382	13.80	28.73	16.96	0.56
10-20 cm	4.50	32.27	27.92	21.7	332	12.24	29.28	16.59	0.50
U3 Western park									
0-5 cm	6.05	46.86	61.66	57.2	610	12.20	46.71	25.54	0.67
5-10 cm	5.80	48.39	65.42	39.3	590	12.62	38.01	20.03	0.63
10-20 cm	5.20	58.32	75.62	33.0	598	11.81	36.27	17.69	0.56
U4 Northern park									
0-5 cm	6.85	32.61	50.21	82.5	1139	19.05	35.77	17.54	0.52
5-10 cm	6.75	42.53	54.55	81.2	1023	21.39	30.32	14.99	0.59
10-20 cm	6.60	40.39	47.93	45.3	1069	18.03	27.79	13.02	0.45

n= 20
* CEC – cation exchenge capacity in pH = 8.2
** SOM – soil organic matter

Table 2. Average contents of heavy metals factions and average total contents (OF) in urban soils (mean ± 0.1)

	F1	F2	F3	F4	F5	F6	OF
	mg/kg						
0-20 cm	Cu						
	0.24±0.0	0.54±0.0	1.57±0.2	5.79±0.4	0.87±0.1	36.27±7	45.27±7
0-20 cm	Zn						
	0.31±0.1	1.13±0.1	5.25±0.6	4.61±0.4	5.45±0.5	42.41±9.0	59.15±8.5
0-20 cm	Pb						
	0.10±0.1	0.91±0.1	1.93±0.4	2.04±0.3	1.68±0.2	22.42±1.3	29.08±1.5
0-20 cm	Cd						
	0.02±0.0	0.03±0.0	0.09±0.1	0.02±0.0	0.05±0.1	0.11±0.1	0.32±0.1

n= 20
*OF – total forms

The highest contents of heavy metals are in the "insoluble residue-pool". This pool is unreachable for plants, and is associated with the crystal lattice of soil minerals.

Generally, the distribution of metals in different fractions follows the order:

- Cu: F6 » F4 > F3 > F5 > F2 >F1
- Zn: F6 » F5 > F3 > F4 > F2 > F1
- Pb: F6 » F4 ~ F3 ~ F5 > F2 > F1
- Cd: F6 > F3 > F5 > F2 > F4 > F1

Copper and Pb are mainly associated with soil organic matter, while Zn and Cd with carbonates and Fe-Mn hydroxides.

Discussion

The analysis of heavy metal pools in soils is used for more detailed study of metals behavior in soils and for clarifying their ability to migrate towards other components of the ecosystem. Determination of the static snapshot of soil structural components, with which metals are associated clarifies the mechanisms of interaction and behavior. Therefore, in many cases, especially when considering the availability of heavy metals and their assimilation by plants, it is important to determine their pools in soils. Heavy metal pools are exclusive prototype of geochemical diversity of different compounds of HM formed as a result of weathering processes (Tchuldzhiyan and Petrov, 1984). Separately, by anthropogenic import various compounds of heavy metals enter the soils and can be transformed depending on soil conditions. Changes in soil conditions (pH, % dust, etc.), as well as enhanced anthropogenic load influence the available pools of heavy metals and their transformations. Therefore, determination of heavy metal pools for particular soil conditions in urban parks is important for clarifying the behavior of metals, their accessibility, impact on mineral nutrition and assimilation by woody plants in urban environment.

The total concentration of the analyzed heavy metals do not

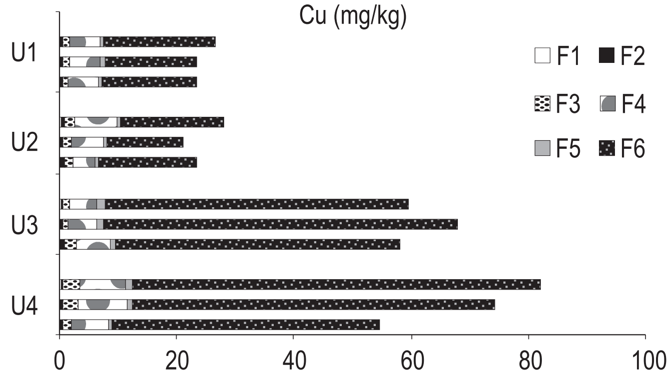

Figure 1a. Sequential fractions of Cu

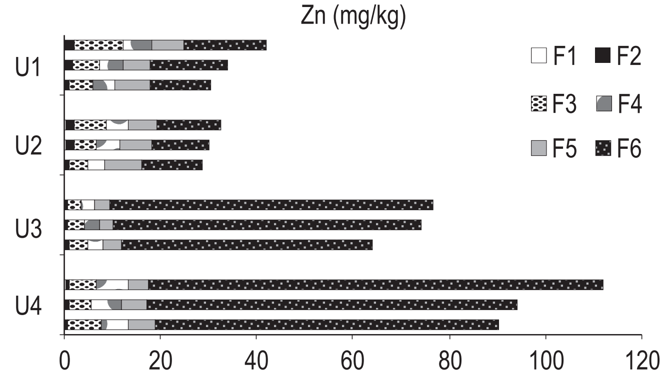

Figure 1b. Sequential fractions of Zn

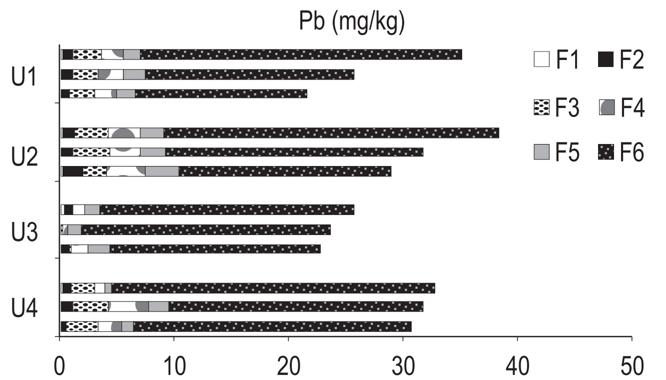

Figure 1c. Sequential fractions of Pb

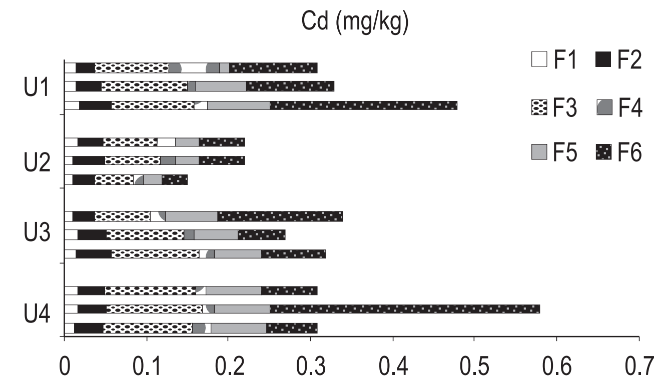

Figure 1d. Sequential fractions of Cd

exceed the official thresholds accepted in Bulgarian standards for soils from public areas (Regulation No. 3/1979; Regulation No. 3/2008).

The highest contents of Cu were in the residual fraction (76 ± 10%) and the lowest in the "soluble fraction" (0.7 ± 0.3%). The organically complexed Cu comprised 15.7 ± 7%. The general Cu distribution was in the order: Total forms (TF) ≈ F6 » F4 > F3 > F5 > F2 >F1. Active Cu is mainly related to soil organic matter (F4 – 16%). This affinity of Cu to soil organic matter was well defined by other authors (McLaren and Crawford, 1973; Alloway, 1995). Atanassova (1995) and Atanassova and Okazaki (1997) showed that at high copper levels, the clay fractions from acid soils could not play a scavenging role because Cu was exchangeable adsorbed by 2:1 clay minerals in soils.

Lead was primarily accumulated in the F6 residual fraction with substantial inputs in the organic fraction (F4 – 7%). Pb distribution followed the order: TF > F6 » F4 ≈ F3 ≈ F5 > F2 > F1. Dąvkovska-Naskręt (2000) found a high percentage of Pb bound to soil organic matter in urban soils of northern Poland. Lead shows high affinity to soil organic matter confirmed by previous studies in connection with the profile distribution of Pb in soils from the Sofia region (Doichinova and Atanassova, 2003). In the urban part of the region, Pb is also bound to carbonates (F3 - 6%) and Fe-Mn hydroxides (F5 - 6%). In F3 fraction are extracted metals from minerals such as: $Cu_2(OH)_2CO_3$, $Pb_3(PO4)_2$, $Pb_5(PO4)_3Cl$, $PbCO_3$, $Zn(OH)_6(CO_3)_2$, $ZnSiO_4$, hydroxides of heavy metals etc., which are present in soils as residual components from the weathering of parent rocks or as intermediates in the transformation of technogenic forms of HM (Allow, 1995). Data on the distribution of Pb among different pools in urban soils support the results of the multiple analyses for anthropogenic load of soils in Sofia with Pb (Doichinova et al., 2006).

Zn also appeared in the residual fraction (63 ± 21.6 %), but higher Zn pools were found in the carbonate and Fe-oxide fraction. The overall trend followed TF ≈ F6 » F5 ≈ F3 ≈ F4 > F2 > F1. Unlike Cu, the active Zn binds slightly less to the soil organic matter, rather than with Fe-Mn hydroxides (F5 – 13%) and carbonates (F3 – 11%). The same was found in studies of other authors concerning urban soils (Lu et al., 2003). Sedberry and Reddy (1976), however establish a higher percentage of organically bound Zn in agricultural soils of Louisiana, USA.

Compared with the other metals, Cd showed the least distribution in the residual fraction (31 ± 12.3%) and highest in the "labile" fraction (11.4 ± 3.9%), indicating potential toxic effects in the urban soils. Substantial proportions were also detected in the carbonate (29.4 ± 5.8%) and the Fe-hydroxide fractions (16 ± 5%).

Increased percentage of labile heavy metals is a characteristic feature of urban environment (Lu et al., 2003; Doichinova et al., 2014). Accessibility and mobility of HM in soils under oak ecosystems of urbanized soils from Sofia decreases in the following order: Cd> Zn> Cu> Pb.

Cadmium is the most mobile and easily accessible element and Pb is the least accessible and has a pronounced accumulation in the top soil surface. The total loading of soils with Cd is results in increase of its active forms, and connected with the expression mostly of Cd-toxicity in the studied soils.

The relationships between various pools of heavy metals in different soils from the urban part (U) of the area and main soil characteristics are shown in Table 3.1, Table 3.2, Table 3.3 and Table 3.4.

Labile Cu (F2) is negatively correlated with pH and humus content. The content of clay is also negatively correlated with fractions F2, F3 and F5 of Zn which means that the surface of the soil of urban forest parks, does not render active clay fraction for adsorption of these Zn-fractions. It is interesting to note the positive correlation between organically bound Zn and pH. In the reported trend towards alkalinization in the surface soil horizons of urban (U)

Table 3. Correlation matrix of various heavy-metal fractions and soil characteristics (n=16)

Table 3/1. Cu

	F1	F2	F3	F4	F5	F6	pH	SOM	Clay	OF
F1	1									
F2	n	1								
F3	n	n	1							
F4	n	n	0.79**	1						
F5	n	n	n	n	1					
F6	n	n	0.59*	n	0.75**	1				
pH	n	-0.81**	n	n	n	n	1			
SOM	n	-0.63*	0.72**	0.82**	n	0.69*	n	1		
Clay	n	n	n	n	0.64*	0.67*	n	n	1	
TF	n	n	0.64*	n	0.73*	0.99**	n	0.73**	0.64*	1

Table 3/2. Zn

	F1	F2	F3	F4	F5	F6	pH	SOM	Clay	OF
F1	1									
F2	n	1								
F3	n	0.73**	1							
F4	n	n	0.62*	1						
F5	n	n	n	n	1					
F6	n	-0.63*	n	n	-0.72**	1				
pH	n	n	n	0.63*	n	n	1			
SOM	n	n	n	n	n	0.72*	n	1		
Clay	n	-0.65*	-0.61*	n	-0.64*	0.59*	n	n	1	
TF	n	n	n	n	-0.65*	0.99***	n	0.77**	n	1

Table 3/3. Pb

	F1	F2	F3	F4	F5	F6	pH	SOM	Clay	OF
F1	1									
F2	n	1								
F3	n	n	1							
F4	n	0.80**	0.76**	1						
F5	n	0.81**	n	n	1					
F6	n	n	n	n	n	1				
pH	n	n	n	n	-0.77**	n	1			
SOM	n	n	n	n	-0.59*	0.59*	n	1		
Clay	n	n	-0.75*	n	n	n	n	n	1	
TF	n	n	0.67*	n	n	0.86**	n	n	-0.64*	1

Table 3/4. Cd

	F1	F2	F3	F4	F5	F6	pH	SOM	Clay	OF
F1	1									
F2	n	1								
F3	n	n	1							
F4	n	n	n	1						
F5	n	n	0.69*	-0.59*	1					
F6	n	n	n	n	n	1				
pH	n	n	0.77**	n	n	n	1			
SOM	n	n	n	n	n	n	n	1		
Clay	n	n	n	n	n	n	n	n	1	
TF	n	n	0.69*	n	0.67*	0.95***	0.65*	n	n	1

*p < 0.05; ** p < 0.01; *** p < 0.001; n – no correlation part of the area it follows that organic matter will have a significant role in regulating the behavior of Zn in soil. Much of rainfall and the dry falloff in the town of Sofia are with alkaline character (Gencheva, 1985).

Phosphorus can form insoluble phosphates with HM in urban soils. This could explain the finding that positive correlation between “insoluble residue” (F6), total phosphorus and total contents of Cu and Zn in the urban soils was obtained.

Simple correlation analysis revealed strong positive relationship between Cu_{tot}, F5, F3, organic matter (OM), silt+clay and P contents and in a multiple regression, as well ($p < 0.05$):

$Cu_{tot} = 4.24 + 3\times10^{-4}*P + 0.02*(silt+clay\ \%) + 0.61*SOM\% + 0.99*F6 - 1.1*F5 + 1.4*F3$ ($R^2=0.99$).

Zn_{tot} was positively correlated with residual forms F6, soil organic matter (SOM) and P and in a multiple regression:

$Zn_{tot} = 12.85 + 0.02*P + 1.08*\%\ SOM + 0.74*F6$ ($R^2 = 0.99$).

Total Pb was correlated with CO_3-bound Pb, residual Pb F6 and negatively correlated with silt+clay content:

$Pb_{tot} = 7.32 - 0.02*\%\ (silt+clay) + 1.9*F3 + 0.84*F6$ ($R^2 = 0.93$).

Labile Pb in F2 was positively correlated with OM-bound Pb (F4) and Fe-oxide bound Pb (F5):

$Pb_{F2} = -0.005 + 0.19*F4 + 0.32*F5$ ($R^2= 0.80$).

Total Cd was positively correlated with CO_3-bound F3, Fe-oxide bound and residual F6 forms and in a multiple regression:

$Cd_{tot} = 0.05 + 1.5*F3 + 0.4*F5 + F6$ ($R^2 = 0.99$).

Regression equations demonstrated that the variations in the total pools of metals were explained by the respective contents in F6, P and other variables in the soil. For Cu and Cd, 99 % of the variability in the total Cu and Cd concentrations is explained by a multiple linear regression model with F6, F5, and F3 as predictor variables.

For the mobile PbF2 contents the explained variance reached 80 % based on F4 and F5 fractions. The observed relatioships can be due to the fact that total contents were mainly concentrated in the silt+clay, SOM and F6 fractions, while Cu (total) might be occluded in insoluble phosphates, as well.

Total contents ($mg.kg^{-1}$) of Cu (36.3 ± 21.8), Zn (59.2 ± 29.8), Pb (29.1 ± 5.3) and Cd (0.32 ± 0.11) do not exceed limits for agricultural, residential, recreational and institutional sites established in the Bulgarian standards (Regulation No. 3/1979, Regulation No. 3/2008), which are the following (pH < 6 and pH 6 -7,4): Cd 1,5 and 2 mg/kg; Cu 80 and 150 mg/kg; Pb 60 and 100 mg/kg; Zn 200 and 320 mg/kg.

A statistically significant ($p < 0.05$) correlation coefficient ($R^2 = 0.65$) between F4 fraction for copper and copper in fine roots was obtained (Figure 2). This dependency shows that in urban soils under oak vegetation, a large part of Cu in F4 might be available and can accumulate in tree roots. The high content of organic matter increases bio-accessibility of Cu, but reduces the accumulation of Pb in fine roots of oak trees. For decreasing bio-accessibility of Pb, Cd and Zn a high level of P in the soil contributed, although the studied urban soils are low in phosphorus (except U4).

Conclusion

The analysis of sequential extractions of heavy metals (Cu, Zn, Pb, Cd) and assessment of various pools contributes significantly to clarifying their behavior in urban soils and their uptake by tree roots. Based on the analysis of the behavior of metals in urban soils under oak ecosystems, we found that heavy metals are mainly represented by their residual pools, which are unavailable to plants. With soil organic matter are related mainly Cu and Pb, while with carbonates and Fe and Mn hydroxides are associated mainly Zn and Cd. Mobility and accessibility of the studied heavy metals in urban soils decreases in the order: Cd> Zn> Cu ⩾ Pb. Lead was imported to the soils mainly with dust particles (particulate matter) and accumulated in the surface layers of soil from urban parks. The lowest percentages of soluble and labile forms are determined in the soils with higher pH and Cation exchenge capacity measured at pH = 8.2 ($CEC_{8.2}$). Mobile forms of Cu, Zn and Pb are highest in top-soils (0-5 cm), and Cd migrates in depth (0-20cm). Carbonate and organic fractions are presented in small amount. In soils with heavy texture and finer texture (Western park), urbanization influence in relation with the available forms is the least. The data on the chemical fractionation and linear and multiple regression analysis confirmed previous results that Cd and Pb are inferred as markers of anthropogenic pollution, Cu contents are attributed to litho(pedo)genic sources, while Zn is both of anthropogenic and litho(pedo)genic origin. The results obtained for the major city forest parks in Sofia, the largest city and capital of Bulgaria, allow for their use for recreation purposes.

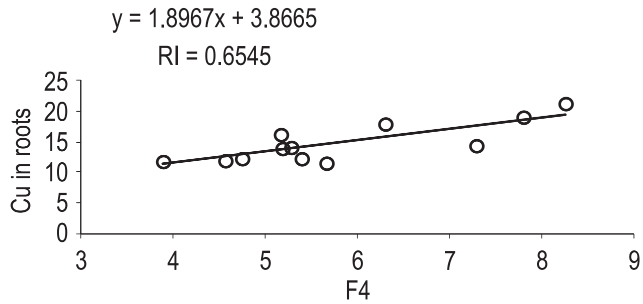

Figure 2. Relationship between Cu in fine roots and "organically bound copper" in soils from urban oak ecosystems of Sofia

References

Alekseenko V and Alekseenko A, 2014. The Abundance of chemical elements in urban Soils. Journal of Geochemical Exploration, 147, B, 245-249.

Arenas-Lago D, Andrade M, Lago-Vila M, Rodríguez-Seijo A and Vega FA, 2014. Sequential extraction of heavy metals in soils from a copper mine: Distribution in geochemical fractions. Geoderma, 230-231, 108-118.

Alloway BJ, 1995. Heavy metals in Soils. Blackie, London.

Atanassova I, 1995. Adsorption and desorption of Cu at high equilibrium concentrations by soil and clay samples from Bulgaria. Environmental Pollution, 87, 17-21.

Atanassova I and Okazaki M, 1997. Adsorption - desorption characteristics of high levels of copper in soil clay fractions. Water, Air and Soil Pollution, 98, 213-228.

Dabkowska-Naskret H, 2000. Chemical Speciation of heavy metals in vegetable garden soils of urban area in northern Poland. First International Conference on Soils of Urban, Industrial, Traffic and Mining Areas (W. Burghard and C. Dornauf (Eds), 12-18 July, University of Essen, Germany, III, 755-760.

Doichinova V, Zhiyanski M and Hursthous A, 2006. Impact of urbanisation on soil characteristics. Environmental Chemistry

Letters (Springer), 3, 160-163.
Doichinova V, Sokolovska M and Velizarova E, 2006. Heavy metals contamination of soils under oak ecosystems in Sofia region. Environmental Chemistry Letters, 4, 101-105.
Doichinova V and Atanassova I, 2003. Behavior of Pb and Zn in Forest Soils under Oak and Pine Plantation. Bulgarian Journal of Ecological Science - Ecology and Future, II, 9-15.
Doichinova V, Zhiyanski M, Hursthouse A and Bech J, 2014. Study on mobility and bioavailability of PTEs in soils from Urban Forest Parks in Sofia, Bulgaria. Journal of Geochemical Exploration, 147, B, 222-228.
Dolotov VA and Ponomareva VV, 1982. Discription of Soils in the Letnii Garden in Leningrad. Pochvovedenie, 9, 134-138 (Ru).
Donov V, Gencheva S and Yorova K, 1974. Guidance for soil analyses, Sofia (Bg).
Du Y, Gao B, Zhou H, Ju X, Hao H and Yin S, 2013. „Health Risk Assessment of Heavy Metals in Road Dusts in Urban Parks of Beijing, China. Environmental Sciences, International Symposium on Environmental Science and Technology (ISEST, 8, 299-309.
Ganev S and Arsova A, 1980. Methods for determination of strongly acid and weakly acid exchange in soils. Soil Science and Agrochemistry, XV, 3, 22-28 (Bg).
Gencheva S, 2000. Actualized classification and diagnoses of anthropogenic soils II. Diagnoses of the Anthopogenic soils. The National conference "75years of forest education in Bulgaria", section Forestry, Sofia, 2000.
Gencheva S, 1985. Classification and some peculiarities of anthropogenic soils. Professorship Thesis, LTU, Sofia, pp. 284 (Bg).
Hou E, Xiang H, Li J, Li J and Wen D, 2015. Soil Acidification and Heavy Metals in Urban Parks as Affected by Reconstruction Intensity in a Humid Subtropical Environment. Pedosphere, 25, 82-92.
Hussain K, Rahman M, Prakash A and Hoque RR, 2015. Street dust bound PAHs, carbon and heavy metals in Guwahati city – Seasonality, toxicity and sources. Sustainable Cities and Society, 19, 17-25.
Janoš P, Vávrová J, Herzogová L and Pilařová V, 2010. Effects of inorganic and organic amendments on the mobility (leachability) of heavy metals in contaminated soil: A sequential extraction study. Geoderma, 159, 335-341.
Kabata-Pendias A and Pendias H, 1992. Trace elements in soils and plants. Second edn, FL: CRC Press, New York.
Kapusta P and Sobczyk L, 2015. Effects of heavy metal pollution from mining and smelting on enchytraeid communities under different land management and soil conditions. Science of the Total Environment, 536, 517-526.
Kuznetsov V and Schimko G, 1990. Methods of sequential extractions in geochemical studies. Ed. Science and Technica, Minsk (Ru).
Ladonin V, 2002. Compounds of heavy metals in soils – problems and methods of studding. Pochvovedenie, 6, 682-692 (Ru).
Ladonin V and Karpukhin M, 2011. Fractional Composition of Nickel, Copper, Zinc, and Lead Compounds in Soils Polluted by Oxides and Soluble Metal Salts. Eurasian Soil Sciences, 44, 874-885.
Li N, Poon C and Liu P, 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied Geochemistry, 16, 1361-1368.
Lu Y, Gong Z, Zhang G and Burghardt W, 2003. Concentration and chemical speciation of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. Geoderma, 115, 101-111.
Manta D, Angelone M, Bellanca A, Neri R and M. Sprovieri, 2002. Heavy metals in urban soils: a case study from city of Palermo (Sicily) Italy. The Science of the Total Environment, 300, 229-243.
McLaren R and Crawford D, 1973. Studies on soil copper. 1. The fractionation of copper in soils. Journal of Soil Science, 24, 173-181.
Machava J, Bublinec E, Gregor J and Kontriov O, 2003. Emission situation in Slovakia, physiochemical properties of heavy metals and their effects in forest ecosystems. The International Conference "75yers of Forest Research Institute -BAS", 1-5 Octobre, Sofia, p. 83-88.
Mehra OP and Jackson ML, 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Minerals, 7, 317-327.
Minkina M, Mandzhieva S, Motusova G, Buravchevskaya, M, Nazarenko O, Sushkova S and Kizilkaya R, 2014.Heavy metal compounds in a soil of technogenic zone as indicate of its ecological state. Euroasian Soil Science, 3, 144-151.
Nowack B, Obrecht JM, Schlue M, Schlulin R, Hansman W and Köppel V, 2001. Elevated lead and zinc Content in Remote Alpine Soils of the Swiss National Park. Journal of Environmental Quality, 30, 919-926.
Obukhov A and Kutukova Yu, 1990. Status of Soils in Kindergartens (by the Example of the Leninskiy District of Moscow). In: Ecological Studies in Moscow and Moscow Municipality, Moscow, 1990b, p. 212-241 (Ru).
Petkov G, Yablanski Ts, Todorova M, Pavlov D, Kostadinova G and Barakova V, 2010. Ecological Assessment of Soils from Parks and Places in Stara Zagora. Ecology and Future, IX, 4, 24-32 (Bg).
Regulation No. 3/1979 for rates of acceptable contents of harmful substances in soils. In: Government gazettes 36 from 08.05.1979, Council of Ministers.
Regulation No. 3/2008 for rates of acceptable contents of harmful substances in soils. In: Government gazettes 71 from 12.08.1979, Council of Ministers.
Qingjie G, Jun D, Yunchuan X, Qingfei W and Liqiang, Y, 2008. Calculating Pollution Indices by Heavy Metals in Ecological Geochemistry Assessment and a Case Study in Parks of Beijing. Journal of China University of Geosciences, 19, 230-241.
Sedberry J and Reddy C, 1976. The distribution of zinc in selected soils in Louisiana. Communication in Soil Science and Plant Analysis, 7, 787-795.
Seleznev A and Yamoshenko I, 2014. Study of Urban puddle Sediments for understanding heavy metal pollution in an urban environment. Environ. Technology & Innovation, 1-2, 1-7
Shao-Lian F, Hashimoto H, Siegel B and Siegel S, 1989. Period of significant source reduction. Water Air and Soil Pollution, 43, 109-118.
Stroganova M and Agarkova M, 1993. Urban Soils: Experimental study and classification (Examlified by the Soils of Southwestern Moscow). Eurasian Soil Science, 25, 59-69.
Stroganova M, Myagkova A, Prokofeva T and Skvortsova I, 1998. Soil of Moscow and Urban Environment. Moskow, p. 178.
Tchuldjian HY and Petrov I, 1984. Heavy metals in soils. Report on contact with Ministry of Environment and waters, Sofia (Bg).
Tchuldjian HY, 2008. Detoxification of Soils, Polluted Jointly by Heavy Metals, Acid Wastes and Acid Precipitations. In: Soil Chemical Pollution, Risk Assement, Remediation, and Security, NATO Science for Peace and Security Series, pp. 1-12.
Xu J and Yang J, 1995. Heavy metals in terrestrial Ecosystem. In: China Environmental Science Society Press, China.

CONTENTS

CONTENTS

Instruction for authors

Preparation of papers

Papers shall be submitted at the editorial office typed on standard typing pages (A4, 30 lines per page, 62 characters per line). The editors recommend up to 15 pages for full research paper (including abstract references, tables, figures and other appendices)

The manuscript should be structured as follows: Title, Names of authors and affiliation address, Abstract, List of keywords, Introduction, Material and methods,Results, Discussion, Conclusion, Acknowledgements (if any), References, Tables, Figures.

The title needs to be as concise and informative about the nature of research. It should be written with small letter /bold, 14/ without any abbreviations.

Names and affiliation of authors The names of the authors should be presented from the initials of first names followed by the family names. The complete address and name of the institution should be stated next. The affiliation of authors are designated by different signs. For the author who is going to be corresponding by the editorial board and readers, an E-mail address and telephone number should be presented as footnote on the first page. Corresponding author is indicated with *.

Abstract should be not more than 350 words. It should be clearly stated what new findings have been made in the course of research. Abbreviations and references to authors are inadmissible in the summary. It should be understandable without having read the paper and should be in one paragraph.

Keywords: Up to maximum of 5 keywords should be selected not repeating the title but giving the essence of study.

The introduction must answer the following questions: What is known and what is new on the studied issue? What necessitated the research problem, described in the paper? What is your hypothesis and goal ?

Material and methods: The objects of research, organization of experiments, chemical analyses, statistical and other methods and conditions applied for the experiments should be described in detail. A criterion of sufficient information is to be possible for others to repeat the experiment in order to verify results.

Results are presented in understandable tables and figures, accompanied by the statistical parameters needed for the evaluation. Data from tables and figures should not be repeated in the text.

Tables should be as simple and as few as possible. Each table should have its own explanatory title and to be typed on a separate page. They should be outside the main body of the text and an indication should be given where it should be inserted.

Figures should be sharp with good contrast and rendition. Graphic materials should be preferred. Photographs to be appropriate for printing. Illustrations are supplied in colour as an exception after special agreement with the editorial board and possible payment of extra costs. The figures are to be each in a single file and their location should be given within the text.

Discussion: The objective of this section is to indicate the scientific significance of the study. By comparing the results and conclusions of other scientists the contribution of the study for expanding or modifying existing knowledge is pointed out clearly and convincingly to the reader.

Conclusion: The most important consequences for the science and practice resulting from the conducted research should be summarized in a few sentences. The conclusions shouldn't be numbered and no new paragraphs be used. Contributions are the core of conclusions.

References:

In the text, references should be cited as follows: single author: Sandberg (2002); two authors: Andersson and Georges (2004); more than two authors: Andersson et al.(2003). When several references are cited simultaneously, they should be ranked by chronological order e.g.: (Sandberg, 2002; Andersson et al., 2003; Andersson and Georges, 2004).

References are arranged alphabetically by the name of the first author. If an author is cited more than once, first his individual publications are given ranked by year, then come publications with one co-author, two co-authors, etc. The names of authors, article and journal titles in the Cyrillic or alphabet different from Latin, should be transliterated into Latin and article titles should be translated into English. The original language of articles and books translated into English is indicated in parenthesis after the bibliographic reference (Bulgarian = Bg, Russian = Ru, Serbian = Sr, if in the Cyrillic, Mongolian = Mo, Greek = Gr, Georgian = Geor., Japanese = Ja, Chinese = Ch, Arabic = Ar, etc.)

The following order in the reference list is recommended:

Journal articles: Author(s) surname and initials, year. Title. Full title of the journal, volume, pages. Example:

Simm G, Lewis RM, Grundy B and Dingwall WS, 2002. Responses to selection for lean growth in sheep. Animal Science, 74, 39-50

Books: Author(s) surname and initials, year. Title. Edition, name of publisher, place of publication. Example:

Oldenbroek JK, 1999. Genebanks and the conservation of farm animal genetic resources, Second edition. DLO Institute for Animal Science and Health, Netherlands.

Book chapter or conference proceedings: Author(s) surname and initials, year. Title. In: Title of the book or of the proceedings followed by the editor(s), volume, pages. Name of publisher, place of publication. Example:

Mauff G, Pulverer G, Operkuch W, Hummel K and Hidden C, 1995. C3-variants and diverse phenotypes of unconverted and converted C3. In: Provides of the Biological Fluids (ed. H. Peters), vol. 22, 143-165, Pergamon Press. Oxford, UK.

Todorov N and Mitev J, 1995. Effect of level of feeding during dry period, and body condition score on reproductive performance in dairy cows,IXth International Conference on Production Diseases in Farm Animals, September 11–14, Berlin, Germany.

Thesis:

Hristova D, 2013. Investigation on genetic diversity in local sheep breeds using DNA markers. Thesis for PhD, Trakia University, Stara Zagora, Bulgaria, (Bg).

The Editorial Board of the Journal is not responsible for incorrect quotes of reference sources and the relevant violations of copyrights.

Animal welfare

Studies performed on experimental animals should be carried out according to internationally recognized guidelines for animal welfare. That should be clearly described in the respective section "Material and methods".

AGRICULTURAL
SCIENCE AND TECHNOLOGY

Volume 9, Number 2
June 2017

Journal web site:
www.agriscitech.eu

Publisher:
www.alfamarket.biz