ECOLOGIA BALKANICA
2019, Vol. 11, Issue 2 December 2019 pp. 215-228

Accumulation of Heavy Metals in the Urban Soils of Natural Monument "Bunardzhik" (Plovdiv, Bulgaria)

Bogdan Nikolov[1], Iliana Velcheva[1], Elena Zheleva[2], Penka Zaprianova[3], Ekaterina Valcheva[3], Tatyana Bileva[3], Slaveya Petrova[1*]

1 - University of Plovdiv "Paisii Hilendarski", 24 Tzar Asen Str., 4000 Plovdiv, BULGARIA
2 – University of Forestry, 10 Kliment Ohridski Str., 1756 Sofia, BULGARIA
3 – Agricultural University, 2 Mendeleev Boul., 4000 Plovdiv, BULGARIA
*Corresponding author: sl.petrova@abv.bg

Abstract. Progressing urbanization makes soils structurally altered and that results in their degradation, so we aimed to analyze the content of some heavy metals in urban soils of the park zone of Natural monument "Bunardzhik", situated in the real center of the city of Plovdiv (Bulgaria). Soil samples were collected from the surface layers of urban soils located to the Western and Eastern park zones of the Bunardzhik Hill, according to transects starting from the main communication routes. Soil content of As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, U, Zn was determined by inductively coupled plasma–mass spectrometry (ICP–MS). The content of V, Mn, Cr, Cu, Zn and Pb is noticeably reduced in the Western park zone ($p<0.05$), leaving from the route and reaching the middle of the park zone. Urban soils from the Eastern park zone are more polluted and there no significant decreases in their content with increasing the distance from the main road artery have been found. All studied heavy metals and toxic elements could be arranged as follows: Mn (436 mg/kg) > Zn (81 mg/kg) > V (40 mg/kg) > Pb (39.7 mg/kg) > Sr (38.3 mg/kg) > Cu (31.3 mg/kg) > Cr (23.7 mg/kg) > Ni (22.0 mg/kg) > As (3.3 mg/kg) > U (1.9 mg/kg) > Cd (0.36 mg/kg) in the Western park zone and Mn (552 mg/kg) > Zn (84 mg/kg) > V (62 mg/kg) > Pb (52.3 mg/kg) > Cr (36.3 mg/kg) > Sr (33.7 mg/kg) > Cu (28.7 mg/kg) > Ni (28.3 mg/kg) > As (6.0 mg/kg) > U (3.1 mg/kg) > Se (1.6 mg/kg) > Cd (0.55 mg/kg) > Hg (0.23 mg/kg) in the Eastern park zone, respectively. The results obtained for the two studied park zones allow for their use for recreational purposes but some exceedance of the precautionary limits should be adressed.

Key words: urban soils, heavy metals, toxic elements, pollution.

Introduction

Heavy metals are natural constituents of the Earth's crust. Anthropogenic activities have drastically disturbed the biochemical and geochemical cycles of some heavy metals. Therefore, the assessment of the environmental risk due to soil pollution is of particular importance for agricultural and urban areas, where heavy metals, which are potentially harmful to human health, persist in soils for a very long time.

Contamination of soil surface layers with heavy metals is mainly associated with urban areas which are intensively managed by humans (Walczak *et al.*, 2011). Heavy metals in urban soils may come from

 Union of Scientists in Bulgaria – Plovdiv
University of Plovdiv Publishing House

various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion (KOMAI, 1981; IKEDA & YODA, 1982; RITTER & RINEFIERD, 1983; CHON *et al.*, 1995; WONG & MAK, 1997; MARTIN *et al.*, 1998; LI *et al.*, 2001). These activities send heavy metals into the air and the metals subsequently are deposited into urban soil as the metal containing dust falls. SAKAGAMI *et al.* (1982) reported that there was a close relationship between heavy metal concentrations in soils and those in the dust falls.

Human health in towns and cities is strongly dependent on the status of urban soils (SIMPSON, 1996). Strong compaction, contamination by wastes and atmospheric depositions, loss of organic matter, changes in soil reaction, structural degradation and infection by pathogenic microorganisms are only few of the many adverse processes that affect and modify the ecological functions of soils in urban areas (BULLOCK & GREGORY, 1991; JIM, 1993; BEYER *et al.*, 1995; BLUM, 1998). Heavy metals in the soils can also generate airborne particles and dusts, which may affect the air environmental quality (CHEN *et al.*, 1997; BANDHU *et al.*, 2000; CYRYS *et al.*, 2003; GRAY *et al.*, 2003). In contrast to agricultural soils, urban soils, especially that in parks and residential areas which are not used for food crops, may also have a direct influence on public health since it can be easily transferred into human bodies (DE MIGUEL *et al.*, 2007; MIELKE *et al.*, 1999; MADRID *et al.*, 2002). In particular, the ingestion of dust and soil has been widely regarded as one of the key pathways by which children are exposed to the heavy metals and metalloids from paint, leaded gasoline, vehicles and local industry (MEYER *et al.*, 1999; RASMUSSEN *et al.*, 2001).

Previous studies indicated that the extent of heavy metal pollution in urban areas varied across time (PFEIFFER *et al.*, 1991) and location (ALBASEL & COTTENIE, 1985), and that increased levels of heavy metals in urban soil was related to the intensity of human activities and traffic volume (ZHENG *et al.*, 2002). The investigation of soil heavy metal concentrations in parks and green areas in Seville, Spain, indicated that the concentrations of Pb, Zn and particularly Cu in the soil often exceeded the acceptable limits for residential, recreational and institutional sites (MADRID *et al.*, 2002). The study of large parks in Stara Zagora (Bulgaria) reveals technogenic loads on soils with heavy metals on the bases of technogenic coefficients 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; KACHOVA & ATANASSOVA, 2017). Recent research in some of the oldest urban parks of Sofia revealed that lead was imported to the soils mainly with dust particles (particulate matter) and accumulated in the surface layers of soil from urban parks (KACHOVA & ATANASSOVA, 2017). The data on the chemical variability in the total Cu and Cd concentrations confirmed 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.

However, differences among cities including population density and industrial activities could have a large impact on the findings of individual studies. Moreover, little information is available on heavy metal concentrations in soils of urban parks located in older cities with large populations.

The aim of this study is to identify the soil environment in terms of the content of selected heavy metals, as well as to identify some of physical and chemical properties of urban soils of Natural monument "Bunardzhik" (Plovdiv, Bulgaria). By analysing the spatial distribution of heavy metal concentrations in relation to the correlations among these elements and distance from the routes, it may be possible to assess the contamination of the soils, the potential hazardous risk both for human health and for protected area.

Materials and Methods

Study area and sampling sites description

Plovdiv (42°9'N, 24°45'E) is situated in south-central part of Bulgaria, in the southern part of the Plain of Plovdiv, on the two banks of the Maritsa River. It is the second-largest city after the capital Sofia with a population of over 347 000 inhabitants (NSI, 2018). Inside the city proper are six syenite hills (including Bunardzhik Hill), several industrial zones, densely populated central area, some moderately populated areas around it, wide network of busy streets and train tracks, big parks and other green yards. Air quality in Plovdiv is quite worsened due to the motor vehicle emissions and residential heating, then the industrial sector, which has a minor impact (ATANASSOV *et al.*, 2006; PETROVA, 2011; PETROVA *et al.*, 2013; 2014a; b; 2015; RIOSV, 2017).

The climate is temperate with mild influence from the Mediterranean Sea and a large temperature range between summers and winters. The average annual temperature is 12.3 °C with maximum in July (32.3 °C) and minimum in January (6.5 °C). The average relative humidity is 73%. It is highest in December (86%) and lowest in August (62%). The total precipitation is 540 mm – the wettest months of the year are May and June with an average precipitation of 66.2 mm, while the driest is August with an average of 31 mm. Gentle winds with speed of up to 1 m s–1 represent 95% of all winds during the year. The prevailing wind direction is from west, rarely from east. Mists are common in the cooler months, especially along the banks of the Maritsa River. On average there are 33 days with mist during the year (National Institute of Meteorology and Hydrology, 2018).

Bunardzhik Hill, also known as the Hill of the Liberators, has an outstanding value in the urban ecosystem as one of the major city-forming factors and it is: *i*) symbol of the city of Plovdiv; *ii*) basic element of his identity; *iii*) unique geomorphological entity; *iiii*) habitat of rare and protected plant species. Functionally, the territory of the hill is assigned to the green system of the city for wide public use according to the General Plan of the Territory of Plovdiv (2007) and the Program for development, maintenance and protection of urban green system (2013). In 1990 Bunardzhik Hill was declared for a Monument of garden-park art, and in 1995 the Ministry of Environment and Waters declared it as a Natural monument (Ordinance RD-466/22.12.1995, MOEW) according to Protected Areas Act (1996) in Bulgaria. The natural character of the territory (including ecosystems and the landscape as a whole) is significantly influenced by the human factor, with most of the habitats characterized by a low degree of naturalness (Management Plan of Natural Monument "Bunardzhik", 2017).

Bunardzhik Hill is situated in the real center of Plovdiv, Bulgaria, along the two of the main road arteries in Plovdiv (Ruski Blvd. and Vassil Aprilov Blvd.) (Fig. 1). Its territory covers an area of 22 ha and is divided to the four functional zones (Table 1) according to the Management Plan of Natural Monument "Bunardzhik" (2017).

Soil sampling

As the park zone is the most influenced area, both from the traffic emissions and from anthropogenic pressure, this study focused on the park soils' investigation. Soil samples are taken in June 2017 from the Eastern and the Western park zones of the hill. These two park zones abut upon Ruski Blvd. and Vassil Aprilov Blvd., respectively, so soil sampling was made along a pollution gradient using the transect method (Fig. 1). Transects started from the road and were directed towards the hill in order to allow the effect of traffic on soil properties be assessed. Soil samples were collected at the 7.5 m, 25 m, and 50 m distance from the route (Table 2) on the depth of 0-20 cm (ISO 10381). Each sample was formed by 5 subsamples. The topsoil horizon was chosen for the analysis because it undergoes the biggest impact of versatile origin – mechanical, physical, chemical and biological. The preparation of soil samples for analysis was carried out, according to ISO 11464.

Soil analyses

Soil pH was measured using pHotoFlex Set, 2512000, WTW-Germany (ISO 10390), and the soil conductivity was measured using Multiset, F340, WTW-Germany (ISO 11265). Soil texture (pipette method by Wigner), humus content (by Turin) has been analyzed in the Laboratory of the Department of Agroecology and Evironmental Protection, Agricultural University of Plovdiv.

Total soil content of As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, U, Zn was determined by inductively coupled plasma–mass spectrometry (ICP–MS) (Agilent 7700). ICP–MS system was calibrated with international standards. Quality control was performed using the standard reference plant material (NCS DC73348): the percent recovery ranged from 91 to 99%, depending on each analyzed element. The extraction of trace elements and analyzes have been made in the Laboratory of Analitical chemistry and Computer chemistry of the University of Plovdiv "Paisii Hilendarski".

Statistical evaluation

Raw data from all analyses were processed using statistical software package Statistica 7.0. for Windows (Stat Soft Inc., 2004). Multi ANOVA (MANOVA) and Student/Fisher test were used for testing the differences of elemental concentrations, both between the soils samples from different road distance and also between the studied sampling sites ($p<0.05$). Relationships between the contents of individual elements in collected soil samples were tested using Pearson correlation coefficients ($p<0.05$). A cluster analysis was used for grouping the studied chemical elements on the basis of their content in studied urban soils from both park zones (Complete linkage, 1-Pearson r).

Results and Discussion

General characteristic of the soils in the studied park zones

Urban soils are composed largely of a mixture of materials differing from those in adjacent agricultural and forest areas, and transformed deeply by human activity through mixing, importing and exporting material, and by contamination (Craul, 1992). Thus human activities modify urban soils thereby setting off anthropogenic lithogenesis and pedogenesis, particularly by imposing very rapid transformation cycles (Blume, 1996; De Kimpe & Morel, 2000).

Based on their genesis, the soils in the Plovdiv area are classified as Fluvisol according to the FAO World Reference Base for Soil Resources (2014). Due to the prolonged human presence on the studied territory (more than 8000 years) and the increasing rate of urbanization in the last decades, soils properties are significantly influenced and now it is more appropriate to discuss them as Technosols and Anthrosol.

Soils in the low and relatively flattened peripheral zones of the Bunardzhik Hill are heterogeneous. They typically have a profile that is disturbed as a result of constructions, ameliorative and reinforcing activities. The terrain surface is typically artificially modeled in terms of alignment, inclination and exposure so as to form a kind of landscape for public service (Fig. 2).

Physical and chemical characteristics of studied urban soils from two park zones of the Natural Monument "Bunardzhik"

The pH values of the studied soil samples from the surface layer (0-20 cm) varied between 6.22 and 6.98 (from light acidic to neutral) in the Western park zone and between 5.87 and 6.22 (from medium acidic to light acidic) in the Eastern park zone (Table 3). Urban soils from the parks of the city of Sofia also showed slightly acidic to neutral reaction (KACHOVA & ATANASSOVA, 2017). DOICHINOVA & ZHIYANSKI (2013) reported similar pH values of urban soils from park zone in Sandanski (Bulgaria). They confirmed that pH intopsoil horizon was greater and tended to decrease in deeper layers which was found as a diagnostic feature for urbanized soils by GENCHEVA (2000). Studies in different environments (agricultural, urban and transition land-use zones) demonstrate that in the acid soils, heavy metals are more mobile than in the alkaline one, and the alkaline environment better sustains metals (KAZLAUSKAITĖ-JADZEVIČĖA *et al.*, 2014).

In an urban environment soil organic matter (SOM) has manifold functions and it is with considerable ecological significance. In the present study, we found that soil organic matter varied between 1.55% (WPZ-50) and 3.41% (EPZ-7.5) (Table 3). So, the studied soils could be characterized as relatively fertile and able to meet the needs of plants. Higher values were measured close to the road and tended to decrease to the inner of two park zones ($p<0.05$). Urban soils of studied parks in Sofia were characterized by significantly higher soil organic matter content – from 5.4% to 8.3% (KACHOVA & ATANASSOVA, 2017), but our findings were close to data from DOICHINOVA & ZHIYANSKI (2013) concerning the SOM content of urban soils from park zone in Sandanski (Bulgaria). As many authors have shown, soil organic matter may be affected by mixing of carbonaceous material like debris, ash, slag, garbage and sewage sludge, as well as from deposition of airborne particles (SCHLEUSS *et al.*, 1998; BEYER *et al.*, 2001). Therefore, the transformed chemistry and structure of soils may lead to serious disturbances in their biological activity and impoverishment of vegetation cover (MIRELES *et al.*, 2012; HU *et al.*, 2013).

Soil texture of urban soils from Bunardzhik Hill varied from light sandy to sandy loam (Table 3). The light soil texture respectively, with the higher sand content, could be related to a potentially higher soil vulnerability to processes of degradation in the presence of pollution, which is characteristic of the urban environment (WU, 2014; MAO *et al.*, 2014). We found that the soils from the Western park zone were with smaller clay fraction than soils from the Eastern park zone ($p<0.05$) (Table 3). As the both studied park soils originated from the same rocks, the variations in the soil texture could be due to the different type of evolution processes, managed by different exposure.

Content of heavy metals and toxic elements in the studied park soils from Natural Monument "Bunardzhik"

In urban areas, a wide range of substances being produced through combustion of fuels, industrial processes, road de-icing, and abrasion of vehicle exploitation materials (mainly tyres) are emitted to the environment. These are toxic gases and dust enriched with heavy metals. Such contamination undergoes deposition and penetrates into soils, damaging the main soil properties (SHANG *et al.*, 2012; MCBRIDE *et al.*, 2014).

The highest content of all the studied heavy metals and toxic elements was found in the sampling plots, situated along the route arteries – at 7.5 meters (Fig. 3 and Fig. 4). This content differed significantly with the concentrations of the same elements measured at the distance of 25 meters and 50 meters ($p<0.05$). So, the traffic inputs could be considered as the leading factor for soil contamination in the periphery of park zones. Our previous studies in Plovdiv revealed that the content of some trace elements in soils along the road network was in direct relationships both with the distance from road and the road location itself according to the wind rose (PETROVA *et al.*, 2018). This situation reflected also on the soil microbial community structure, leading not only to the damages in the physico-chemical properties of soils but to the decrease into their quality and functions.

As a whole, park soils in the east side of Natural Monument "Bunardzhik" are more contaminated then the park soils from the west side. Exceptions were found only for Cu and Sr (Fig. 3 and Fig 4). Heavy metals (mainly Cu, Pb, Zn, Cd, Ni, V) are derived by many anthropogenic processes and activities, such as domestic activities, residential heating, petrol and diesel vehicles (JOHNSON *et al.*, 2011). Copper (Cu) is yet another lithogenous trace element found in soil, but the increased levels of it, as they are observed in the topsoil, can be put down on anthropogenic activity. Strontium (Sr) is usually linked to carbonaceous soil material of large scale broken rock, and so in this case, as its content do not vary very much (38 mg/kg average in soils from Western park zone and 34 mg/kg average in those from Eastern park zone). Soil content of Hg and Se in the Western park zone is under the detection limit of 0.1 mg/kg but in soils from the other park these elements are more abundant ($p<0.001$) (Fig. 3 and Fig. 4). Compared to data from park zones in Sofia, the studied urban soils from Plovdiv (Bunardzhik Hill) have about 40% lower content of Cu, but are significantly more polluted with Pb (up to 3 fold), Cd (up to 2 fold) and Zn (up to 2 fold) (KACHOVA & ATANASSOVA, 2017).

Table 1. Functional zoning of the Bunardzhik Hill's area.

Zone	Area, ha	%	Functional purpose
Park zone (Zone 1)	4.55	20.5	Recreation, public services, sports and cultural events
Forest park zone (Zone 2)	10.81	49	Recreation in semi-natural (forest-park) natural environment, conservation of plant and animal species and typical landscapes
High zone (Zone 3)	5.61	25.5	Maintaining natural vegetation and endangered, rare and endemic species
Memorial zone (Zone 4)	1.07	5.0	Preservation of the memorials
Total:	22.04	100	-

Fig. 1. Functional zoning of Natural Monument "Bunardzhik" and sampling plots location.

Table 2. Sampling plots description.

Park zone	Along Boulevard	Distance from the road	Soil sample symbol
Western park zone	Vassil Aprilov	7.5 m	WPZ-7.5
		25 m	WPZ-25
		50 m	WPZ-50
Eastern park zone	Ruski	7.5 m	EPZ-7.5
		25 m	EPZ-25
		50 m	EPZ-50

Fig. 2. Landscape in Western park zone (A) and Eastern park zone (B).

Table 3. Physical and chemical characteristics of studied urban soils from two park zones.

Soil sample	pH	Organic C, %	SOM, %	Soil texture
WPZ-7.5	6.41	1.75	3.02	Sandy soil
WPZ-25	6.98	1.35	2.33	
WPZ-50	6.22	0.90	1.55	
EPZ-7.5	5.87	1.98	3.41	Sandy loam soil
EPZ-25	5.90	1.81	3.11	
EPZ-50	6.22	1.28	2.21	

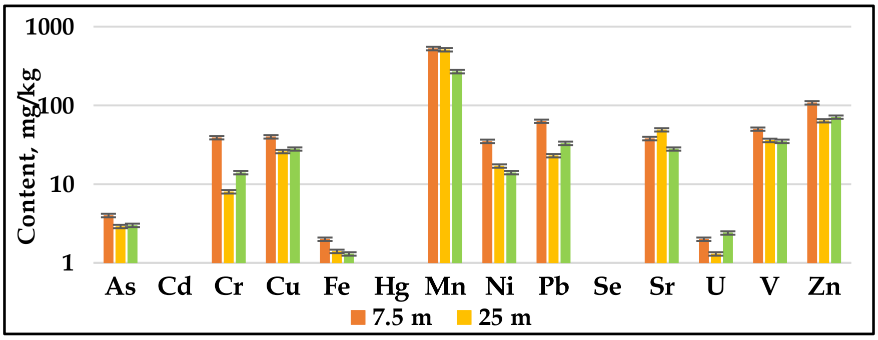

Fig 2. Content of heavy metals and toxic elements in soils from Western park zone of Natural Monument "Bunardzhik" (mg/kg, logarithmic scale).

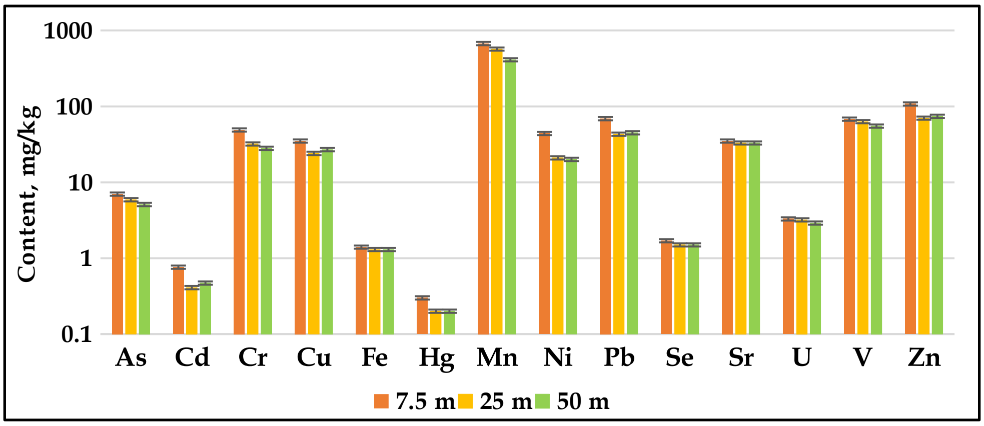

Fig 3. Content of heavy metals and toxic elements in soils from Eastern park zone of Natural Monument "Bunardzhik" (mg/kg, logarithmic scale).

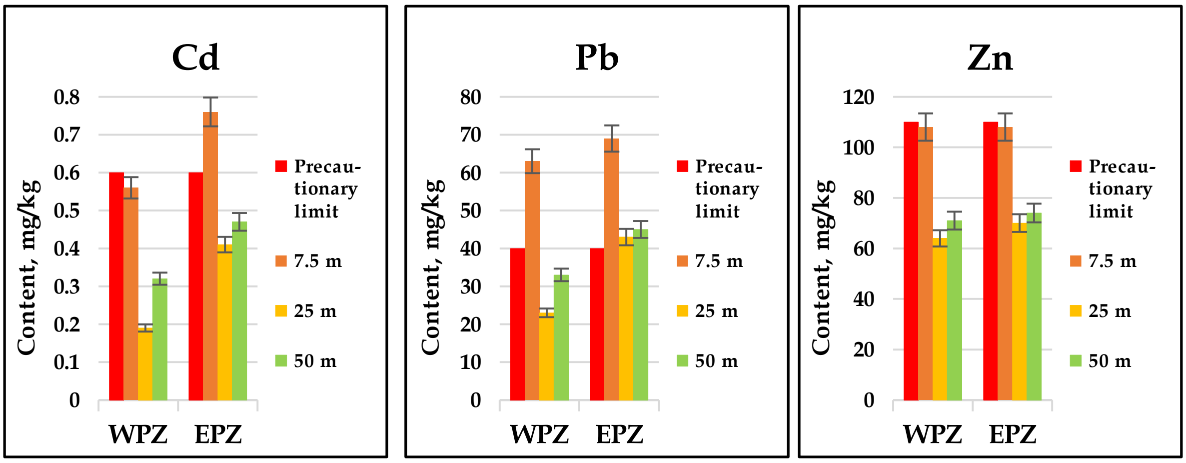

Fig 4. Comparison of our results with the precautionary limits (Regulation Norm №3/2008) about Cd, Pb and Zn content in soils of Natural Monument "Bunardzhik".

A comparison has been made with the national precautionary limits and threshold values accepted in Bulgarian standards for soils from public areas (Regulation Norm №3, 2008). Although our results are quite below the maximal limits some problems were found with the precautionary values (Fig. 4). Lead in soils from the Eastern park zone exceeds these values up to 170% at distance of 7.5 m, and to a lesser extend at 25 m and 50 m, while in soils from Western park zone an increment of 155% have been found only at 7.5 m distance from road ($p<0.05$). Cadmium content in Western park zone is below the limits but the closest sampling plot to the road in Eastern park zone was contaminated up to 125% above the precautionary values ($p<0.05$). Zink content in both sampling plots at 7.5 m distance was found to be 1% below the precautionary limits so some attention should be paid. Our findings are in good agreement with the statement of Kachova & Atanassova (2017) that Cd and Pb are inferred as markers of variables. Anthropogenic pollution, Cu contents are attributed to litho(pedo)genic sources, while Zn is both of anthropogenic and litho(pedo)genic origin.

These results give us a reason to assume that in the area of our research, these elements have a common origin, namely as waste products from road transport. This includes both exhausted gases and waste products from brake systems, tire wear, etc. A number of publications indicate that Fe is emitted from vehicle braking systems, Pb and Cd - from the exhaust gases, V from different metal composites (MAHER *et al*., 2008). Cr and V are considered indicative of vehicle emissions (GARTY *et al*., 1996) and partly associated with tire and brake abrasion, as we have shown in our previous studies (PETROVA, 2011; PETROVA *et al*., 2013; PETROVA *et al*., 2014a, b; PETROVA *et al*., 2015). So, the significant correlation with the elevated content of other studied elements in soil samples from 7.5 m distance from road lets to conclude that the traffic is the main emitter of toxic substances in the central city part of Plovdiv.

The results achieved in the cluster analysis of soil contamination showed some different relationships between heavy metals and toxic elements in the two investigated park zones (Fig. 5). Two main groups have been formed in the Western park zone, first of which included 10 of studied elements, and the second – only two (Mn and Sr) (Fig. 5A). According to BURAU & ZASOSKI (2002), it is possible to explain a stronger relationship between lithogenous elements as strontium (Sr) and manganese (Mn). When regarding the other elements, the strongest accumulation associations were formed by As-Cr-Cu, Cd-Pb-Zn and Fe-Ni-V, among which a strong linear interdependence is observed and it could be related to the pollution levels in the city. The weakest genetic links of these metals connect them with uranium (U) that is found in their cluster. Two main groups were observed in the cluster analysis of soils from Eastern park zone too (Fig. 5B), but they significantly differ from data obtained by the Western park zone. Similar accumulation tendency was found only for associations Cd-Pb-Zn and Fe-Ni ($p<0.05$).

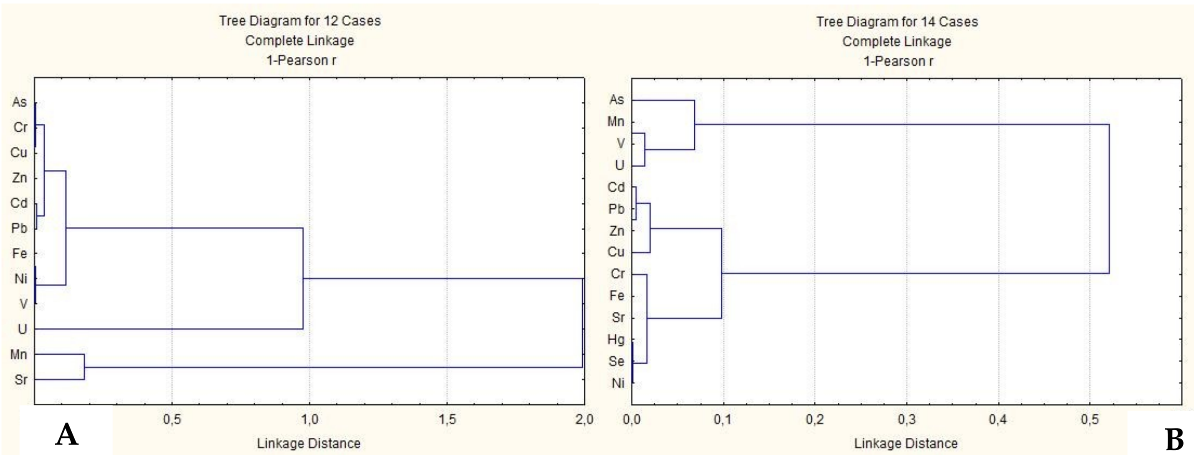

Fig 5. Cluster analysis of heavy metals and toxic elements in soils from Western park zone (A) and Eastern park zone (B) of Natural Monument "Bunardzhik".

Our previous studies have shown significant differences in the trace elements content both in some herbs (PETROVA *et al*., 2013, 2014a) and in the leaves of some ornamental trees, growing in these two park zones (PETROVA *et al*., 2014b). For example, average Pb content in tree leaves from the Western park zone was 6.7 mg/kg while in the Eastern park zone was 8.9 mg/kg, average content of Cu was 9.1 mg/kg and 12.4 mg/kg, respectively, while average content of Ni was 2.2 mg/kg and 3.0 mg/kg, respectively (PETROVA *et al*., 2014b). Thereby, some activities in collecting and removing the fallen autumn leaves in park zones could be recommended as a practical measure for limiting the entry of pollutants in urban soils by the decomposition of organic matter.

Conclusions

The studied soils from the Eastern and Western park areas of the Natural monument "Bunardzhik" have different characteristics that are probably due to the complex impact of natural and anthropogenic factors. In the soils from the western side of the hill, the content of vanadium, manganese, chromium, copper, zinc and lead is noticeably reduced, leaving from Vassil Aprilov Blvd. and reaching the middle of the park zone. In the soils on the eastern side of the hill, as a whole, higher amounts of the majority of the studied elements are reported, and there is a lack of significant decreases in their content, increasing the distance from the main road artery - Ruski Blvd.

Based on the results obtained, all studied heavy metals and toxic elements could be arranged as follows: Mn (436 mg/kg) > Zn (81 mg/kg) > V (40 mg/kg) > Pb (39.7 mg/kg) > Sr (38.3 mg/kg) > Cu (31.3 mg/kg) > Cr (23.7 mg/kg) > Ni (22.0 mg/kg) > As (3.3 mg/kg) > U (1.9 mg/kg) > Cd (0.36 mg/kg) in the Western park zone and Mn (552 mg/kg) > Zn (84 mg/kg) > V (62 mg/kg) > Pb (52.3 mg/kg) > Cr (36.3 mg/kg) > Sr (33.7 mg/kg) > Cu (28.7 mg/kg) > Ni (28.3 mg/kg) > As (6.0 mg/kg) > U (3.1 mg/kg) > Se (1.6 mg/kg) > Cd (0.55 mg/kg) > Hg (0.23 mg/kg) in the Eastern park zone, respectively.

The comparison with the normative base showed that the precautionary limits of zinc, cadmium and lead in the roadside sections of the Eastern and Western Park zone and of lead in the middle part of the Eastern park zone of Natural monument "Bunardzhik" were exceeded. The main source of these pollutants is urban traffic, and a possible reason for the higher concentrations in the Eastern park zone is the lack of wind, dust recirculation, canyon street effect, etc.

Elevated concentrations of heavy metals in the topsoil negatively affect soil biota and plant biodiversity 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, and especially of the protected area Natural monument "Bunardzhik". Some adequate measure for future prevention of soil pollution should be implemented, i.e. removing of the fallen tree leaves in the autumn season, traffic optimization and restriction, etc.

Acknowledgements

This research work was carried out with the support of the Fund "Scientific research" at the Plovdiv University "Paisii Hilendarski" by contract MU17-BF022.

References

ATANASSOV D., S. SPASSOVA, D. GRANCHAROVA, S. KRASTEV, T. YANKOVA, L. NIKOLOV, M. CHAKAROVA, P. KRASTEVA, N. GENOV, J. STAMENOV, E. DIMITROV. 2006. Air pollution monitoring and modeling system of the town of Plovdiv (Phase I). - *Journal of Environmental Protection and Ecology*, 7(2): 260-268.

ALBASEL N., A. COTTENIE. 1985. Heavy metal contamination near major highways, industrial and urban areas in Belgian grassland. - *Water Air and Soil Pollution*, 24: 103-109. [DOI]

BANDHU H.K., P. SANJIV, M.L. GARG, B. SINGH, J.S. SHAHI, D. MEHTA, E. SWIETLICKI, D.K. DHAWAN, P.C. MANGAL, N. SINGH. 2000. Elemental composition and sources of air pollution in the city of Chandigarh, India, using EDXRF and PIXE techniques. - *Nuclear Instruments and Methods*, 160: 126-138. [DOI]

BEYER L., P. KAHLE, H. KRETSCHMER, Q. WU. 2001. Soil organic matter composition of man-impacted urban sites in North Germany. – *Journal of Plant Nutrition and Soil Science*, 164: 359-364. [DOI]

BEYER L., H.P. BLUME, D.C. ELSNER, A. WILLNOW. 1995. Soil organic matter and microbial activity in urban soils. - *The Science of the Total Environment*, 168: 267-278. [DOI]

BLUM W. 1998. Soil degradation caused by industrialization and urbanization. - *Advances in Geoecology*, 31: 755-766.

BLUME H.P. 1996. *Boden stadtisch-industrieller Verdichtungsrume*. In: Blume, H.P., Felix-Henningsen, P., Fischer, W.R., Frede, H.G., Horn, R., Stahr, K. (Eds.), Handbuch der Bodenkunde-Boden als Teile von Landschaften. Ecomed Verlag, Landsberg

BULLOCK P., P.J. GREGORY. 1991. *Soils in the Urban Environment*. Blackwell, London

BURAU R. G., R. J. ZASOSKI. 2002. *Soil and water chemistry*. California, 153 pp

CHEN T.B., J.W.C. WONG, H.Y. ZHOU, M.H. WONG. 1997. Assessment of trace metal distribution and contamination in surface soils of Hong Kong. - *Environmental Pollution*, 96: 61-68. [DOI]

CHON H.T., J.S.G. AHN, M.C. JUNG. 1995. Metal contamination of soils and dusts in Seoul metropolitan city, Korea. - *Environmental Geochemistry and Health*, 17: 23-37. [DOI]

CRAUL P.J. 1992. *Urban Soil in Landscape Design*. John Wiley, New York.

CYRYS J., M. STOLZEL, J. HEINRICH, W.G. KREYLING, N. MENZEL, K. WITTMAACK, T. TUCH, H.E. WICHMANN. 2003. Elemental composition and sources of fine and ultrafine ambient particles in Erfurt, Germany. - *The Science of the Total Environment*, 305: 143-156. [DOI]

DE KIMPE C.R., J.L. MOREL. 2000. Urban soil management: a growing concern - *Soil Science*, 165: 31-40. [DOI]

DE MIGUEL E., I. IRIBARREN, E. CHACON, A. ORDONEZ, S. CHARLESWORTH. 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). - *Chemosphere*, 66: 505-513. [DOI]

DOICHINOVA V., M. ZHIYANSKI. 2013. Studies on Characteristics of Soils in Urban Forest Parks and in Natural Forest Plantations in the Region of Town Sandanski. - *Soil science, agrochemistry and ecology*, vol. XLVII, № 2: 68-75.

FAO. 2014. *World Reference Base for Soil Resources*. 2014. Available at: [www.fao.org]. Accessed: 10.10.2018.

GARTY J., M. KAUPPI, A. KAUPPI. 1996. Accumulation of airborne elements from vehicles in transplanted lichens in urban sites. - *Journal of Environmental Quality*, 25 (2): 265-272. [DOI]

GENCHEVA S. 2000. Actualized classification and diagnoses of anthropogenic soils II. Diagnoses of the Anthopogenic soils. - In: *Proceedings of the National conference "75 years of forest education in Bulgaria", section Forestry*, University of Forestry, Sofia, pp. 196-204.

General Plan of the Territory of Plovdiv. 2007. Available at: [www.plovdiv.bg]

GRAY C.W., R.G. MCLAREN, A.H.C. ROBERTS. 2003. Atmospheric accessions of heavy metals to some New Zealand pastoral soils. - *The Science of the Total Environment*, 305: 105-115. [DOI]

HOU E., H. XIANG, J. LI, D. WEN. 2015. Soil Acidification and Heavy Metals in Urban Parks as Affected by Reconstruction Intensity in a Humid Subtropical Environment. - *Pedosphere*, 25: 82-92. [DOI]

HU Y., X. LIU, J. BAI, Y. SHIH, E.Y. ZENG, H. CHENG. 2013. Assessing Heavy Metal Pollution in the Surface Soils of a Region that Had Undergone Three Decades of Intense Industrialization and Urbanization. - *Environmental Science and Pollution Research*, 20(9): 6150-6159. [DOI]

IKEDA A., K. YODA. 1982. Soil pollution by heavy metals in Sakai City. - *Japanese Journal of Ecology*, 32: 241-249

ISO 10381: 2002. Soil quality - Sampling - Part 1: Guidance on the design of sampling programs. Available at: [www.iso.org]

ISO 10390: 2005. Soil quality – Determination of pH. Available at: [www.iso.org]

ISO 11265: 1994. Soil quality - Determination of the specific electrical conductivity. Available at: [www.iso.org]

ISO 11464: 2006. Soil quality - Pretreatment of samples for physico-chemical analysis. Available at: [www.iso.org]

JIM C. 1993. Soil compaction as a constraint to tree growth in tropical and subtropical urban habitats. - *Environmental Conservation*, 20: 35-49. [DOI]

JOHNSON C., A. DEMETRIADES, J. LOCUTURA, R.T. OTTESEN (Eds.). 2011. *Mapping the Chemical environment of Urban areas*. John Wiley & Sons Publishing House, UK, 640 p.

KACHOVA V., I. ATANASSOVA. 2017. Heavy metal pools in urban soils from city parks of Sofia, Bulgaria. - *Agricultural science and technology*, 9(2): 144-150. [DOI]

KADŪNAS V., V. KATINAS, A. RADZEVIČIUS, R. TARAŠKEVIČIUS, R. ZINKUTĖ. 2005. Geochemical Atlas of Lithuania – A Basis for Detailed Geochemical Investigations of LongTerm Ecological Research Sites. - *Acta Zoologica Lituanica*, 15 (2): 131-135. [DOI]

KAZLAUSKAITĖ-JADZEVIČĖ A., J. VOLUNGEVIČIUS, V. GREGORAUSKIENĖ, S. MARCINKONIS. 2014. The role of pH in heavy metal contamination of urban soil. - *Journal of Environmental Engineering and Landscape Management,* 22:4, 311-318. [DOI]

KOMAI Y. 1981. Heavy metal pollution in urban soils. - In: Kitagishi K., I. Yamaha (Ed.). *Heavy metal Pollution in soils of Japan*. Sci. Soc. Press, Tokyo, pp. 193-217.

LI N., C. POON, P. LIU. 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. - *Applied Geochemistry*, 16: 1361-1368. [DOI]

LUND E.D., C.D. CHRISTY, P.E. DRUMMOND. 1998. *Applying Soil Electrical Conductivity Technology to Precision Agriculture*. Proceedings of the 4th International Conference on Precision Agriculture, St. Paul MN.

MADRID L., F. DIAZ BARRIENTOS, F. MADRID. 2002. Distribution of Heavy Metal Contents of Urban Soils in Parks of Seville. - *Chemosphere,* 49(10): 1301-1308. [DOI]

MAHER B.A., C. MOORE, J. MATZKA. 2008. Spatial variation in vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves. - *Atmospheric Environment*, 42: 364–373. [DOI]

Management Plan of Natural Monument "Bunardzhik". 2017. Available at: [www.plovdiv.bg]

MAO Q., G. HUANG, A. BUYANTUEV, J. JIANGUOWU, S. SHANGHUALUO, K. KEMINGMA. 2014. Spatial Heterogeneity of Urban Soils: The Case of the Beijing Metropolitan Region, China. - *Ecological Processes,* 23: 23-28. [DOI]

MARTIN A.C., V.C. RIVERO, M.T.L. MARIN. 1998. Contamination by heavy metals in soils in the neighborhood of a scrapyard of discarded vehicles. - *The Science of the Total Environment*, 212: 142-152. [DOI]

MCBRIDE R.A., A.M. GORDON, S.C. SHRIVE. 1990. Estimating Forest Soil Quality from Terrain Measurements of Apparent Electrical Conductivity. - *Soil Science Society of America Journal*, 54: 290-293. [DOI]

MCBRIDE M.B., H.A. SHAYLER, H.M. SPLIETHOFF, R.G. MITCHELL, L.G. MARQUEZ, G.S. FERENZ, J.M. RUSSEL, A.L. CASEY, S. BACHMAN. 2014. Concentrations of Lead, Cadmium and Barium in Urban Garden Grown Vegetables: The Impact of Soil Variables. - *Environmental Pollution,* 194: 254-261. [DOI]

MEYER I., J. HEINRICH, U. LIPPOLD. 1999. Factors affecting lead, cadmium and arsenic levels in housedust in a smelter town in Eastern German. - *Environment Research,* 81: 32-44. [DOI]

MIELKE H.W., C.R. GONZALES, M.K. SMITH, P.W. MIELKE. 1999. The urban environment and children's health: soils as an integrator of lead, zinc and cadmium in New Orleans, Louisiana, USA. - *Environment Research*, 81: 117-129. [DOI]

MIRELES F., J.I. DAVILA, J.L. PINEDO, E. REYES, R.J. SPEAKMAN, M.D. GLASCOCK. 2012. Assessing Urban Soil Pollution in the Cities of Zacatecas and Guadalupe, Mexico by Instrumental Neutron Activation Analysis. - *Microchemistry Journal*, 103: 158-164. [DOI]

Municipal Strategy and Plan for the Sustainable Development of Tourism in Plovdiv for the 2014-2020 period. 2014. Available at: [www.plovdiv.bg]

National Institute Of Meteorology And Hydrology. 2018. Month Bulletin. Avalable at: [www.stringmeteo.com].

National Statistics Institute (NSI). 2018. Available at: [nsi.bg].

Ordinance RD-466/22.12.1995, MOEW. Available at: [government.bg]

Petkov G., Ts. Yablanski, M. Todorova, D. Pavlov, G. Kostadinova, V. Barakova. 2010. Ecological Assessment of Soils from Parks and Places in Stara Zagora. - *Ecology and Future*, IX, 4: 24-32

Petrova S. 2011. Biomonitoring study of air pollution with *Betula pendula* Roth., Plovdiv (Bulgaria) – *Ecologia Balkanica*, 3 (1): 1-10.

Petrova S., L. Yurukova, I. Velcheva. 2013. *Taraxacum officinale* as a biomonitor of metals and toxic elements (Plovdiv, Bulgaria). - *Bulgarian Journal of Agricultural Science*, 18 (5): 742-748.

Petrova S., I. Velcheva, L. Yurukova, M. Berova. 2014a. Possibilities of Using *Plantago lanceolata* L. as a Biomonitor of Trace Elements in an Urban Area. - *Bulgarian Journal of Agricultural Science,* 20 (2): 325-329.

Petrova S., L. Yurukova, I. Velcheva. 2014b. Possibilities of using deciduous tree species in trace element biomonitoring in an urban area (Plovdiv, Bulgaria). - *Atmospheric Pollution Research,* 5 (2): 196-202. [DOI]

Petrova S., L. Yurukova, I. Velcheva. 2015. Lichen-bags as a biomonitoring technique in an urban area. - *Applied Ecology and Environmental Research*, 13 (4): 915-923. [DOI]

Petrova S., B. Nikolov, I. Velcheva, M. Yankova, E. Kogan, E. Zheleva, E. Valcheva, A. Alexandrov, M. Marhova, M. Tsankova, I. Iliev. 2018. Dynamics of soil properties under a pollution gradient in urban areas (Plovdiv, Bulgaria). - *Scientific Papers, Series A. Agronomy*, Volume LXI, No. 1: 109-116.

Pfeiffer E.M., J. Freytag, H.W. Scharpenseel. 1991. Investigation of heavy metal and arsenic pollution of soils and plants in the urban area of Manila, Philippines. - *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft,* 66: 1169-1172.

Plyaskina O., D. Ladonin. 2009. Heavy metal pollution of urban soils. - *Eurasian Soil Science*, 42 (7): 816-823. [DOI]

Program for development, maintenance and protection of urban green system. 2013. Available at: [www.plovdiv.bg]

Protected Areas Act. 1996. Available at: [mrrb.bg]

Rasmussen P.E., S.K. Subramanian, B.J. Jessiman. 2001. A multi-element profile of housedust in relation to exterior dust and soils in the city of Ottawa, Canada. - *The Science of the Total Environment,* 267: 125-140. [DOI]

Regulation Norm №3 of August 1, 2008. Standards for harmful substances in soil. - *State Gazette,* No. 71, 2008.

RIOSV. 2017. Annual Report for the environmental state in the Plovdiv region. Available at: [plovdiv.riosv.com].

Ritter C.J., S.M. Rinefierd. 1983. Natural background and pollution levels of some heavy metals in soils from the area of Dayton, OH. - *Environmental Geology*, 5: 73-78. [DOI]

Sakagami K.I., R. Eamada, T. Kurobe. 1982. Heavy metal contents in dust fall and soil of the National Park for Nature Study in Tokyo. - *Mitteilungen der Deutschen Bodenkundlichen Gessellscaft,* 33: 59-66.

Schleuss U., Q. Wu, H.P. Blume. 1998. Variability of soils in urban and periurban areas in Northern Germany. – *Catena,* 33: 255-270. [DOI]

Shang L.Y., R.H. Sun, Z.M. Wang, Y.H. Ji. L.D. Chen. 2012. Assessment of Heavy Metal Pollution in Surface Sediments of Rivers in Northern Area of Haihe River Basin. - *China Journal of Environmental Sciences*, 33: 606-611.

Simpson T. 1996. Urban soils. - In: McCall G.J.H., E.F.J. De Mulder, B.R. Marker (Eds.), *Urban Geoscience*, pp. 35-60.

StatSoft Inc. 2004. STATISTICA (*Data Analysis Software System*), Vers. 7. Computer Software. Available at: [statsoft.com]

WALCZAK B., A. GREINERT, L. GOSK, K. GORKA. 2011. Influence of Soil Geomechanical Transformations in Urban Communication Areas on their Physicochemical Properties. - *Soil Science Annual*, 62(2): 412-419.

WONG J.W.C., N.K. MAK. 1997. Heavy metal pollution in children playgrounds in Hong Kong and its health implications. - *Environmental Technology*, 18: 109-115. [DOI]

WU J., 2014. Urban Ecology and Sustainability: The State of-the-Science and Future Directions. - *Landsc. Urban Plan.*, 125: 209-221. [DOI]

ZHENG Y.M., K. YU, H.T. WU, Z.C. HUANG, H. CHEN, X. WU, Q.Z. TIAN, K.K. FAN, T.B. CHEN. 2002. Lead concentrations of soils in Beijing urban parks and their pollution assessment. - *Geographical Research*, 21: 418-424. [DOI].

Received: 23.05.2019
Accepted: 12.12.2019