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MACRO AND MICROELEMENTS CONTENT OF URBAN SOILS FROM PLOVDIV (BULGARIA)

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Abstract

The accumulation of some macro- (N, P, K) and microelements (Co, Cu, Mn, Zn) in urban soils has been studied by the analysis of topsoil horizon. Soil samples from the big park areas and along the main boulevards in the city of Plovdiv (Bulgaria) were collected. The chemical elements content was determined using standardized analytical methods. Data obtained showed significant differences, from a low up to excessive pollution level. The majority of investigated roadside soils recorded heavy metal loading when compared to the park soils from the same area. Generally, the K and P content was high in all soil samples and varied in the range 291.9-825.4 mg/kg for potassium and 410.5- 1216.0 mg/kg for phosphorus, respectively. Nitrogen content was not so abundant and varied from low/insufficient (14.17-19.4 mg/kg) in some park soils to medium (20.85-31.36 mg/kg) in the rest samples.

Key words*: traffic pollution, heavy metals, park soils, roadside soils.*

INTRODUCTION

Urbanization is the main driver of rapid land-use change around the world with important consequences for soil quantity and quality (Zhiyanski et al., 2017). Urban soils are formed under the combined effect of both natural soil formation factors and anthropogenic factors (Stroganova & Prokofieva, 2001). Soil degradation is often observed in urban areas and is expressed as a complete or partial loss of individual soil functions.

Accumulation of heavy metals and toxic elements into surface layers is one of the main characteristics of urban soils. A wide range of substances being produced through combustion of fuels, abrasion of vehicle exploitation materials (mainly tyres), road de-icing, and industrial processes are emitted to the urban environment. These are mainly toxic gases and dust enriched with heavy metals. Such pollution undergoes dry and wet atmospheric deposition and penetrates into urban soils (Mcbride et al., 2014; Shang et al., 2012). Transformed structure and chemistry of soils may lead to serious disturbances in their physio-chemical properties, biological activity and functioning, as well to the impoverishment of vegetation cover (Hu et al., 2013; Mao et al., 2014; Nikolov et al., 2019; Swiercz & Zajecka, 2018; Wu, 2014).

Urban soils derive from natural soils to the anthropogenic influence, caused by human settlement construction and their development. The transformation level is directly proportional to the intensity of urbanization process, human activities and traffic volume, as well as the type of land use and land cover changes (Zheng et al., 2002). Based on the above-mentioned reasons, the soil cover of the settlements could be divided to: *i)* soils consisting of a mixture of materials other than those in adjacent agricultural or forest areas that form a surface layer with a power of > 50 cm, greatly altered by human activity; *ii)* soils in parks and gardens that differ from natural forest or agricultural soils by composition, type of land use and management; *iii)* soils that are the result of construction activities in urban areas and are often sealed (Morel et al., 2005).

Soil, as the component of urban green spaces (Setälä et al., 2013), plays a pivotal role in maintaining urban ecosystem services, such as biodiversity maintenance, water resources protection, microclimate regulation, carbon sequestration, food production, and fulfilment of cultural or recreational needs (Lovell & Taylor, 2013; Neil et al., 2014; Wu, 2014). Urban soils are well known as large pools of carbon, nitrogen, and other elements, serving as the foundation of urban ecosystems by supporting plant growth and sustaining biogeochemical cycles (Pouyat et al., 2002). However, the protection of urban soils is still poorly considered in the planning and development of urban areas, and there is a lack of profound knowledge regarding the potential of different types of vegetation cover and plant species to moderate the degradation or to improve the state of urban soils (Zhiyanski et al., 2017).

Quantifying soil properties and understanding soil conditions are essential for assessing ecosystem services provided by urban green spaces and detecting pollution in them (Mao et al., 2014). Having in mind that the urban soils going into different use, including vegetable and/or trees cultivation in the small gardens around the houses (Lăcătușu et al., 2008), the nutritive chemical elements level knowledge is of a great importance for the sustainable management of the urban green infrastructure.

In this context, the aim of the present study concerns the urban soil chemistry, especially about macro- and microelements contents as premise for urban green spaces supporting and urban agriculture developing.

MATERIALS AND METHODS

Study area

The city of Plovdiv is located at 24°45' east longitude and 42°09' north latitude, at an altitude of 160 m a.s.l. It is the second largest city in Bulgaria after Sofia, and is also one of the most densely populated cities in the country with almost 350,000 inhabitants per 102 km^2 (NSI, 2018). Inside the city proper are six syenite hills, 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.

Sample collection

Soil samples were taken in Mart 2019 according to the administrative regulation of the city of Plovdiv, urban gradient and the type of land use (Figure 1). Sampling plots have been chosen in permanent grassland areas along the main boulevards in the city, as well as in permanent grassland areas of park zones (as away from the traffic as possible). Soil samples were collected on the depth of 0-20 cm and each sample was formed by 5 subsamples (Petrova et al., 2013).

Laboratory analyses

Soil pH was measured using pHotoFlex Set, 2512000, WTW-Germany, and the soil organic matter content (SOM) was analysed using the weight loss method (Nikolov et al., 2019).

Analyses of the mobile forms of studied macro-elements (N, P and K) followed ISO/TS 14256-1:2003 and GOST 26209:1991, respectively.

Total content of studied microelements (Co, Cu, Mn, and Zn) in air dried soil samples was estimated after MW digestion in closed PTFE vessels (ETHOS ONE, Milestone) by using a mixture of $HNO_3 + H_2O_2$. All reagents used are high purity analytical grade. For a control of possible contamination due to the regents or sample preparation procedure, balk samples are prepared and analysed for every sample batch.

The total content of Cu (324.754 nm), Mn (348.291 nm) and Zn (206.200 nm) were determined by ICP-OES (iCAP 6300 Duo,S, Thermo Scientific) at the appointed spectral lines by axial plasma observation with an exception of Mn (for which radial plasma view mode was used). For quantification of low Co content the method ICP-MS (Agilent 7700) was used. The following isotopes were monitored: ^{54}Mn, ^{59}Co, ^{63}Cu, ^{65}Cu, ^{64}Zn and, ^{66}Zn.

The calibration solutions were prepared after appropriate dilution of Multi VI (30 elements in HNO_3, Merck, Darmstadt, Germany), traceable to NIST. For on-line correction of non-spectral matrix effect in ICP-MS the method of internal standard (^{103}Rh) was applied. Both instrumental methods have been validated (for the total content of elements) via analysis of certified reference material (CRM) Loam Soil ERM -

CC141. The same material was used for quality control purposes. A portion of CRM was digested and analysed together with samples. The measured concentrations of all tested elements were statistically comparable with the declared certified values (for extraction with Aqua Regia).

Statistical analyses
Descriptive analysis was obtained using the following variables: arithmetic mean, median, range, standard deviation (SD), and coefficient of variation (CV). The cluster analysis was carried out, based on Ward's method in which the similarity criterion is the squared Euclidean distance. Euclidean distance provides a measure of the similarities between samples. The distance coefficients express the degree of similarity as distance in multidimensional space and thus, as the distance value decreases, the similarity increases (Melegy & El-Agami, 2004).

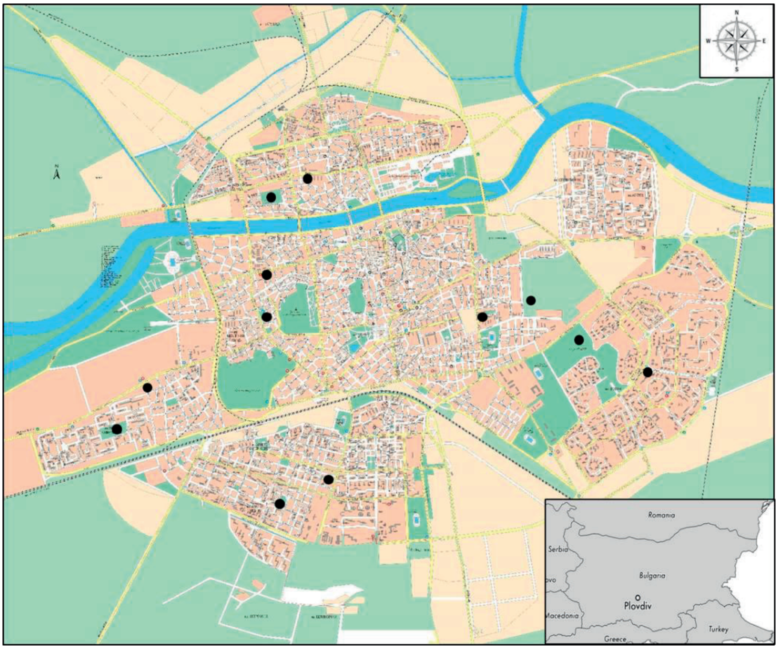

Figure 1. Map of Plovdiv and locations of sampling plots

RESULTS AND DISCUSSIONS

The influence of the anthropogenic factor on the contemporary soil formation process is well known and soils with the distinct influence of this factor are diagnosed as "Anthropogenic soils" (Anthrosols) (Ivanov et al., 2010). Depending on the main directions of anthropogenic activity, at the next taxonomic level Gencheva (2000) divides three soil types: agrogenic, urbogenic and technogenic.

According to their genesis, the soils in the Plovdiv area are classified as Fluvisols (FAO, World Reference Base for Soil Resources, 2014). Our previous studies on some park soils from the city of Plovdiv have shown that they exhibit urban changes not only in the topsoil horizon but in deeper soil layers too, so they could be referred to Urbic Anthrosols (WRB, 2006). When regarding the soils of small green belts, especially roadside, we found that soil properties are significantly influenced and it is more appropriate to discuss them as Technosols (WRB, 2006) (Petrova et al., 2018).

The pH values of soils samples from the surface layer (0-20 cm) varied from 5.57 (medium acidic) up to 6.70 (close to neutral) (Table 1). The prevailing part of studied urban soils had a light acidic reaction with a median value of 6.37 in both park and roadside samples. Our findings well correspond with data about the pH of some urban garden soils from the Ferneziu area (NW Romania) - medium acid-neutral (5.7-7.5) (Mihali et al., 2013). Similar results have been also obtained for soil pH of some industrial areas (median 6.46) in the city of Skarżysko-Kamienna (Poland) (Swiercz & Zajecka, 2018), while the pH values of urban green areas (median 5.64) and allotment gardens (5.57) in this city are significantly lower from our data. Physio-chemical properties of urban soils are dependent on the characteristics of geological substrate as well as the conditions and structure of the urban environment (Greinert, 2015). As noted by Park et al. (2010), physio-chemical properties of soils are derivatives of the city age and spatial structure. It is caused by the factors influencing soils in various stages of urban development and concerns both industry and transportation growth, as well as the intensity of urbanisation. Moreover, soils are subject to numerous land-use treatments and thus unequivocally transform their structure and physio-chemical properties.

Soil organic matter (SOM) in the present study varied in the range of 3.18% to 7.21% (park) and between 2.36-4.37% (roadside) (Table 1). As a whole, SOM in Plovdiv was quite elevated, more expressed in park samples. SOM is necessary for all soil functions, and it is the most important indicator of soil health. It consists of varying proportions of small plant residue (fresh), small living soil organisms, decomposing (active) organic matter, and stable organic matter (humus) in varying stages. SOM is a mineralizable source of nutrients for plants. It increases the availability of most nutrients, buffers the effects of high acidity, increases the available water capacity and moisture retention of the soil, helps to minimize compaction and surface crusting, increases water infiltration, provides food for micro-organisms that facilitate the availability of nutrients, holds soil aggregates together, decomposes pesticides, and acts as a carbon sink.

Soil organic carbon (SOC) is a function of SOM, so we found the same tendency. All studied urban soils samples are above the recommended range of soil SOC (> 10 g/kg) for healthy plant growing (Whitcomb, 1987). It could be assumed that these soils possess significant potential for plant growing and provide a good media for urban greening. Data from Plovdiv are significantly higher than the organic carbon content in some urban soils from Romania whit medium values about 1.7% (Lăcătușu et al., 2008).

Table 1. General characteristics of studied urban soils

Parameter	pH		Organic C, %		SOM, %	
	Park soil	Road-side soil	Park soil	Road-side soil	Park soil	Road-side soil
Mean	6.25	6.40	2.61	1.99	4.50	3.43
Median	6.37	6.37	2.42	1.91	4.17	3.29
Min	5.57	6.23	1.84	1.37	3.18	2.36
Max	6.63	6.70	4.18	2.71	7.21	4.67
SD	0.39	0.17	0.89	0.55	1.54	0.95
CV, %	7	3	34	28	34	28

Data concerning the content of main macro-elements (N, P and K) as mobile forms are presented on Table 2. Although the studied urban soils are rich in total nitrogen (data not shown), the level of mobile nitrogen is very low. The values range between 14.17 and 31.36 mg/kg with a median of 20.13 mg/kg. These values meaning a low level of nitric azote supplying, are specific for the soils that have not received any organic or mineral fertilizers. Therefore, the urban soils are poorly supplied with mobile nitrogen forms, that representing one of the specific chemical property of these soils (Lăcătușu, 2005).

Median values of mobile phosphorus in urban soils from all studied locations are 525 mg/kg (park) and 540 mg/kg (roadside), respectively, values that, without exception, defining a very high content domain.

Regularly, the potassium is in large quantities in urban soils. Medium total potassium values, rounding about 2.5%, are revealing a very good soil supplying with this macro-element. In our study, the mobile potassium content is very high, reaching a maximum value about 826 mg/kg in park soils. Median values of mobile potassium from all studied samples are 660 mg/kg (park) and 722 mg/kg (roadside), making point very high mobile potassium content in urban soils from Plovdiv.

Therefore, the analysed urban soils are containing low quantities of mobile nitrogen, but are highly supplied with mobile phosphorus and potassium. These findings are in agreement with data from Ferneziu area (NW Romania), reported by Mihali et al. (2013). An exception was found only for nitrogen supply - it's content in Romanians urban soil is medium due to natural content and anthropogenic inputs (as consequence of the fertilization of the soils in the vegetable gardens).

Table 2. Agrochemical characteristics of urban soils

Parameter	N, mg/kg		P, mg/kg		K, mg/kg	
	Park soil	Road-side soil	Park soil	Road-side soil	Park soil	Road-side soil
Mean	20.69	23.44	557.8	613.5	667.5	623.2
Median	20.13	24.03	525	540	660	722
Min	14.17	15.57	77	354	463	292
Max	31.36	28.17	1216	1117	826	745
SD	6.05	4.18	394.1	280.9	146.9	183.9
CV, %	29	18	71	46	22	30

The C/N ratio is very low for urban soils in Plovdiv (< 10). This shows that in these soils with more anthropogenic influence, the organic matter is subjected to a higher degree of mineralization and carbon loss in the atmosphere, while the humus accumulation process is weaker. We aimed to analyse also the content of some microelements with biogenic role - Co, Mn, Cu, Zn, and the results are shown in Table 3. According to content level or their abundance, these chemical elements could produce negative effects on environmental factors. In fact, from environmental sciences point of view, all these chemical elements are included in heavy metals generic terms.

Analytical dates, statistically calculated, have been reveal differences between both chemical elements and locations ($p < 0.05$). The content of Co varied between 5.6 mg/kg and 15.4 mg/kg in the park soils and between 6.1 mg/kg and 8.8 mg/kg in the roadside soils. It was found to be the microelement with the most significant differences in CV according to the type of land use - 38% (park) and 12% (roadside) ($p < 0.05$). Our data are 3 fold lower than the median values for Co content (24 mg/kg) in Romanian urban soils, reported by Lăcătușu et al. (2008) and Mihali et al. (2013). However, there is no Co deficiency in studied urban soils from Plovdiv (Bulgaria).

The content of Cu varied in the range 23-56 mg/kg, Mn content was between 421 and 891 mg/kg, while Zn ranged from 74 mg/kg to 193 mg/kg. The median content of Cu, Mn and Zn in our study was also quite the median values of these element, revealed by Lăcătușu et al. (2008) and Mihali et al. (2013) in Romanian urban soils. This fact could be due mainly to the genesis of microelements in the urbanized areas. Han et al. (2006) reported that coefficients of variations (CV) of heavy metals dominated by natural sources are relatively low, while those of heavy metals affected by anthropogenic sources are quite high. Thus, based on the CV values which all are below 0.40, the microelements in studied urban soils from Plovdiv seem to be associated mainly with natural sources, although some anthropogenic inputs to Co, Cu and Zn should be considered.

Table 3. Content of microelements in studied urban soils

Parameter	Co, mg/kg		Cu, mg/kg		Mn, mg/kg		Zn, mg/kg	
	Park soil	Road side soil	Park soil	Road side soil	Park soil	Road side soil	Park soil	Road side soil
Mean	9.3	7.6	38	46	640	540	111	113
Median	8.85	7.5	38	49.5	564	516	96	113
Min	5.6	6.1	23	32	494	421	81	74
Max	15.4	8.8	56	56	891	691	193	160
SD	3.5	0.9	12.6	9.9	157	93	42	35
CV, %	38	12	33	22	25	17	38	31

To differentiate distinct groups of macro- and microelements as tracers of natural or anthropogenic sources, an explorative hierarchical cluster analysis has been performed (Figure 2), which maximises the variance between groups and minimizes the variance between members of the same group (Lee et al., 2006).

As can be noticed from Figure 2, the elements were grouped in two clusters: cluster I (N, Co, Cu, Zn) and cluster II (K, P, Mn). The similarity axes represent the degree of association between the elements, as follows: the higher their value, the higher the degree of association between the elements. The first cluster may be influenced by the anthropogenic pollution by means of the activities in the area (urban greening and road traffic), while cluster II seem to be associated with the geogenic and pedogenic sources.

Heavy metal content in street dust and upper soil horizons in cities is an index of pollution originating from various forms of human activity - operation of industrial plants, fuel consumption, exhaust emissions and the wear of various vehicle parts (Al-Khashman, 2007; Bilos et al., 2001). As Zglobicki et al. (2019) revealed, Zn was the element with the greatest enrichment in street dust in relation to the geochemical background for both fractions (63-200 μm and < 63 μm) for the whole 6-years period of survey in Lublin, Poland. The concentrations of Zn and Cu in the urban soils of Plovdiv could be influenced by the road traffic, while N and Co concentrations could be related with the mineral fertilisers used in landscaping activities (Maas et al., 2010). Cu abundance may be also influenced by the fertilisers and pesticides used in park areas (Nikolov et al., 2019).

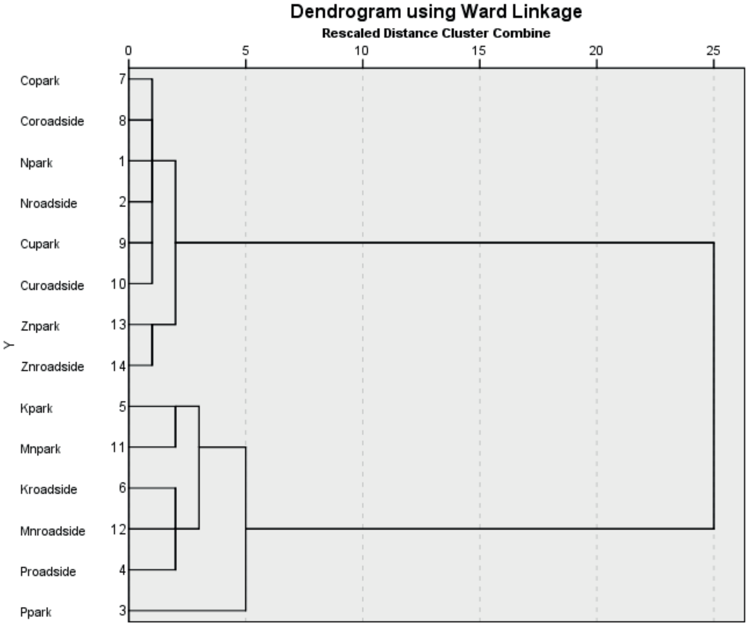

Figure 2. Hierarchical cluster analysis of macro- and microelements content of studied urban soils

CONCLUSIONS

As a whole, SOM in Plovdiv was quite elevated, more expressed in park samples. All studied urban soils are above the recommended range of soil SOC (> 10 g/kg) for healthy plant growing. It could be assumed that these soils possess significant potential for plant growing and provide a good media for urban greening. Generally, the K and P content was high in all soil samples and varied in the range 291.9-825.4 mg/kg for potassium and 410.5-1216.0 mg/kg for phosphorus, respectively. Nitrogen content was not so abundant and varied from low/insufficient (14.17-19.4 mg/kg) in some park soils to medium (20.85-31.36 mg/kg) in the rest samples. The C/N ratio is very low (< 10) which means that the organic matter is subjected to a higher degree of mineralization and carbon loss in the atmosphere, while the humus accumulation process is weaker.

Urban soils of Plovdiv are well supplied with microelements. Based on the CV values, which all are below 0.40, these microelements seem to be associated mainly with natural sources, although some anthropogenic inputs to Co, Cu and Zn should be considered.

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