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Air Pollution Biomonitoring in Urban Ecosystems with Aesculus hippocastanum

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Abstract. Several phytomonitoring surveys in urban ecosystems have been undertaken during the last years. The questions about the role of natural variables in conditions of increased anthropogenic pressure, as well as the background levels of pollutants in the background sites in urban areas, are still open. Our study was focused on bioaccumulation of heavy metals and toxic elements in leaves of *Aesculus hippocastanum* L. from two air quality station types: background and traffic. Consequently, the pollutant levels in 3 Bulgarian cities with different geographical characteristics were compared. Nevertheless, results revealed similar levels of heavy metals and toxic elements in the studied cites, which suggested the anthropogenic factor as a major for deposition. In addition, all three cities are at risk of atmospheric deposition of Pb in the areas located around intensively loaded road arteries. PCA illustrated that the concept of "urban background sites" is disputable in some cases.Based on the results horse chestnut is recommended for urban green infrastructures.

Key words: Horse chestnut, air quality, traffic, background station.

Introduction

Air pollutants are emitted from a variety of natural and anthropogenic sources, e.g. combustion processes, various industrial activities, traffic, state of road infrastructure, construction and repair activities. The distribution of pollutants in the air is directly related to weather conditions and can be described by the following cycle: (i) emitting from source into the air; (ii) dilution; (iii) sedimentation or absorption from the surface, e.g. plants (NIKOLOVA, 2008). Urban growth has strong environmental impact including air quality deterioration. Automobile exhaust emission is the main source of air pollution in major cities as it is a source of atmospheric pollution throughout the year. Domestic heating through wood and coal can be a significant source of emissions (fine particulate matter, benzene) in the cold winter days. Chemical composition of tree leaves provides data on the spatial distribution of atmospheric pollutants. Plants absorb heavy metals mainly through the leaf pores till the concentration in the ambient air is reached, regardless of the additional quantities that flow from the soil into the plant (HEINZ & REINHARD, 1991).

Aesculus hippocastanum L. is a large deciduous tree native to the Balkan Peninsula (THOMAS *et al.*, 2019). Horse chestnut was found to be in the group of the most effective net particle accumulating plant species among investigated 96 perennial urban plant species (MUHAMMAD *et al.*, 2019). Aesculus hippocastanum was an object of biomonitoring study in the capital of Serbia for a 5-year period (Cr, Fe, Ni, Zn, Pb, Cu, V, As and Cd) and was recommended to be used as bioaccumulator (KOCIĆ *et al.*, 2014).

Although tree species, and particularly horse chestnut were applied in urban biomonitoring studies for many years, it has not given completely satisfactory data about the role of the natural features of urban ecosystems and are there really background city sites. The aim of this study was to determine the variation of airborne heavy metal and toxic element concentrations in the horse chestnut leaves depending on (i) geographical characteristics of selected urban systems and (ii) traffic impact.

Materials and Methods

The passive biomonitoring was carried out in 3 major Bulgarian cities (Sofia, Plovdiv and Burgas), which are characterized by different natural and anthropogenic factors influencing air quality. The location of Sofia in the Sofia valley, surrounded by mountains, reduces the possibility of self-cleaning of the atmosphere. The air in the capital is polluted mainly by transport, heating with solid and liquid fuels, contaminated road surfaces and thermal power plants. The main sources of pollution in the city of Plovdiv are industrial, domestic and public heating, transport and non-organized emissions (Regional Inspectorate of Environment and Water - Plovdiv, 2016). The main sources of pollution in Burgas are predominantly the transport, heating and industrial sectors (Burgas Municipality, 2016). "Lukoil Neftohim Burgas" AD is the largest refinery in the country. Refiners can be a source of a wide range of pollutants (fine particulates, hydrocarbons, nitrogen oxides, sulfur dioxide, hydrogen sulfide) from both production processes and accidental leakage and reservoir fleets.

In order to achieve maximum accumulation, representative samples of leaves of *Aesculus hippocastanum* were collected from 6 monitoring stations at the end of the vegetation season (end of August-September) in 2016. Selected air quality stations are classified as traffic or background type according to the dominant emission source.

Aesculus hippocastanum is Balkan endemic and tertiary relic species (BISERKOV *et al.*, 2015). It was chosen on the basis of its proven qualities as a biomonitor and its distribution and representativeness in the three cities. In each city, 2 stations were selected: urban background and traffic (Fig. 1). At each point, leaves of between 3 and 5 trees were sampled (GORELOVA *et al.*, 2011). The leaves were usually harvested at a height of 1.5 - 2 m and placed in polyethylene bags. All samples consisted from green undamaged leaves. The elements P, K, Ca, S, Na, Mg, Mn, Fe, Al, Zn, Cu, Pb and Sr were determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES) using iCAP 6300 Duo,S, Thermo Scientific, at the Department of Analytical and Computer Chemistry, Faculty of Chemistry, University of Plovdiv. The elements Cr, Co, Cd, V, Ni, As, Hg, Se and Sb Mo were determined by ICP-MS (Agilent 7700).

Principal component analysis (PCA) in programme CANOCO was used to study relationships between the different elements in monitoring stations (TER BRAAK & ŠMILAUER, 2002).

Results and Discussion

Six stations were selected to correspond to the requirements of urban background and traffic sites (Table 1).

In the analyzed leaves of *Aesculus hippocastanum*, the leading macroelement is calcium, which represents between 1.5 and 2.6% of the content (Table 2). Similar values are considered as a signal for Ca and are associated with contamination conditions (JITEREANU *et al.*, 2010). Comparison of K levels with optimal values published for other tree species (0.6-1.8%) indicates that the trees subject to the present study do not show a deficiency on this element. At the same time, phosphorus has levels that are linked to suppression of metabolism. The descending rows of the analyzed macro- and microelements are presented below.

Site1:
Ca>Mg>K>Na=Al>S>P>Fe>Mn>Sr>Zn>Cu>Cr>Pb>V>Ni>Sb>Mo>As>Co>Hg>Se>Cd
Site2:
Ca>K>Mg>Al>=Na=S>P>Fe>Zn>Mn>Sr>Cu>Pb>Cr>As>Ni>Mo>V>Se>Sb>Co=Hg>Cd
Site3:
Ca>K>Mg>Al>Na=S>P>Fe>Mn>Sr>Zn>Cu>Pb>Cr>V=Ni>As>Mo>Sb>Co>Hg>Se>Cd
Site4:
Ca>K>Mg>Al=Na=S>P>Fe>Mn>Sr>Zn>Pb>Cu>Ni>Cr>As>V>Se=Mo>Co>Sb>Cd>Hg
Site5:
Ca>K>Mg>Al>Na=S>P>Fe>Sr>Zn>Mn>Cu>Pb>Cr>Ni>V>As>Mo>Cd>Se=Co>Sb>Hg
Site6:
Ca>K>Mg>Al=Na=S>P>Fe>Sr>Zn>Mn>Cu>Cr>Pb>V>Ni>As>Mo>Se=Co>Sb>Hg>Cd

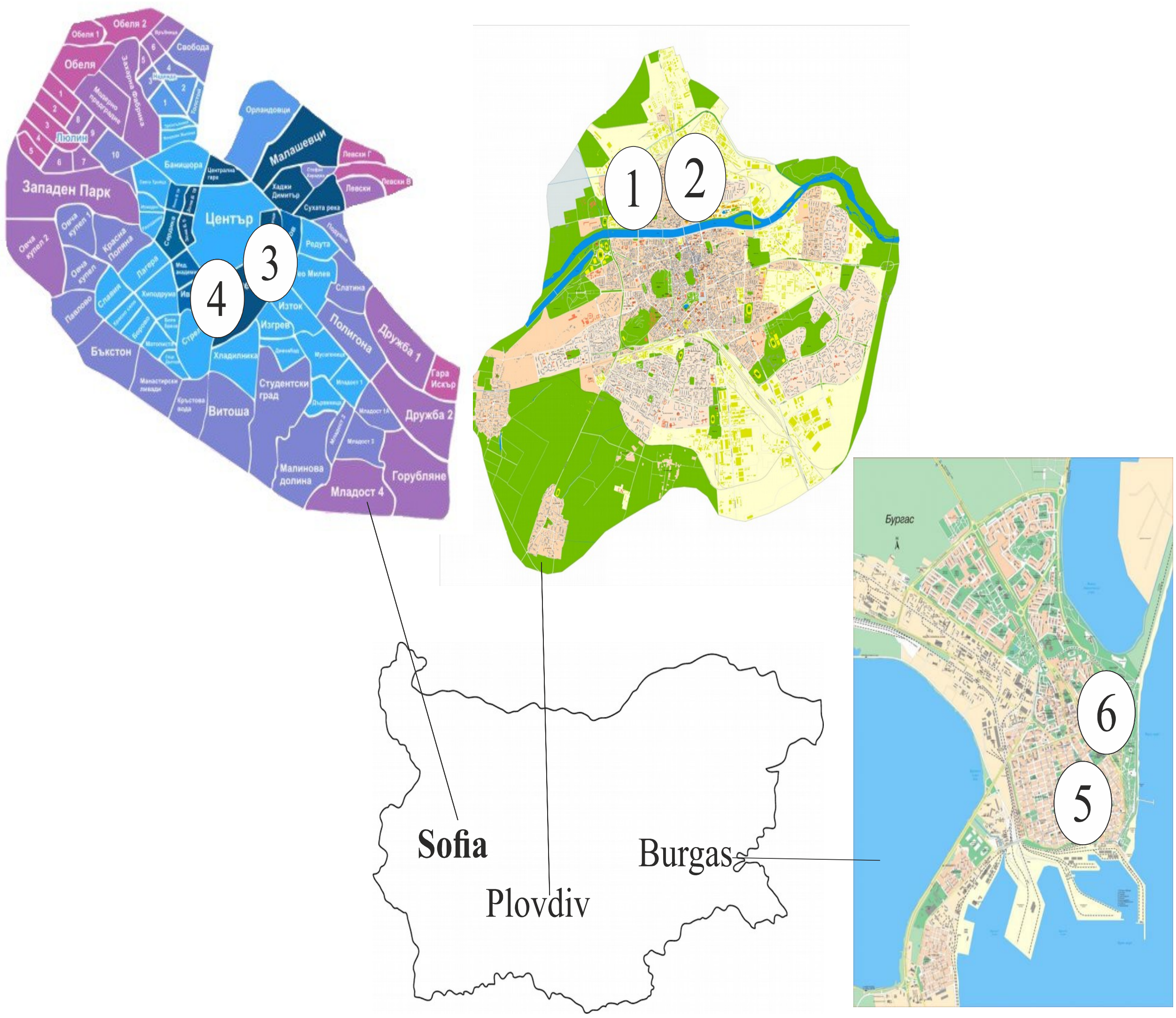

Fig. 1. Location of monitoring stations.

Table 1. Description of the monitoring stations.

	Site	Description
1	Plovdiv, Pobeda Str.	Situated in the northwest part of the city, conditionally accepted as a city-wide background. The vegetation is represented by tree species and low grasses.
2	Plovdiv, Maritsa Blvd., to the Bridge of the Fair	Located in the northwestern part of the city, next to one of the busiest boulevards. Nearby is Maritsa River.
3	Sofia, Faculty of Chemistry	Located in the central part of the city, which is extremely busy throughout the day.
4	Sofia, Lozenets, Korab mountain Str.	The site is located near a small street without significant traffic. Conspicuously accepted for urban background.
5	Burgas, center	Located near a main thoroughfare in the central city area. Conforming to the requirements for a transport-oriented point.
6	Burgas, Zornitsa district	The point is located in a residential area in the Zornitsa residential district, on the outskirts of Burgas; with features of an urban background site.

Table 2. Minimum and maximum accumulated levels in the leaves of *A. hippocastanum* in Sofia, Plovdiv and Burgas. Legend: * - concentrations were presented in %.

	Minimum			**Maximum**		
Element	%/mg kg $^{-1}$	RSD %	Site N	%/mg kg $^{-1}$	RSD %	Site N
Al*	0.1	5.6	4	0.2	5.0	6
Na*	0.1	4.5	2	0.2	4.5	1
K*	0.4	4.4	1	1.2	4.8	2
Mg*	0.2	4.4	4	0.5	4.4	1
Ca*	1.5	4.7	2	2.6	4.4	1
S*	0.1	4.3	1- 5	0.2	4.2	6
Mn	28	4.1	2	98	4.9	1
Fe	236	4.6	4	879	4.8	1
P	1189	5.9	1	2887	5.2	5
Cu	4	5.8	4	23	4.8	5
Sr	27	4.6	2	217	4.1	6
Zn	41	5.1	4	67	4.9	1
V	0.4	3.5	2	1.4	3.9	1
Cr	1.0	3.4	4	2.8	4.8	1
Co	0.1	4.6	2	0.3	3.7	1
Ni	0.6	4.9	2	1.3	4.7	1
As	0.3	5.4	6	0.7	3.7	2
Se	0.05	6.1	3	0.3	2.6	4
Mo	0.23	5.3	6	0.65	4.2	1
Cd	0.03	7.7	3	0.25	4.9	5
Sb	0.11	4.5	4	0.78	4.7	1
Pb	1.7	4.1	6	6.3	4.1	2
Hg	0.07	12.2	4	0.18	10.7	1

Plovdiv town suffers from dirt comes from climate and topography due to the temperature inversion which acts as a "cover" over the city, preventing the dispersion of pollutants. Dissipation is further hampered by the location in the Maritsa valley, which is reflected in the established maximum value of twelve elements in the leaves from traffic station: Mg, Ca, Mn, Fe, V, Cr, Co, Ni, Mo, Sb, Hg and Zn. In the second point observed in the city were reported maximum of the macroelement potassium and the heavy metals arsenic and lead. For most of the above elements, anthropogenic pollution is mainly due to metallurgy, the quantity of motor vehicles and the type of burned petrol. One of the major negative effects of the city's current transport system is the high level of air pollution throughout the year.

In the selected background station in Sofia was found the highest concentration of element Se. Since selenium falls mainly in the burning of fossil fuels, paper and tires (STOYANOV, 1999), it can be assumed that the increased level in the point as a result of the increased traffic on Tsarigradsko shosse Blvd. A minimum concentration of selenium (0.05 mg kg-1), which is up to 6 times the concentration difference, was analyzed in the transport-oriented station in Sofia (N3).

For the traffic station in Burgas, the leaves of the selected biomonitor show the maximum accumulations of copper and cadmium, while the highest levels of sulfur, strontium and vanadium were analyzed at the point on the periphery of the city. The is about 3 times higher in the leaves from the center of Burgas compared to the other stations. The reason for the presence of high concentrations of cadmium in the measured samples is probably the periodic emission surges from the transport through the center of Burgas towards the southern Black Sea coast. The reported maximum of sulfur illustrates the impact of Lukoil Neftochim Burgas AD. In station 5, the highest content of macroelement phosphorus is also recorded.

Principal Component Analysis showed that the first axis (eigenvalue 0.589) was positively correlated with Cr, Hg, Mo, Pb, Sb, Se, Sr and V, while the second axis (eigenvalue 0.205) had strongest correlation with Cd and Mn. Stations with high accumulated levels of Mn, Ni, Co, Sb, Sr, Cr, Hg and V were located in the upper left of the plot (stations N1, 3 and 6). Traffic station in Burgas illustrated specific bioaccumulation model with elevated values for Zn, Cu and Cd (bottom left), while traffic site in Plovdiv is separated in the bottom right part of the plot. Only station N4 could be assumed as background urban station (upper right). It could be concluded that in the studied cities, the central urban areas with dense human structures and intensive traffic, possess risk towards air quality.

When comparing the traffic-oriented points and those conventionally accepted for urban backgrounds, the lead difference is significant, which confirms the effect of the vehicle on the atmospheric air load. In Plovdiv the difference was above 2 times, almost twice for Sofia and Burgas. This is due to the fact that despite the ban on leaded petrol in Bulgaria, a significant number (68%) of the vehicles are over 15 years of age (EVTIMOV, 2014), which contributes significantly to the atmospheric air pollution. These results conclude that the major cities of the country are at risk of atmospheric deposition of lead in the areas located around intensively loaded road arteries. Most often these areas have line character, covering a strip with a width of up to 100 m on both sides of busy streets and boulevards.

The iron content of tree species in urban environments in the order of 48-376 mg kg^{-1} is taken as an indication of no emission (GORELOVA *et al.*, 2011). In the present study, only samples from Points 2 and 4 have levels below the above upper range. Despite the commented results for a low content of Zn in the form of 16 to 32 mg kg^{-1}, we found from 41 to 67 mg kg^{-1}.

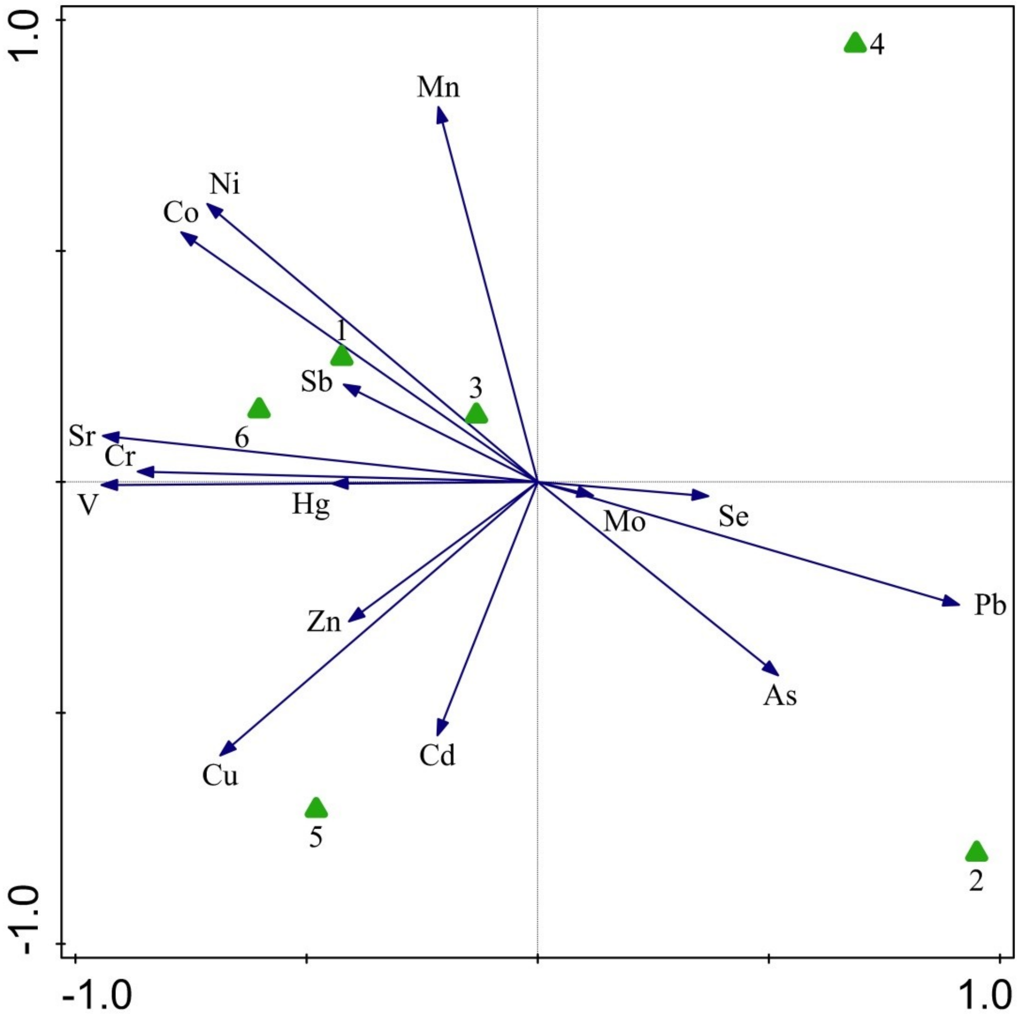

Fig. 2. PCA ordination plot of accumulated heavy metals and toxic elements in the studied monitoring stations.

Reported Pb levels in *Aesculus hippocastanum* from Bulgaria, Serbia, Turkey and Russia were between 0.5-1.6 mg kg^{-1} (GORELOVA *et al.*, 2011). Biomonitor's leaves from Sofia accumulated 0.68 mg kg^{-1} lead. The research emphasized that horse chestnut in metallurgic region could accumulate up to 5.6-8.1 mg kg^{-1}, similar to the registered value in the traffic site in Plovdiv. Highest value of Pb was found in *A. hippocastanum* in areas with high traffic density in recent research of four tree species frequently used in landscaping studies (TURKYILMAZ *et al.*, 2018). Background levels in all three cities studied in 2016 had similar to the average for trees in Europe concentrations (1.5 и 2.1 mg kg^{-1}; IZRAELY, 1989).

The relation between Fe/Mn varied in the range 2.6 и 9.8 which confirmed the assessed link between these two elements and plant resistance towards toxic elements (KABATA-PANDIAS & PENDIAS, 2001).

Comparison with data from the same species from Plovdiv for a period of 6 years ago (PETROVA *et al.*, 2012) showed that the average Cu levels remained the same, while Pb was nearly 2 times higher, Cr close to 8, V 18 times higher concentrations. Only cadmium had 2 times lower average levels in the leaves of *Aesculus hippocastanum*.

Increased levels of lead, chromium and vanadium could be linked to the increased traffic, as well as the expansion of industrial zones and construction activities in the city's area.

The comparison with published data on lead, cadmium, zinc and copper in the chestnut leaves in the region of Trasse, the European part of Turkey again showed higher levels in Bulgaria. For instance, lead variation at 20 sampling points was between 0.023-0.119 (Yilmaz *et al.*, 2006), while in the three Bulgarian cities in the range between 1.7 - 6.3 mg kg^{-1}. Cadmium in neighboring Turkey - 0.002-0.068 mg kg^{-1}, while bioaccumulation levels in our study were within the range 0.03-0.25 mg kg^{-1}. Zinc in leaf samples from the territory of Turkey was 0.374-0.532 mg kg^{-1}; in Bulgaria - from 41 to 67 mg kg^{-1}. Copper was 0.322-0.466 mg kg^{-1}, compared to the Bulgarian samples with concentrations from 4 to 23 mg kg^{-1}. The above illustrates the impact of major industry emission sources, including energy, as well as the transport sector on the territory of studied three Bulgarian cities.

Conclusion

Despite difference in natural characteristics of the three cities, they showed similar pollutants levels. Based on the above, it could be suggested that the major factor for pollutants deposition is anthropogenic.

The largest number of maximum concentrations was found in Plovdiv (As, Co, Cr, Hg, Mo, Ni, Pb, Sb, V), followed by Burgas (Cd, Cu, Se).

The 9 maximum measured at the two points on the territory of the city of Plovdiv can be related to the physico-geographic conditions, namely the high frequency of the temperature inversions and the high percentage of the low wind speeds, which do not allow the dispersion of the pollutants.

The point considered as a city background for Plovdiv, apart from showing maximum of 8 pollutants, has an established difference between 2 and 3 times in the levels of Cr, Co, Ni and V with the nearby traffic-oriented (Point 2).

PCA illustrated that one single station could be definitely separated from traffic stations. Thus, we consider that the concept of "urban background sites" in some cases is compromised.

Leaves of deciduous tree species *Aesculus hippocastanum* with proven biomonitor qualities may be used to assess atmospheric pollution in urban settings. Additionally, the species has advantages as a relief of taxonomic identification, easier sampling due to the size of the leaves and the high frequency of afforestation in the settlements in the country. High levels of the Fe/Mn ratio have been established, indicating the resistance of the selected biomonitor to pollutants. This gives grounds for recommending afforestation in urban environment.

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