Survey of the concentration of heavy metals in beech leaves in the region of Central Balkan National Park, Bulgaria

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Abstract. Since 1986 Bulgaria has been part of the International Cooperative Program on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) which contributed to accumulating a significant database on the chemical composition of leaf samples from some widely distributed tree species in Bulgaria. In line with the applied methodology, the set network of sample plots did not extend to the territory of the Central Balkan National Park. The present survey is aimed at expanding the database on the content of some heavy metals (Cu, Zn, Pb, Cd) in leaf samples of beech (*Fagus sylvatica*) collected within the framework of ICP Forests. In addition, some new information about the territory of the Park necessary for its future monitoring is also presented. After expansion and supplementing, the created database makes it possible to determine the mean values of heavy metal content in beech leaves for the region of Central Balkan National Park.

Key words: database, leaf analysis, monitoring, tree species

Introduction

The network of protected areas provides conditions for protection of the rich biodiversity in Bulgaria. Irrespective of the applied environmental regimes, as a result of transfer or naturally enriched geochemical background, plants accumulate heavy metals and metalloids which influence their metabolic processes and their health status.

The Central Balkan National Park is one of the three national parks in Bulgaria (http://www.moew.government.bg/?show=top&cid=195). It occupies the central part of the Balkan Range and with an area of 72 021.07 ha it is the second largest national park in the country (Apostolova 2015). Broad-leaved forests prevail in the Park, among which the beech forests are of particular value, as some of the best protected forest massifs of this type in Europe.

The forests of beech cover totally an area of 29 761 ha and 99 % of them are of natural seed origin. The average age of the beech communities in the Park is 133 years, and on an area of 24 401 ha they are over 100 years old (Apostolova 2015).

The forest area of the Park was classified into 69 landscape units relatively homogeneous in relation to the rock composition and terrain characteristics (Karatoteva 2016).

Four habitats of beech woodlands have been identified under Directive 92/43/EEC (1992): 9130 *Asperulo-Fagetum* beech forests; 9110 *Luzulo-Fagetum* beech forests; 9150 Thermophylous beech forests, and 91W0 Moesian beech forests (Central Balkan protected area (BG0000494), www.2000 natura2000.moew.government.bg).

Since 1986, Bulgaria has been part of the International Cooperative Program on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests), which resulted in the accumulation of a significant database on the chemical composition of leaf samples from prevalent

tree species in Bulgaria (Doncheva & al. 1994; Malinova & al. 1998; Pavlova & Tzvetkova 2000; Pavlova & al. 2000). Owing to the accepted scheme of plot-setting according to the methodology of ICP Forests, sample plots under the forest monitoring system did not fall into the territory of Central Balkan National Park.

No norms and criteria have been set for assessment of the content of macro- and microelements in different plant species, because plants react differently to the same concentrations of heavy metals, depending on the growing conditions, ecological requirements of the species, etc. Owing to absence of admissible levels for the content of heavy metals in the tree species, variation limits have been set for the different elements and plant species (Stefan & al. 1997). When using some of the limits and values mentioned in literature, it is necessary to bear in mind that they have been established for different regions, under different soil conditions and anthropogenic impact. This explains why during the analyses and assessments of heavy metal content in plants, besides comparisons with literature data, mean values are actually determined for the respective region and species, as well as assessment of variation in them.

Under the implementation of the ICP Forests for Europe, variation limits have been set for some macro elements, heavy metals, as well as for the correlations of nutrients for pine, spruce, oak and beech. Considering the wide range of these limits, some specific regional threshold values have been accepted and used for Bulgaria (Doncheva 1995; Pavlova 2000; Pavlova & al. 2006).

The aim of this study was to investigate the content of heavy metals and metalloids in leaf samples of beech. The results will expand the database accumulated within the framework of ICP Forests and will provide new information about the territory of the Park needed for its future monitoring.

Material and methods

Eight sample plots (BS1-BS8) were set in beech woodlands along the borders of the Park (five and three sample plots on southern and northern slopes, respectively – Fig. 1; BS – book sample). Seven of them (BS1 – BS7) are referred to 9130 *Asperulo-Fagetum* beech forest and one (BS8) to 9110 *Luzulo-Fagetum* beech forest habitat. The altitudinal range is between 1050–1555 m a.s.l.

Samples were collected and prepared for analysis (dried and crushed) according to the ICP-Forests Manual (2010). Samples for leaf analysis (leaves of common beech) were taken from dominant trees accepted for a standard. The place of sampling was the lit-up part of the crown of five trees, in equal proportion from the four main directions of the world. Sampling was done in July–August 2014.

The chemical analyses were run at the Central Laboratory for Chemical Testing and Control of the Bulgarian Agency for Foods Safety with the Ministry of Agriculture and Foods, with Accreditation Certificate 17-LI/28.02.2014, valid until 30.06.2016 and issued by the Executive Agency of the Bulgarian Accreditation Office, according to the requirements of the Bulgarian State Standard EN ISO IEC 17025:2006.

Standard methods (BSS EN 14084:2003) were used for determining the content of microelements (Cu, Zn, Pb, Cd) in the plant samples. Results of the chemical analyses were recalculated in absolutely dry matter.

In the present survey, the regional values set for the Central Balkan Range were used as criteria for assessment of the leaf analyses of beech samples obtained after statistical processing of the database for leaf analyses in a 20-year forest monitoring period (Pavlova & al. 2006). Some basic parameters of descriptive statistics are determined, such as: Median; Minimum and Maximum; Range; Quartile Range; Lower 25 % Quartile; Upper 75 % Quartile; Coefficient of variation (CV).

Statistical processing of the results was done with SPSS Statistics 19 (2010).

Results and discussion

In most sample plots, the content of Cu in the beech leaves varied within comparatively narrow limits: 5.8–6.6 $mg.kg^{-1}$ DW. In BS3 and BS5, slightly higher values were recorded: 8.6 $mg.kg^{-1}$ DW and 8.9 $mg.kg^{-1}$ DW, respectively. The highest content of Cu was recorded in the beech leaves from BS1 – 12.39 $mg.kg^{-1}$ DW – which exceeded by about 20 % the upper variation limit of Cu for the region of the Central Balkan Range (Fig. 2). Variation differed within the framework of sample plots and the variation coefficient varied from 12 % (BS6) to 42 % (BS1).

Copper is an important microelement for plants, so its deficiency should be also recorded. The signs of Cu deficiency in trees are dry treetops and chlorosis of

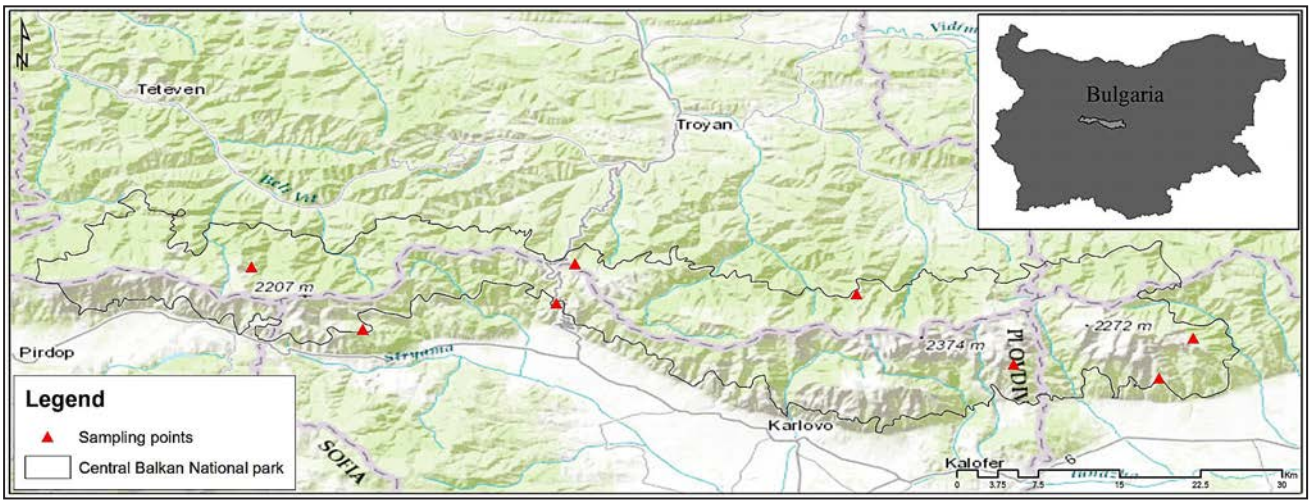

Fig. 1. Map of distribution of sample plots on the territory of Central Balkan National Park.

young leaves (Kolarov & Tsvetkova 2006). According to some authors, the limit of deficiency for this microelement is 5 mg.kg^{-1} (Smith 1985). In our case, such values were found only in single trees, which prevailed in number in BS7.

According to the concentration of Zn in beech leaves, the sample plots can be divided into two groups. The first group comprises the sample plots with relatively low concentrations of Zn in the leaves, which varied within the range of 14.3 mg.kg^{-1} DW to 18 mg.kg^{-1} DW (Fig. 3). These were found for samples BS7, BS8, BS3, and BS4. In these sample plots the values of Zn in the leaves remained under the lower limit of the natural variation range of the elements in the region of the Central Balkan Range. The second group includes sample plots with higher concentrations of Zn, varying between 25 and 26.3 mg.kg^{-1} DW (Fig. 3) which are within the limits of natural variation.

Lead is a microelement that plants do not need for their development, but it is accumulated in their vegetative parts owing to its presence in soil, air aerosols and precipitations. The natural order of Pb content in the leaves of tree species without harmful impact is 5–10 mg.kg^{-1} DW (Kabata-Pendias & Pendias 2001).

Generally, Pb was found in small concentrations in the beech leaves in all sampling plots (Fig. 4). The average values for the sampling plots did not exceed 1.5 mg.kg^{-1} DW, while in four plots they were under

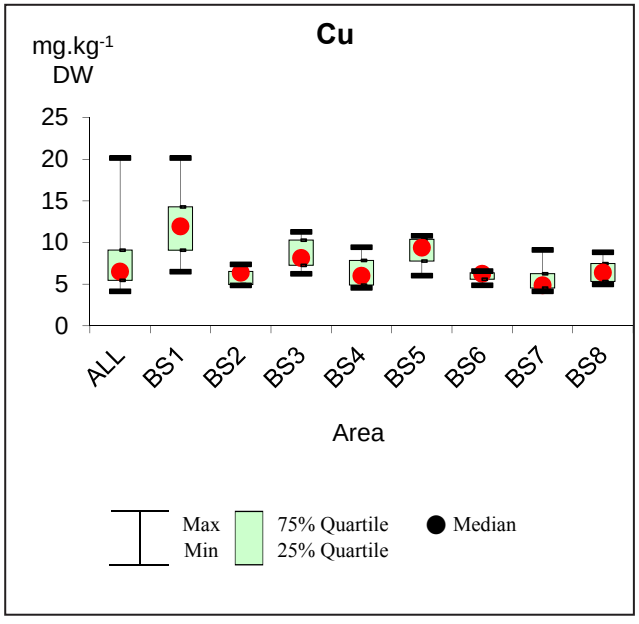

Fig. 2. Variation of Cu content in beech leaves per sample plots.

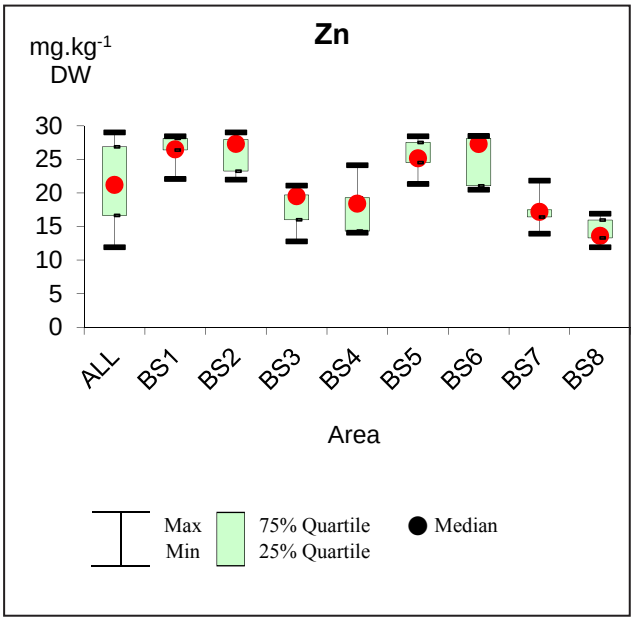

Fig. 3. Variation of Zn content in beech leaves per sample plots.

0.9 mg.kg^{-1} DW. The results obtained during this survey on the content of Pb were considerably lower than the established variation limits (2 mg.kg^{-1} up to 4 mg.kg^{-1}) for the region of the Central Balkan Range.

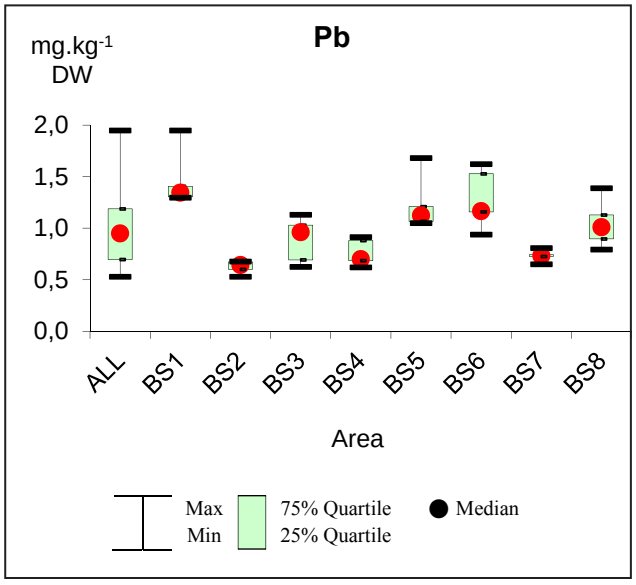

Fig. 4. Variation of Pb content in beech leaves per sample plots.

The average concentrations of Cd in the sample plots varied comparatively within the widest limits. The difference between the lowest and highest value was 3.3 times (Fig. 5). The minimum value was recorded in BS6, and the maximum in BS2 and BS5. The established content of Cd in the beech leaves in all sampling plots was lower than the variation limit

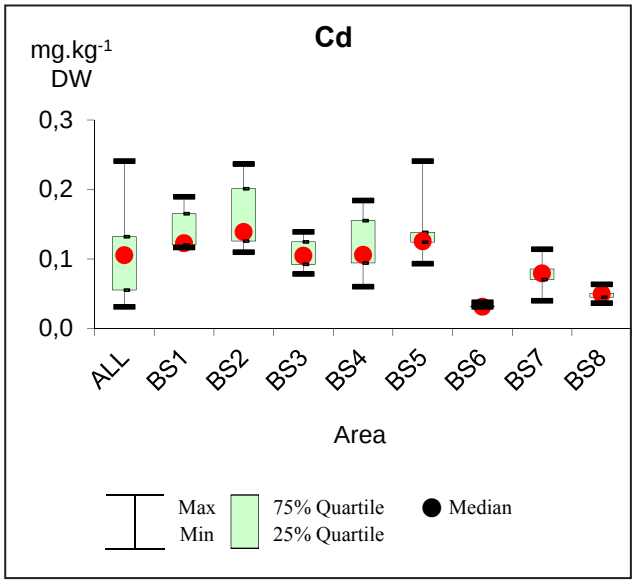

Fig. 5. Variation of Cd content in beech leaves per sample plots.

established for the region. The average variation limits of Cd in the beech leaves for the Central Balkan Range are relatively higher than the reported in literature natural limits of variation – 0.05 mg.kg^{-1} up to 0.2 mg.kg^{-1} (Lozanovskaya & al.1998). In our case, the reported concentrations were lower than these limits. Earlier surveys of the content of macro- and microelements in beech leaves in the region have also shown values lower than 0.02 mg.kg^{-1} (Bezlova & al. 1997).

Conclusion

In the present study, the concentrations of Cu, Zn, Pb, and Cd in beech leaf samples from eight sampling plots (BS) in the region of Central Balkan National Park were recorded. Our results showed that with the exception of Cu, all other micro elements were present in concentrations within or below the variation limits for the respective elements established for this territory. The highest concentration of Cu was recorded in BS1, exceeding by 20 % the upper variation limit.

The accumulated database, after expansion and supplementing, makes it possible to set up median values for the content of heavy metals in beech leaves in the region of Central Balkan National Park.

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