DISTRIBUTION OF HEAVY ELEMENTS IN SOIL FROM COUNTRIES OF THE BALKAN REGION

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Abstract
The study is dealing with the distribution of heavy elements (Cd, Cr, Cu, Ni, Pb and Zn) in surface soil from eight countries of the Balkan region. Comparison of the heavy element contents in neighboring countries gives an overview of the regional distribution of heavy elements and assessment of possible pollution. Application of principal component analysis (PCA) provided a framework for differentiation of dominant sources of elements in the analyzed data set.
Key Words: *soil, heavy elements, principal component analysis*

Introduction

Heavy elements are always present in soils due to natural weathering of parent rock material and pedogenesis processes. However, their accumulation in soils has been the subject of attention since they do not decay with time and they may become toxic to biota when exceeding threshold values. Since top soils are main "receptors" of elements from various sources as motor exhaust pipes, industrial activities, waste disposal and incineration, heavy metal concentrations in top soils are considered as tracers of environmental pollution. Furthermore, any contamination of soils could in turn cause groundwater contamination because the contaminants of polluted soils tend to be more mobile than those of unpolluted ones (Davydova, 2005). Thus, environmental concerns have resulted in many studies of the heavy elements in soils, including also the Balkan region (Ubavić et al., 1993; Bojinova et al., 1996; Jakovljević et al., 1997; Atanasov et al., 2001; Šajn, 2001; Škrbić and Miljević, 2002; Šajn, 2003; Vasin et al., 2004; Dolenec et al., 2007; Jemec and Šajn, 2007; Dragović et al., 2008; Christoforidis and Stamatis, 2009; Tersić et al., 2009; Stafilov et al., 2010a; Stafilov at al., 2010b; Škrbić and Đurišić-Mladenović, 2010; Alijagić and Šajn, 2011; Gojka et al., 2011; Škrbić et al., 2011). However, comparison of the available literature data on the heavy elements presence in soils of a wider geographical region are rare (Škrbić and Đurišić-Mladenović, 2010), particularly in the region of countries with less stringent regulations for environmental protection, like it is the case with majority of (Western) Balkan countries.

The aim of this study was to compare the content of six heavy elements (Cd, Cr, Cu, Ni, Pb and Zn) in surface soils on the base of literature available data for eight countries from the Balkan region. These six elements are the most frequently analyzed in soils and they are often used as indicators of the anthropogenic pollution. For instance, the key product that has contributed especially to the large quantities of Pb into the environment is organo-Pb anti-knock additives to gasoline. Tetra-ethyl lead was used until the 1990s as an additive in gasoline to prevent the engine from premature detonation ("knocking"). Although leaded gasoline has been banned within the EU from 2000 on following the Directive 98/70/EC and its amendment (Directive 2003/ 17/EC), some European countries like Serbia and Bosnia and Hertzegovina are still selling the leaded gasoline along with unleaded gasoline. The sources of Cu, Zn and Cd are car components, tyre abrasion, lubricants, industrial and incinerator emissions. In the past, Cd was a trace contaminant of Zn used in tires and it is also used in alloys to harden engine parts. Furthermore, combustion of fuel (oil, coal) in stationary sources could be regarded as main emission source for Cr and Ni. In order to analyze relationships between the observed variables and samples principal component analysis (PCA) was used. The intention was to clarify also the general distribution patterns or similarities of heavy metals occurring in soils collected at various sites in the region with different contribution of potential sources.

Material and methods

Data sets

Set of data consisted of the results on heavy elements occurrence in 96 surface soils (in depth down to 30 cm) available in the literature concerning the Balkan region. Only those studies comparable with each other were taken into consideration. As it was found that Zn, Cu, Cr, Cd, Pb and Ni were the only elements commonly analyzed in these studies, they were taken into account here.

Data analyses

For the purpose of elucidation of data structure, a data table with 96 soil samples and log-transformed contents of six heavy elements were formed and submitted to standard principal component analysis (PCA) procedure as a common data reduction tool (Varmuza and Filzmoser, 2009).The principal of PCA is to characterize each sample (named also as object or case) not by analyzing every variable (heavy metal content), but projecting the data in a much smaller sub set of new variables called principal components (PCs). These new variables are linear combinations of the initial variables that highlight the variance within a data set and remove the redundancies. Successive principal components arranged in decreasing order of eigenvalues account for decreasing amounts of variance; they are ordered in such a way that the variance of the first PC (PC1) is the greatest, the variance of the second PC (PC2) is second greatest, and so on, whereas that of the last one is the smallest. The relevant portion of information is carried out by the first PCs. The coefficients between the old and new variables are called the loadings. They explain how the new PCs are composed from the original variables (Héberger et al., 2005). The PCs are orthogonal (independent), in other words uncorrelated. The solution is obtained by an eigenvalue calculation. Thus, a basic assumption in the use of PCA is that the score and loading vectors corresponding to the largest eigenvalues contain the most useful information relating to a specific problem and that the remaining ones constitute mainly noise, i.e. for a practical problem it is sufficient to retain only a few components accounting for a large percentage of the total variance (Héberger et al., 1999).

Results and discussion

The basic statistics of the data set divided in accordance to the country of the Balkan region are summarized in Table 1. Moreover, Figure 1 gives an illustrative overview of the collected data for each country (except for Croatia represented with only one sample – average obtained for a survey of 916 surface soil samples). Taking into account the uneven number of samples in different countries and absence of knowledge regarding parent material and anthropogenic activities such as industry, agriculture and transportation, comments on the given below Table 1) based on extensive studies of both the human and ecotoxicological effects of soil contaminants. As can be seen from Figure 1, median values above the Dutch reference values (i.e. levels at which there is a sustainable soil quality) were found for Cd in Bosnia and Herzegovina and Slovenia, for Cr in Albania and Greece, for Cu in Albania, Bulgaria and Republic of Macedonia, for Ni in Albania, Bulgaria, Bosnia and Herzegovina, for Pb in Greece, and for Zn in Slovenia. It can also be observed that median content of nickel (Ni) in examined soils from Albania was, unlike others, above the intervention value (210 mg/kg) for which a serious case of soil contamination exists.

As a multivariate pattern recognition tool, principal component analysis was used to extract as much as possible information from the presented data set. PCA have been widely used in identifications of pollution sources and to apportion natural vs. anthropogenic contribution (Luo et al., 2007; Dragović et al., 2008; Škrbić and Đurišić-Mladenović, 2010). This method of data analysis helps the data interpretation in order to identify the underlying pattern in the data set and distributional structure of the samples regarding the analyzed variables (in this study, they are heavy metals contents). Two principal components were retained for further analysis accounting a sufficiently high amount of total variance of data, i.e. 75.8%. Figure 2 represents a biplot PC1 vs. PC2 as a graphical view of relationship among heavy elements and soil samples.

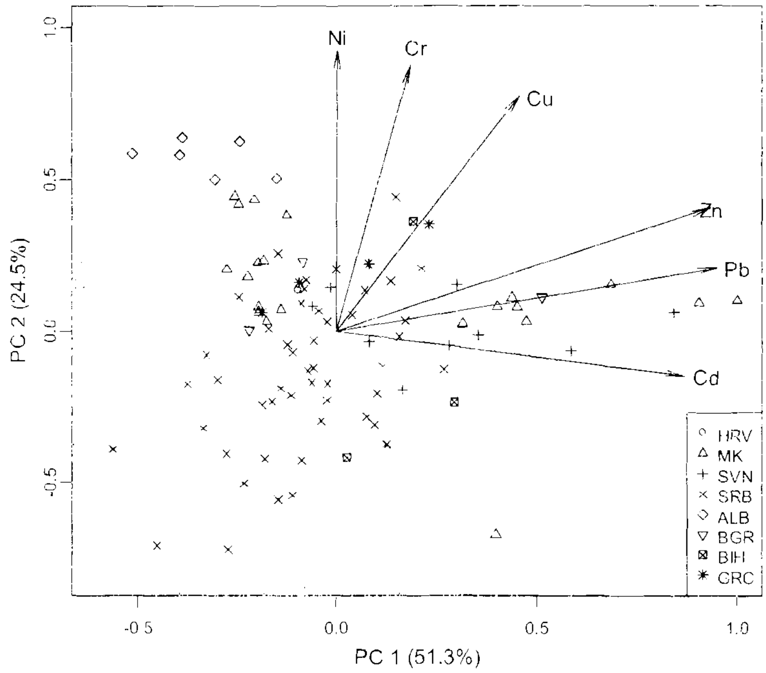

Figure 2. The PC1 vs. PC2 biplot of the analyzed data set (% presented in parentheses represents the percentages of the total data variance explained by particular PC)

During the biplot construction, each loading and score values were divided with the respective maximum values obtained for particular PC; thus, the biplot presented the relative positions of the element loadings and the sample scores within the range from−1 to +1. On a given biplot, the data set was separate on two groups of variables (heavy metal contents): one containing elements with the significant loadings on PC1 (Pb, Zn and Cd) and the other with elements significantly loaded on PC2 (Ni, Cr and Cu). Similarly to our previous study (Škrbić and Đurišić-Mladenović, 2010), PC1 reflected the variability of the Pb, Zn and Cd contents in soils influenced most probably by traffic either through vehicular exhaust fumes

(Pb) or non-exhaust emissions (Cd, Zn) from the abrasion of tyres/brakes and/or from lubricants; the physical meaning of PC2 could be attributed most probably to the combined effects of background (pedogenic) and/or stationary anthropogenic sources of Cr and Ni in soils, as well as to the agricultural practice as the Cu source.

Figure 2 also revealed that some of the samples from Slovenia and Macedonia had increased content of Zn, Pb and Cd, which could be linked to the location of these samples. Namely, these soil samples were taken from the city center of Celje, Slovenia and around a lead and zinc smelter in the Republic of Macedonia. According to the position of samples along PC2, it could be seen that outliers with the elevated content of Ni are all soil samples from Albania and some of the Macedonian samples. Considering the biplot position of soil samples from Serbia, similarity with the other countries of the region is observed, with only three outliers due to lowest levels of the analyzed elements belonging to the soil samples from national parks of Vojvodina Province (Vasin et al. 2004) (3 samples in the third quadrant of the biplot, Figure 2) and one with elevated Cr/Cu content representing soil from the Velika Morava river valley, used for intensive agricultural and food production (Jakovljević et al., 1997).

Conclusion

This study was carried out as a preliminary survey on heavy element distribution in soils from the Balkan region. This region was selected as study area in order to compare heavy element contents among neighboring countries with similar industrial development and to get an overview about levels of heavy element pollution. Comparing the data from different countries similar order of heavy elements among Bulgaria, Macedonia and Slovenia, as well as Serbia and Bosnia and Herzegovina was observed. The application of principal component analysis to the data set consisting of the contents of six heavy elements revealed distribution patterns specific for the region. The first PC was correlated with Pb, Zn and Cd, while the second PC was correlated with Ni, Cr and Cu. An extensive data collection followed by geochemical interpretation of the data will allow the discrimination of lithogenic and anthropogenic sources of heavy metal pollution of soils which represents future research requirements.

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