

Metal Levels in Surface Soils after Different Extraction Procedures

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Article info

Received: 03/07/2013
Accepted: 12/11/2013

Keywords:

Metals
Soil
Extraction
Kiseljak

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Abstract: Surface soil samples collected from the Kiseljak area, Bosnia and Herzegovina, were analyzed for eight different heavy metals (Cd, Cr, Cu, Fe, Hg, Mn, Pb and Zn) using atomic absorption spectrometry – flame and cold vapour techniques. Three procedures of extraction of metals from soil were used: 1) extraction with ethylenediamine tetraacetic acid (EDTA), 2) extraction with HNO₃ solution, and 3) extraction with aqua regia. Results for metals are reported for the first time in soils for this region. Pseudo total metal content in soil samples can be presented by the following descending series: Fe > Mn > Pb > Zn > Cu > Cr > Cd > Hg. The categories of increased pollution and highly polluted soils are almost equally presented in the Kiseljak area. Location Kiseljak-Centar by the content of Pb and Cu belong to the contaminated soil. In the case of Cd all analyzed soil samples belong to contaminated soils.

INTRODUCTION

Soil is a medium of interaction between the atmosphere, the biosphere and the lithosphere, and the presence of toxic elements in soil can be harmful to plants, animals and humans, under certain circumstances (Kelepertsis, Argyraki, and Alexakis, 2006). Although some metals are essential for biological functions and most occur naturally in the soil environment, the soils of urban environments commonly hold increased metal contents due to the contamination from surrounding traffic and industries (Ljung, Oomen, Duits, et al., 2007). Soils represent an excellent media to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in topsoils (Dantu, 2009). Independent of the correlations found in each of the particular cases studied, data available

in the bibliography indicates that pH, organic matter content, cation exchange capacity, specific surface area, carbonate content and iron oxide content are the principal soil characteristics that determine the capacity

to retain heavy metal pollutants (Lafuente, Gonzalez, Quintana, et al., 2008). The total heavy metal content in soils provides a convenient means of expressing a measure of pollution, but numerous reports have highlighted that such measures are deficient in predicting toxicity of metal pollutants. Heavy metals may be distributed among many components of the soil or sediment and may be associated with them in different ways (Yusuf, 2007). Extraction tests are commonly used to study the mobility of metals in soils and sediments by mimicking different environmental conditions or dramatic changes on them. The results obtained by determining the extractable elements are dependent on the extraction procedure applied. In the literature, EDTA is the most frequently cited as a chelating agent for extracting potentially toxic trace metals from soils for its efficiency, availability and low cost, relative to other synthetic aminopolycarboxylic acids (Andrade, Prasher, and Hendershot, 2007). Also, most studies on helate-

induced phytoextraction have focused on EDTA phytoextraction (Epelde, Hernandez-Allica, Becerril, et al., 2008). On the other hand, extraction with aqua regia is often referred to as pseudo total concentrations.

The study site has been the subject of numerous investigations, particularly those pertaining to the chemistry of mineral waters. The main goal of this study was to investigate chemical characteristics of the surface soil after different extraction procedures in the area of Kiseljak.

EXPERIMENTAL

Study area

The broader Kiseljak area is characterized by the relatively long and narrow Lepenica Valley, which extends from Han Ploča in the southeast to Kiseljak in the northwest. The Kiseljak area is in a belt with a moderate continental climate, while the southwestern sections of the terrain have high peaks and a harsh alpine climate. The climate is characterized by harsh winters, moderately warm summers, rainy autumns, relatively high precipitation irregularly distributed through the year and a lack of strong winds (Skopljak and Vlahović, 2012). What makes this place known, and by which the city was named, is certainly natural source of mineral water - kiseljak.

Soil sampling

Sampling locations in the Kiseljak area are shown in Figure 1. Soil samples were collected in December 2009, at six locations: Gromiljak (L1), Lepenica (L2), Kiseljačić (L3), Topole (L4), Kiseljak-Centar (L5), and Bilalovac (L6). Larger particles, e.g. stones and plant residues, were firstly removed. Samples were placed in polyethylene bags, and dried to constant weight at 105 °C (for mercury determination at 35 °C) in a drying oven. Samples were then grounded and homogenized in an agate mortar. The results were expressed on a dry weight basis.

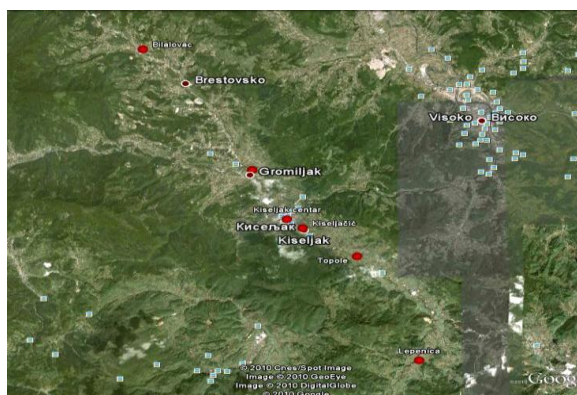


Figure 1. Satellite image of the Kiseljak area with sampling locations (lat. 43°56'24.75", lon. 18°04'43.86", elev. 490 m; background image GoogleEarth)

Soil pH determination

Soil pH is determined potentiometrically in a slurry system using pH meter (CG 841, Schott). Soil pH was determined in water (soil:water 1:2.5).

Extraction of metals from soil

In this work the three procedures of extraction of metals from soil were compared: 1) extraction with ethylenediamine tetraacetic acid (EDTA), 0.05 mol/L; 2) extraction with HNO₃ solution (1:2 v/v) and 3) extraction with aqua regia which is often referred to as pseudo-total concentrations. Extraction was performed on shaker, 10 hours.

Determination of the metals

Metal (Cd, Cr, Cu, Fe, Mn, Pb and Zn) content was determined by atomic absorption spectrometry (SpectraAA-10, Varian), flame technique (FAAS) and Hg by cold vapor technique (CVAAS). To ensure the reliability of the results, appropriate quality procedures and precautions were taken. All the reagents were of analytical grade. Glassware was properly cleaned. Blank and standards were run repeatedly after set of five measurements to calibrate the instrument. Spike sample analysis (or known addition) is used to test the method at varying concentrations of analyte. Known amounts of analyte were added to a sample and the percent recovery was calculated. The acceptable percent recovery of known additions were obtained (extraction with EDTA: Fe (85-93 %); Zn (96-109 %); Pb (80-86 %); Mn (84-88 %); Cr (106-117 %); Cu (86-104 %); Cd (100-108 %); extraction with nitric acid solution: Fe (81-87 %); Zn (99-108 %); Pb (80-85 %); Mn (90-94 %); Cr (80-86 %); Cu (98-103 %); Cd (94-114 %); extraction with aqua regia: Fe (80-86 %); Zn (98-101 %); Pb (81-85 %); Mn (81-87 %); Cr (83-86 %); Cu (100-105 %); Cd (93-110 %). The sample and blank analyses were performed in triplicate.

The obtained metal contents were interpreted on the basis of the limit values specified by the Regulation of determination permitted quantities of harmful and hazardous substances in the soil and methods of their analysis (Sl. novine FBiH, 52/09) and the classification of soil contamination by Basić (1994). The classification was done by comparison of obtained values and limit values, i.e. by the degree of contamination - Cd:

% Cd = obtained pseudo total metal content in soil (mg/kg)*100/limit value

On this basis, the soils are classified into five groups:

GROUP I: clean soil - Cd up to 25%

GROUP II: increased pollution - Cd 25-50%

GROUP III: high pollution - Cd 50 - 100%

GROUP IV: polluted soil - Cd 100-200%

GROUP V: contaminated soil - Cd more than 200%

RESULTS AND DISCUSSION

Soil pH

The pH of the soil samples ranged from 6.66 to 7.15. According to data for soil pH, the following can be concluded:

- soil samples at locations Gromiljak, Lepenica and Bilalovac belong to slightly acid soil;
- soil samples at locations Kiseljačić, Topole and Kiseljak - Centar fall into weakly alkaline soils.

Extraction of metals

EDTA has been widely used to express metal availability to plants or other biological organisms (Dai, Nahmani, Becquer, et al., 2002; Wang, Shan, Zhang, et al., 2004; Meers, Laing, Unamuno, et al., 2007). The aqua regia of extractable content is considered as the pseudo total metal fraction.

Limit values of metal content in soil are defined by Regulation (Sl. novine FBiH, 52/09) depending on the soil texture (sandy, silty-clay and clay). The texture of the soil was not determined, so threshold for clay soil was selected with the highest metal content. Limit values (mg/kg air dried soil) are as follows: 1.5, 100, 80, 1.5, 100 and 200 for Cd, Cr, Cu, Hg, Pb and Zn, respectively. Concentration of Hg was the lowest at all locations and ranged from 0.36 to 5.67 mg/kg. Mercury content was exceeded at one location, Kiseljak-Centar. At the same location the highest concentrations of Cu (103.41 mg/kg) and Pb (166.13 mg/kg) were found and obtained concentrations exceeded the limit value. The content of cadmium in all locations was above the limit value. The lowest variability in the pseudo total Fe content was observed at all sites (2466.47 to 2640.27 mg/kg), while Mn content considerably vary (345.03-1000.82 mg/kg) with the location. Chromium content ranged from 48.52 to 70.80 mg/kg, and was below the limit values.

In most cases the lowest pseudo total contents of all analyzed metals were found at two sites, Bilalovac and Kiseljačić. Pseudo total metal content in soil samples can be presented by the following descending series: Fe > Mn > Pb > Zn > Cu > Cr > Cd > Hg. The Kiseljak area is characterized by frequented roads, gasoline stations, mineral water processing plants, textile and military industry which can be potential sources of the metals in the soil.

Results of multielemental (Cd, Cr, Cu, Fe, Hg, Mn, Pb and Zn) analysis of the surface soil samples after different extraction procedures are given in Figure 2. The extractions were performed in triplicates and the results are presented as averages of the triplicate extracts.

In all soil samples, the metal concentrations after extractions with EDTA and HNO₃ solution were lower than the pseudo total amount. The highest amount of extracted Mn was obtained with EDTA in comparison to the pseudo total content. The content of all metals after extraction with EDTA was below the limit value.

The degree of soil contamination with heavy metals in Kiseljak area is given in table 1.

Table 1. The degree of soil contamination with heavy metals in the Kiseljak area

Sample	% C _d					
	Zn	Pb	Cr	Cu	Cd	Hg
Gromiljak	43	86	71	58	788	33
Lepenica	44	84	57	40	668	16
Kiseljačić	59	78	54	47	525	24
Topole	72	99	68	48	759	36
Kiseljak Centar	45	166	49	129	523	410
Bilalovac	14	60	59	21	687	34

The categories of increased pollution (25-50% C_d) and highly polluted (50 to 100% C_d) soils are almost equally presented in the Kiseljak area. Location Kiseljak-Centar by the content of Pb and Cu can be considered as contaminated soil. In the case of Cd all analyzed soil samples belongs to V group - contaminated soils.

Taking into account that the metals from natural and anthropogenic sources accumulate together, it is difficult to determine which metal fraction in the soil is natural, and which is of anthropogenic origin. Any study of the soil requires basic information about the chemical properties before any assessment of the presence of anomalous metal concentrations. A reliable method for this assessment is the normalization of geochemical data. Aluminum, iron, lithium, scandium, titanium and zirconium can be used for normalization and detection of anomalous concentrations of trace elements. In this work normalization of elements in relation to iron was used (Trefry, and Presley, 1976; Yanguo, Shijun, Xianguo, et al. 2002; Suh, and Birch 2005; Vreca, and Dolenec, 2005). Values of Pearson's correlation coefficients are: Cd-Fe (r=0.24), Cr-Fe (r=0.03), Cu-Fe (r=0.15), Hg-Fe (r=0.38), Mn-Fe (r=0.35), Pb-Fe (r=0.30) and Zn-Fe (r=0.39). A positive correlation exists between Fe and all other elements but values are very low which can indicate that only low percentage of metals natural variability can be attributed to the textural and mineralogical variability of the soils (Sakan, Đorđević, and Trifunović, 2011).

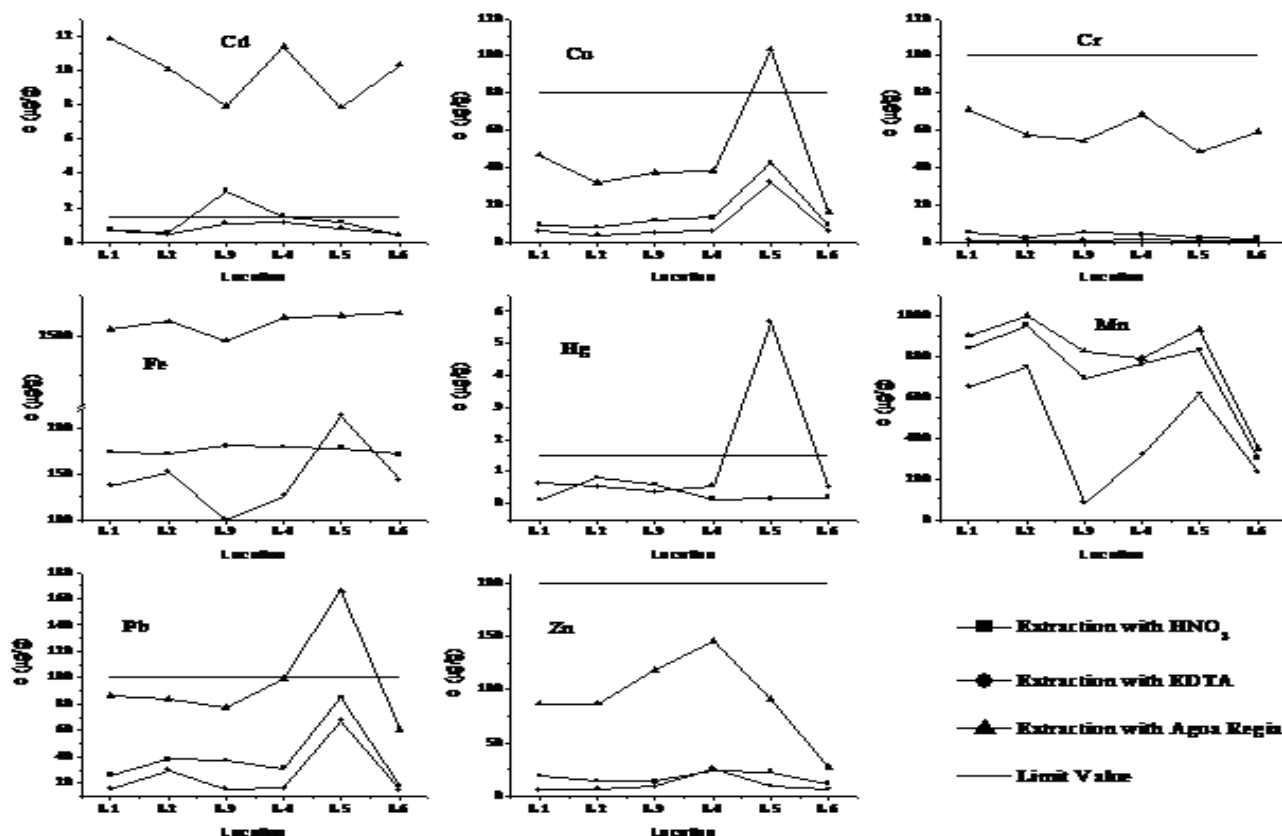


Figure 2. Metal content in soil samples from the area Kiseljak after different extraction procedures

CONCLUSIONS

Soils represent an excellent media to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in topsoils. Surface soil samples collected from the Kiseljak area, Bosnia and Herzegovina. In all soil samples, the metal concentrations after extractions with EDTA and HNO₃ solution were lower then the pseudo total amount. In most cases the lowest pseudo total contents of all analyzed metals were found at two sites, Bilalovac and Kiseljačić. The highest concentrations of Cu, Hg and Pb were found at the Kiseljak area Pseudo total metal content in soil samples can be presented by the following descending series: Fe > Mn > Pb > Zn > Cu > Cr > Cd > Hg.

To assess the presence of anomalous metal concentrations normalization of elements in relation to iron was used. A positive correlation exists between Fe and all other elements ,but values are very low which can indicate that only low percentage of metals natural variability can be attributed to the textural and mineralogical variability of the soils.

The categories of increased pollution (25-50% C_d) and highly polluted (50 to 100% C_d) soils are almost equally presented in the Kiseljak area. Location Kiseljak-Centar by the content of Pb and Cu can be cosidered as contaminated soil. In the case of Cd, all analyzed soil samples belongs to V group - contaminated soils.

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Summary/Sažetak

Analizirano je osam teških metala (Cd, Cr, Cu, Fe, Hg, Mn, Pb i Zn) u uzorcima površinskih tala sakupljenih na području Kiseljaka, Bosna i Hercegovina. Korištena je metoda atomske apsorpcione spektrometrije, plamena i tehnika hladnih para. Za ekstrakciju metala iz tla korišteni su sljedeći postupci: 1) ekstrakcija sa etilendiaminotetraacetatnom kiselinom (EDTA), 2) ekstrakcija sa HNO₃, i 3) ekstrakcija sa zlatotopkom. Pseudo ukupni sadržaj metala u uzorcima tla predstavljen je sljedećim opadajućim nizom: Fe > Mn > Pb > Zn > Cu > Cr > Cd > Hg. Kategorije povećanog onečišćenja (25-50% So) i visokog onečišćenja tala (50 to 100% So) su gotovo podjednako zastupljene na području Kiseljaka. Lokacija Kiseljak-Centar po sadržaju Pb i Cu pripada zagađenim tlima. U slučaju Cd svi analizirani uzorci tla spadaju u kontaminirana tla.