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Phytoavailability of potentially toxic elements from industrially contaminated soils to wild grass

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ABSTRACT

Topsoil and grass samples from 14 sites located in different distances from three copper mining factories and a copper smelter were collected in Srednogorie, Bulgaria. The paper discusses results of studies on the mobility of potentially toxic elements (As, Cd, Cr, Cu, Mn, Ni, Pb, Zn) from contaminated soils to wild grass *Cynodon dactylon* in terms of transfer (TF: soil to plant) and phytoavailability (PF: EDTA (ethylenediaminetetraacetic acid)-soluble to plant) factors. Soils located close to mine and smelter factories were heavily contaminated by As and Cu reaching levels up to 500 mg/kg and 2400 mg/kg, respectively for As and Cu. At seven sites arsenic and copper in grass were over the normal levels (1 mg/kg As; 20 mg/kg Cu). The content of Cu in grass averaged 63 mg/kg exceeding the maximum allowable for sheep. Relationship between PF and TF values was found for As, Cd, Cu, Ni, Pb, Zn but not for Mn and Cr. To some extent the soil pH, TOM (total organic matter) and $CaCO_3$ content are related to the phytoavailability of As, Cd and Cu since for Zn and Pb this relation is attributed to Al- and Fe-content of soil. Statistically significant correlation coefficients were determined between the EDTA-soluble fraction of soil and content in grass in the case of As, Cd, Cr, Cu, Mn and Pb indicating the suitability of the short procedure for phytoavailability studies of those elements. The application of hierarchical cluster analysis and self-organizing maps of Kohonen made it possible to reveal specific hidden relationships between the soil variables and transfer factors as well as between the sampling locations. This additional information helps in more detailed interpretation of phytoavailability and transfer processes in the region of interest.

The novelty in this study is achieved by careful consideration of the possibility of using EDTA extracts of the toxic metals in investigating of the phytoavailability and transfer processes soil/plant. Additionally, chemometric expertise used makes it possible to differentiate the behavior of each toxic metal in the processes studied. The combination of easy option for rapid extraction and intelligent data analysis gives a new perspective for contributions in explanation of the complex interactions between soils and plants when assessing pollution events in a certain environment.

1. Introduction

World primary production of Cu has increased from 9.2 Mt in 1990–13.7 Mt in 2003 (USGS, 2004). In the 20th century its utilization increased rapidly and now the mining and refining of Cu takes place on all six continents, as an important by-product from non-ferrous Cu ores is Au (Kabata-Pendias and Mukherjee, 2007).

The largest Bulgarian companies for mining and processing of copper, gold-containing ores and copper concentrate are located on the southern flank of the Balkan ranges, Central Sredna Gora Mountain, central-western Bulgaria. All the leading copper mining companies and the biggest in South-Eastern Europe facility for smelting and refining of copper are located approximately between the 60th and 90th kilometers east of the capital Sofia. The country basic industries of copper mining and smelting are concentrated on a relative small territory. The factories are located in the suburbs of cities and villages surrounded of a grassland used for animal feeding. The activities of all these factories for mining and smelting of copper ores may contribute to elevated levels of heavy metals in the environment, their accumulation in soils and plants, followed by their transport in terrestrial food chains (Kloke et al., 1984). The high concentration levels of elements as As, Cd, Cu, Pb, Zn observed in areas of close proximity to copper factories could

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Fig. 1. Map of the study area and location of the sampling sites.

cause serious environmental problems (Kuo et al., 1983; Karszewska et al., 1998; Maiz et al., 2000; Kabala and Singh, 2001; Burt et al., 2003; Pope et al., 2005; Yan et al., 2007; Ge and Zhang, 2015). Although the currently strong control on the managing and handling the industrial wastes (due to tight legislation implementation), pollution due to previous activities connected with deposition of potentially toxic elements (PTE) in soil over very long periods still exist. The long-term persistence of heavy metals in the environment presents potential human health risk. The risk is associated with plant consumption or direct soil dust inhalation by inhabitants. PTE-related concerns have not to be overlooked despite the lower levels of industrial pollution in the last years (Antoniadis et al., 2017). A continuous monitoring of toxic element uptake and allocation in the selected plants must be carried out in order to avoid a consistent transfer of these elements along terrestrial food chains (Madejón et al., 2002). In order to enhance the effectiveness of the analytical work for regular quality control of the contaminated areas, considerably reducing the experimental task, procedures for fast and simple estimation of the available, mobile and mobilizable fraction of PTE have to be applied (Alvarez et al., 2006). Short single extraction procedures for assessing the plant available forms in soils have been proposed (Quevauviller et al., 1996; Pueyo et al., 2001; Chojnacka et al., 2005; Alvarez et al., 2006). Despite the multitude of attempts to elaborate a standard extraction procedure that would represent the content of PTE available to plants, there is still a need to obtain new additional information for a particular soil and plant genotype (Alvarez et al., 2006). The prediction of phytoavailability of potentially toxic elements is very difficult for contaminated environments (Kabata-Pendias, 2004). There are several models that can be used to predict the phytoavailability of microelements (Rodrigues et al., 2012; Liu et al., 2015; Chen et al., 2016; Lim et al., 2016). But these models are limited to a given plant and local soil conditions. It means that environmental control requires comprehensive separate study of specific contaminated sites. Native plants are tolerant to toxic elements and often better in terms of survival and growth under environmental stress (Yoon et al., 2006). Therefore, the wild grass *Cynodon dactylon* (Bermuda grass) was used in the present study for investigation of contaminated sites around the copper mines and the copper smelter.

The objectives of this research were as follows:

- to evaluate the soil pollution around three copper mines and a copper smelter;
- to find the availability of potentially toxic elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) from contaminated soil to grass (*Cynodon dactylon*) and to interpret the relationships between soil-plant transfer processes and basic soil characteristics using multivariate techniques;
- to evaluate the potential of EDTA soil extraction procedure for rapid regular monitoring of PTEs uptake and food chain risk assessment.

2. Materials and methods

2.1. Study area

Grass samples together with the associated soil samples were collected in September of 2016. A total of 14 topsoil (0–20 cm) samples together with the wild grass *Cynodon dactylon* growing on this soils were selected: a) eight samples along the three Bulgaria's leading copper ore mining and processing companies Elatsite Med (flotation factory near the village of Mirkovo, 60 km east of Sofia) – sampling sites 1, 2; Chelopech Mining (processing of copper-bearing massive sulphide and porphyry copper deposits, in the village of Chelopech, 70 km east of Sofia) – sampling sites 3–5; and Asarel-Medet (open pit mining and copper ore processing factory located at an altitude of about 1000 m in the Sashtinska Sredna Gora Mountain, near to the city of Panagyurishte, 90 km east of capital Sofia) – sampling sites 10–12; b) four sampling sites around the copper smelter and refinery, situated between the towns of Zlatitsa and Pirdop (located seven kilometers east of Chelopech) – sampling sites 6–9; c) two sampling sites at the two ends of a Topolnitsa dam, serving as collector of waste waters from the copper industry activities in the study area – sampling sites 13, 14 (Fig. 1). The sites and the general characteristics of the soil samples are specified in Table 1. The pH was measured in a 1:5 suspension of soil in pure water (ISO 10390:2005). Equivalent calcium carbonate (%) and total organic matter content (TOM %) were determined according to ISO 10693:1995 and ISO 10694:1995, respectively. The content of Al and Fe was determined in *aqua regia* soil extracts by ICP-OES (inductively coupled optical emission spectrometry).

2.2. Sample preparation and chemical analysis

The digestion of soil samples was performed by adopted method of ISO 11466:1995. A 1.0 g of sample was weighed and transferred into a tall form conical beaker. To each sample 30 ml of *aqua regia* was added. The beakers were covered with appropriate small glass funnels and left