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Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia)

Vojtěch Ettler [a,*], Bohdan Kříbek [b], Vladimír Majer [b], Ilja Knésl [b], Martin Mihaljevič [a]

[a] Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Faculty of Science, Albertov 6, 128 43 Praha 2, Czech Republic
[b] Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic

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ABSTRACT

Differences in the total and bioaccessible concentrations of As and metals (Co, Cu, Pb, Zn) in topsoils ($n = 107$) from the mining and smelting areas in the Zambian Copperbelt were evaluated. The mean total concentrations of metals and As in topsoils were generally 2 to 7× higher in the smelting area, indicating significantly higher effect of smelter dust fallout on the degree of topsoil contamination. The contaminant bioaccessibility was tested by an US EPA-adopted *in vitro* method using a simulating gastric fluid containing a 0.4 M solution of glycine adjusted to pH 1.5 by HCl. Higher bioaccessibilities in the smelter area were observed for As and Pb, attaining 100% of the total metal/metalloid concentration. The maximum bioaccessibilities of As and Pb in the mining area were 84% and 81%, respectively. The ranges, mean and median bioaccessibilities of Co, Cu and Zn were similar for the two areas. The maximum bioaccessibilities of Co, Cu and Zn were 58–65%, 80–83% and 79–83%, respectively. The obtained data indicate that a severe health risk related to topsoil ingestion should be taken into account, especially in smelting areas.

1. Introduction

The mining and smelting activities are responsible for extensive contamination of soils. The smelter emissions as well as wind-blown dust from mine tailings and smelter slag dumps are generally the main point sources of soil pollution (Ettler et al., 2005a, 2009, 2011; Kříbek et al., 2010; Šráček et al., 2010; Vítková et al., 2010). Studies dealing with the bioavailability and bioaccessibility of metals/metalloids contaminants in highly-polluted soils are extremely useful in understanding the possible effect on biota (Bosso and Enzweiler, 2008; Chen et al., 2009; Douay et al., 2008; Juhasz et al., 2011; Roussel et al., 2010). In particular, human exposure to contaminants in mining/smelting areas has implications for health risk assessment (Banza et al., 2009; Roussel et al., 2010).

The “bioaccessible” fraction is defined as the amount of contaminant that is mobilized from the solid matrix (e.g. soil) in the human gastrointestinal tract and becomes available for intestinal absorption. The “bioavailable” fraction is the fraction of contaminant that can reach the blood stream from the gastrointestinal tract (Morrison and Gulson, 2007; Roussel et al., 2010; Ruby et al., 1999). In the last two decades, a number of laboratory methods (often called PBET, physiologically-based extraction tests) have been developed to investigate *in vitro* the oral (ingestion) or respiratory bioavailability/bioaccessibility of metals from polluted geomaterials (soils, wastes) (Oomen et al., 2002, 2003a, 2003b; Ruby et al., 1993; Schroder et al., 2004). These methods and their applications have recently been reviewed by Plumlee and Ziegler (2006) and Plumlee et al. (2006) and have led to the development of standardized tests adopted by the U.S. Environmental Protection Agency (US EPA, 2007). Although this test was validated by *in vivo* tests only for Pb and As (Ruby et al., 1993, 1996; Schroder et al., 2004), it has also been widely adopted to study the bioaccessibility of other inorganic contaminants in polluted soils (e.g., Kim et al., 2002; Madrid et al., 2008a, 2008b).

The present study is based on our previous screening soil survey discriminating the contaminant sources in the area of intense copper–cobalt mining and smelting in the Zambian Copperbelt (Kříbek et al., 2010). It has been reported that children can ingest between tens and hundreds of milligrams of soil per day via hand-to-mouth behaviour. Up to 200 mg soil/day was observed by van Wijnen et al. (1990) and, for the 90th percentile, typically between 40 and 100 mg/day. More recently, Özkaynak et al. (2011) used a USEPA Stochastic Human Exposure and Dose Simulation Model (SHEDS) to show that up to 1367 mg soil/day can be ingested with a 95th percentile of 176 mg/day and mean value of 41 mg/day. Thus, a severe risk of exposure to metallic contaminants in highly polluted areas of the Zambian Copperbelt can be anticipated. High exposure to metal contaminants expressed particularly as high urinary Co concentrations was also reported from the nearby Copperbelt mining and smelting district in the Democratic Republic of Congo (Banza et al., 2009). As a result, this study is focused on investigation of the differences in gastric bioaccessibility of metals (Co, Cu, Pb, Zn) and As in topsoils from two distinct areas with contrasting pollution sources (mining vs. smelting).

* Corresponding author. Tel.: +420 221 951 493; fax: +420 221 951 496.
E-mail address: ettler@natur.cuni.cz (V. Ettler).

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2. Materials and methods

2.1. Soil sampling

Based on extensive data on the spatial distribution of inorganic contaminants in the Zambian Copperbelt district (Kříbek et al., 2010), two hot-spots with contrasting sources of pollution were selected for investigation of the metal/metalloid bioaccessibility: 1) a mining area in the vicinity of Chingola with a number of active open-pit mines (Nchanga and Chingola) ($n = 52$ soil samples) and 2) a smelting area in the vicinity of Kitwe with the Nkana Cu smelter active between 1932 and 2009 ($n = 55$ soil samples) (Fig. 1). According to Mihaljevič et al. (2010), the prevailing wind direction in the studied areas is NE–SW between November and February (wind speed up to 2 m/s) whereas, during the rest of the year, stronger winds with a velocity of >3 m/s in the direction SE-NW prevail. The wind direction has a significant effect on the spatial distribution of airborne contamination in the vicinity of point pollution sources in the Zambian Copperbelt (Ettler et al., 2011; Kříbek et al., 2010; Mihaljevič et al., 2010). In the mining area, the dust fallout originates mainly from open-pit mining operations, ore crushers, ore/concentrate transport and mine tailings. In contrast, the areas around smelters are mainly affected by the smelter emissions and fine-grained slag dust generated by slag treatment plants (crushing prior to further re-smelting and further metal recovery) (Kříbek et al., 2010; Vítková et al., 2010).

Only topsoil samples (0–2 cm depth) were considered in this study, being the most probable source of potential health risk due to ingestion. According to Soil Taxonomy (Soil Survey Staff, 2010), the soils were characterized as Oxisols. The samples were stored in polyethylene (PE) bags, air-dried to constant weight on returning to the laboratory and sieved through a clean 0.25-mm stainless steel sieve (Retsch, Germany). The 0.25-mm sieved fraction was used for the pH determination and bioaccessibility testing, because this particle size is representative of that which adheres to children's hands (US EPA, 2007). An aliquot part of each sample was finely ground in an agate mortar (Fritsch Pulverisette, Germany) and used for subsequent bulk chemical analysis.

2.2. Soil analysis

The pH measurements were performed according to Pansu and Gautheyrou (2006) in a 1:5 (w/v) soil-deionized water suspension after 1-h agitation using a Schott Handylab pH meter. Total organic carbon (C_{org}) and total inorganic carbon (C_{carb}) contents were determined using Eltra CS 500 analyzer (Eltra, Germany). Total sulphur (S_{tot}) was determined on Eltra CS 530 analyzer (Eltra, Germany).

The pseudo-total digests of soil samples were obtained by a standardized *aqua regia* extraction protocol according to ISO Standard 11466 (ISO, 1995). Certified reference material (CRM) BCR-483 (sewage sludge-amended soil) and standard reference material (SRM) NIST 2711 (Montana soil) were used to control the accuracy of the *aqua regia* pseudo-total digestion, yielding satisfactory values (Table 1). Although NIST 2711 has element values certified for total digests, the *aqua regia* pseudo-total digests were in good agreement with the certified values as well as with the *aqua regia* data recently published for this SRM (Karadaş and Kara, 2011). Total digests were analyzed for the content of Co, Cu, Pb and Zn by a Perkin Elmer 4000 flame atomic absorption spectrometer (FAAS) or by a Thermo Scientific Xseries 2 inductively coupled plasma mass spectrometer (ICP-MS). The As concentrations were determined by a Perkin Elmer 503 hydride generation atomic absorption spectrometer (HG-AAS) or by ICP-MS.

The bioaccessibility test was performed according to the US EPA (2007) protocol, identical with the Simple Bioaccessibility Extraction Test (SBET) adopted by the British Geological Survey (Oomen et al., 2002). The extraction fluid contained 0.4 M glycine (30.028 g glycine dissolved in 800 ml of deionized water), adjusted to pH 1.5 ± 0.05 by reagent grade HCl (Merck, Germany), finalized by diluting to 1 l by deionized water (MilliQ+, Millipore Academic, USA) and pH verification. A

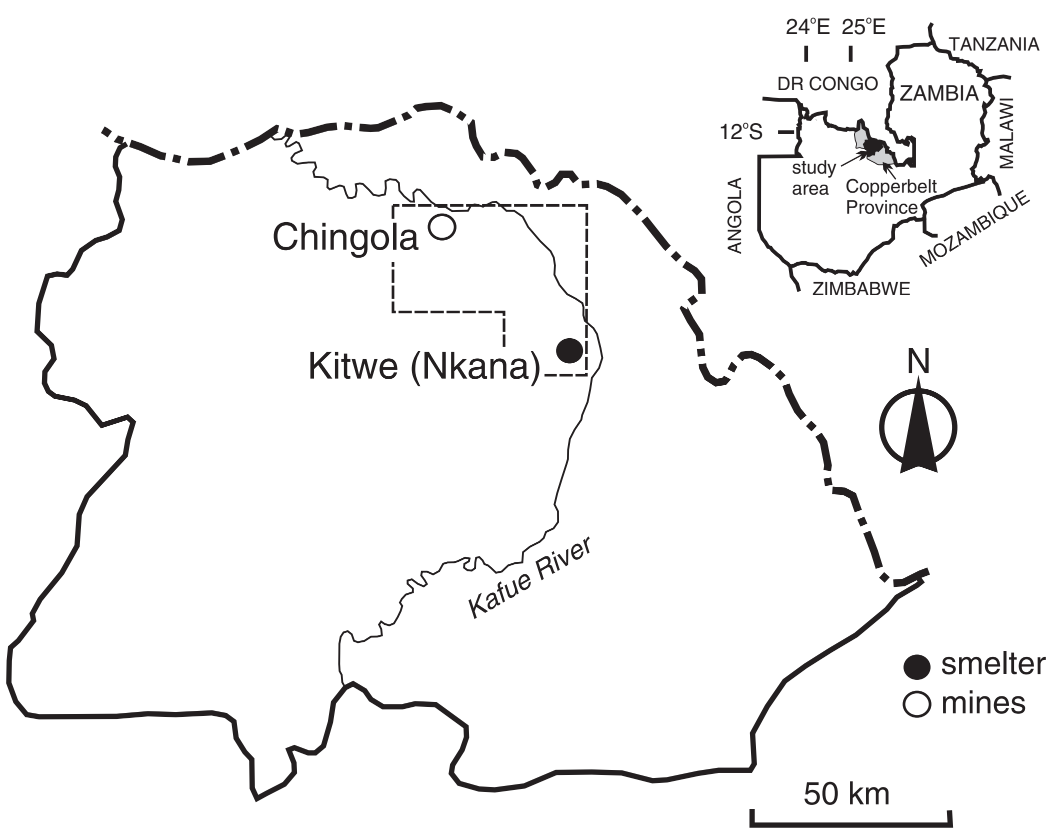

Fig. 1. The map of the Zambian Copperbelt location and study area (dashed line).