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Composition and fate of mine- and smelter-derived particles in soils of humid subtropical and hot semi-arid areas

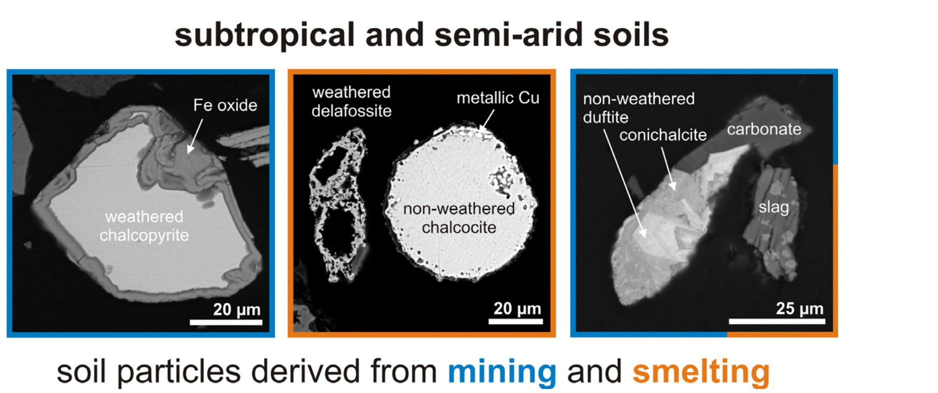
Vojtěch Ettler [a,*], Zdenek Johan [b,1], Bohdan Kříbek [c], František Veselovský [c], Martin Mihaljevič [a], Aleš Vaněk [d], Vít Penížek [d], Vladimír Majer [c], Ondra Sracek [e], Ben Mapani [f], Fred Kamona [f], Imasiku Nyambe [g]

[a] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic
[b] BRGM, Avenue Claude Guillemin, 45082 Orléans Cedex 2, France
[c] Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic
[d] Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 21 Praha 6, Czech Republic
[e] Department of Geology, Faculty of Science, Palacký University in Olomouc, 17. listopadu 12, 771 46 Olomouc, Czech Republic
[f] Department of Geology, Faculty of Science, University of Namibia, Private Bag 13301, Windhoek, Namibia
[g] University of Zambia, School of Mines, P. O. Box 32 379, Lusaka, Zambia

HIGHLIGHTS

- Mining- and smelter-derived particles identified in subtropical and semi-arid soils
- Sulphides, oxides, and metal-bearing arsenates most frequently encountered
- Soluble sulphates and arsenolite from primary smelter dusts not detected in soils
- Higher metal availability and greater weathering of particles in subtropical soils
- Complex Ca–Cu–Pb arsenates efficiently control mobility of metal(loids).

GRAPHICAL ABSTRACT



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ABSTRACT

We studied the heavy mineral fraction, separated from mining- and smelter-affected topsoils, from both a humid subtropical area (Mufulira, Zambian Copperbelt) and a hot semi-arid area (Tsumeb, Namibia). High concentrations of metal(loid)s were detected in the studied soils: up to 1450 mg As kg^{-1}, 8980 mg Cu kg^{-1}, 4640 mg Pb kg^{-1}, 2620 mg Zn kg^{-1}. A combination of X-ray diffraction analysis (XRD), scanning electron microscopy (SEM/EDS), and electron probe microanalysis (EPMA) helped to identify the phases forming individual metal(loid)-bearing particles. Whereas spherical particles originate from the smelting and flue gas cleaning processes, angular particles have either geogenic origins or they are windblown from the mining operations and mine waste disposal sites. Sulphides from ores and mine tailings often exhibit weathering rims in contrast to smelter-derived high-temperature sulphides (chalcocite [Cu_2S], digenite [Cu_9S_5], covellite [CuS], non-stoichiometric quenched Cu–Fe–S phases). Soils from humid subtropical areas exhibit higher available concentrations of metal(loids), and higher frequencies of weathering features (especially for copper-bearing oxides such as delafossite [$Cu^{1+}Fe^{3+}O_2$]) are observed. In contrast, metal(loid)s are efficiently retained in semi-arid soils, where a high proportion of non-weathered smelter slag

* Corresponding author.
E-mail address: ettler@natur.cuni.cz (V. Ettler).
[1] Deceased February 13, 2016.

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particles and low-solubility Ca–Cu–Pb arsenates occur. Our results indicate that compared to semi-arid areas (where inorganic contaminants were rather immobile in soils despite their high concentrations) a higher potential risk exists for agriculture in mine- and smelter-affected humid subtropical areas (where metal(loid) contaminants can be highly available for the uptake by crops).

1. Introduction

Emissions from mines and non-ferrous metal smelters are responsible for the contamination of various environmental compartments in the vicinity of such industrial operations (Csavina et al., 2012, 2014; Shukurov et al., 2014). Soils represent major sinks for emitted metal(loid)-bearing particulates (aerosol size; <10 μm), and also for larger particles. As a result, high levels of inorganic contaminants have been observed, especially in the surficial soil layers around mines and smelters (Ettler (2016) and references therein). The prevailing wind direction and the size of particulates/particles are key parameters affecting the spatial distribution of smelter- and mine-related contamination, with higher rates of dispersion in dry and semi-arid areas (e.g., Csavina et al., 2011, 2012; Ettler, 2016; Kříbek et al., 2014a, 2014b, 2016; Mihaljevič et al., 2015). Thus, in terms of spatial distribution, the contamination hotspots in soils are generally elongated, and exhibit their highest metal(loid) concentrations downwind from the mines and smelters (Ettler et al., 2011, 2014a; Ettler, 2016; Kříbek et al., 2010, 2016). Csavina et al. (2011, 2014) reported that ultrafine smelter-derived aerosols (<0.5 μm in size) are particularly rich in contaminants, and they may travel over long distances. Moreover, variability in dry and wet deposition can also affect the distribution of particulates/particles near smelters. Schindler et al. (2012) and Caplette et al. (2015) studied alteration crusts on rocks near several Canadian smelters. They found that an increase in metal(loid) concentrations and the greater occurrence of metal(loid)-bearing particulates embedded in these black rock coatings 2 km from the smelter stack may be attributed to a "shadow effect", which results from precipitation events and the gravitational settling of larger particulates causing their deposition. It was argued that especially the smaller metal-sulphate aerosols might be washed out from the atmosphere during precipitation events, and thus their spatial influence might be limited during wet periods (Schindler et al., 2012; Sorooshian et al., 2012).

A number of studies have been devoted to mineralogical investigations of particulates (<10 μm) as well as larger particles, collected near mining and smelting operations: encapsulated in alteration layers on rocks (Caplette et al., 2015; Mantha et al., 2012; Schindler et al., 2012), trapped in soils from temperate areas (Adamo et al., 1996; Cabala and Teper, 2007; Henderson et al., 1998; Knight and Henderson, 2006; Lanteigne et al., 2012, 2014), or in snowpack (Gregurek et al., 1998, 1999). Interestingly, except for a few studies (e.g., Chopin and Alloway, 2007; Ettler et al., 2014a, 2014b; Gutiérrez-Ruiz et al., 2012), the mineralogical and chemical compositions of mining- and smelter-derived particulates and particles in soils of subtropical and tropical climatic zones have not yet been studied.

The aim of this study was to provide insights into the variability of chemical and mineralogical compositions of particulates/particles emitted from non-ferrous metal mining and smelting operations and deposited into the soils of humid subtropical and dry semi-arid areas in southern Africa. We also focused on the assessments and comparisons of their weathering features, as well as their potential role in the release and fate of metal(loid) contaminants into these soil systems.

2. Materials and methods

2.1. Study areas and soil sampling

The studied soils were sampled in two mining and smelting areas (Fig. 1): (i) Mufulira in the Zambian Copperbelt (mean annual precipitation 1270 mm, mean annual temperature 19.7 °C, humid subtropical climate [Cwa] according to the Köppen climate classification); (ii) Tsumeb in northern Namibia (mean annual precipitation 550 mm, mean annual temperature 22 °C, hot semi-arid climate [BSh] according to the Köppen climate classification) (climate-data.org). In both regions, there is a distinct rainy season (November–April) and a dry season (May–October); the strongest winds occur during the dry seasons, these being south-easterly (Fig. 1).

Mufulira is located in a Cu—Co mining and smelting area, where ore extraction and processing activities date back to the 1930s. The ore in the Mufulira deposit is characterised by a stratabound disseminated mineralisation in footwall arkoses and conglomerates; the main ore minerals being bornite (Cu_5FeS_4), followed by chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), covellite (CuS), and cobaltiferous pyrite. The Mufulira copper smelter was initially commissioned in 1937, and was equipped with reverbatory furnaces and later with electric furnaces; in 2006, the smelting process was upgraded, when Isasmelt technology was commissioned (more information is given in Kříbek et al. (2010); Schlesinger et al. (2011); and Vítková et al. (2010)). The offgas is first cooled in heat recovery boilers, and afterwards electrostatic precipitators (ESP) are used for dust removal.

The Tsumeb deposit belongs to the northern Namibian sulfidic metallogenic province, which is part of the Otavi group formed of limestones and dolomites of Neoproterozoic age. This deposit is predominantly of a Pb–Cu–Zn type and contains a large variety of metal(loid)-bearing ore minerals, which also exhibited economic concentrations of Ag, Cd, Ge, and As. The deposit was mined in large open pits and several shafts from the beginning of the 20th century until 2006. The smelter at Tsumeb began operations in 1907, when blast furnaces were constructed to process the local Pb—Cu ores. In 1963, new smelters were constructed, consisting of a Cu smelter with a reverbatory furnace and a Pb smelter with a shaft furnace. In the 1980′s, a slag mill was constructed for the processing of old Cu reverbatory slags, in which Pb and Cu were subsequently separated and granulated slags were produced. Currently, the Pb smelter is being dismantled, but the Cu smelter equipped with Ausmelt and reverbatory furnaces is still in operation, and now processes Cu concentrates from other localities (mainly from the Chelopech mine in Bulgaria). The offgas from the furnaces and converters is cooled in heat recovery boilers, and the dust is subsequently removed in baghouse facilities. The Tsumeb smelter is now one of the few in the world producing Cu from As-containing ores, with production of As_2O_3 as an intermediate product (more information about the mining and smelting activities is given in Bowell (2014); Ettler et al. (2009); Mihaljevič et al. (2015); Schlesinger et al. (2011), and at the company's website www.dundeeprecious.com).

The most polluted topsoils from profiles having been sampled during previous screening research in the Mufulira and Tsumeb areas (Ettler et al., 2014a; Mihaljevič et al., 2015; Podolský et al., 2015) were selected for this study. Soils from wooded (predominantly with miombo trees [*Brachystegia*, *Julbernardia*, and *Isoberlinia* spp.]) and grassland plots were sampled at three locations in the vicinity of Mufulira: (i) 3.6 km downwind from the Cu smelter, 2.5 km downwind from a mine tailing site; (ii) 8 km downwind from the Cu smelter, 5.5 km downwind from a mine tailing site; (iii) reference soils 25 km upwind from the Cu smelter and mine tailing sites (Fig. 1 and Table 1). Two soils were collected 1 km downwind from the Cu—Pb smelters and a few hundred meters from the tailing disposal sites in Tsumeb, where a mix of flotation mine wastes and slag dust are