



Transformation of arsenic-rich copper smelter flue dust in contrasting soils: A 2-year field experiment[☆]

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ABSTRACT

Dust emissions from copper smelters processing arsenic-bearing ores represent a risk to soil environments due to the high levels of As and other inorganic contaminants. Using an *in situ* experiment in four different forest and grassland soils (pH 3.2–8.0) we studied the transformation of As-rich (>50 wt% As) copper smelter dust over 24 months. Double polyamide bags with 1 g of flue dust were buried at different depths in soil pits and in 6-month intervals; then those bags, surrounding soil columns, and soil pore waters were collected and analysed. Dust dissolution was relatively fast during the first 6 months (5–34%), and mass losses attained 52% after 24 months. The key driving forces affecting dust dissolution were not only pH, but also the water percolation/retention in individual soils. Primary arsenolite (As₂O₃) dissolution was responsible for high As release from the dust (to 72%) and substantial increase of As in the soil (to a 56 × increase; to 1500 mg kg⁻¹). Despite high arsenolite solubility, this phase persisted in the dust after 2 years of exposure. Mineralogical investigation indicated that mimetite [Pb₅(AsO₄)₃(-Cl,OH)], unidentified complex Ca-Pb-Fe-Zn arsenates, and Fe oxyhydroxides partly controlled the mobility of As and other metal(loid)s. Compared to As, other less abundant contaminants (Bi, Cu, Pb, Sb, Zn) were released into the soil to a lesser extent (8–40% of total). The relatively high mobility of As in the soil can be seen from decreases of bulk As concentrations after spring snowmelt, high water-extractable fractions with up to ~50% of As(III) in extracts, and high As concentrations in soil pore waters. Results indicate that efficient controls of emissions from copper smelters and flue dust disposal sites are needed to prevent extensive contamination of nearby soils by persistent As.

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1. Introduction

Soils represent a direct sink for contaminants emitted to the atmosphere by non-ferrous metal smelters (Ettler, 2016). Numerous investigations have been conducted to describe the spatial distribution, mobility, and forms of inorganic contaminants (metals and metalloids) in smelter-affected soils using bulk or sequential extraction analyses (Clemente et al., 2008; Kríbek et al., 2010), isotope tracing techniques (Cloquet et al., 2006; Ettler et al., 2004, 2011; Šillerová et al., 2017), and/or mineralogical analyses of

smelter-derived particulates (Bromstad et al., 2017; Ettler et al., 2016a; Gutiérrez-Ruiz et al., 2012). However, experiments simulating the reactivity of smelter-derived materials in soils are extremely rare in the literature. The first approach for understanding the reactivity of anthropogenic materials (e.g., slag, fly ash) is based on a pH-dependent laboratory leaching test (e.g., Jarošíková et al., 2017, 2018), because pH is also the key parameter affecting contaminant releases in soil systems (e.g., Bataillard et al., 2003). A step forward is the laboratory testing of the weathering of materials using pot or column experiments with soils, which for the sake of simplicity are often conducted with pure compounds as proxy materials (Bataillard et al., 2003; Chrástný et al., 2012; Ettler et al., 2016b; Robson et al., 2014; Yue and Donahoe, 2009). However, long-term weathering in real soil systems is very complicated, and the first field experiments aimed towards understanding the

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reactivity of minerals in soils have indicated that along with the basic soil parameters, many other factors such as vegetation cover (the presence of certain tree species) can significantly affect the dissolution processes (e.g., Augusto et al., 2000; Mihaljević et al., 2010). Only a few long-term *in situ* experiments dealing with the reactivity of metal(loid)-bearing particles have thus far been conducted. Birkefeld et al. (2006, 2007) studied the reactivity of PbO, Cu concentrates, and Cu slags in acidic forest soils over 18 months. Whereas PbO particles were highly reactive and became covered with secondary carbonates within 2 months of incubation, the other materials were rather resistant to weathering (Birkefeld et al., 2006, 2007). Pareuil et al. (2010) studied the dissolution in soil of a Mn-bearing smelting slag by means of a 1-year *in situ* incubation experiment, and found that less than 0.01% of the Mn had been released. Compared to slags, smelter dusts are significantly more reactive in soil systems due to their small grain size and the presence of highly soluble compounds (Jarošíková et al., 2017; Skeaff et al., 2011; Vítková et al., 2011). Nowack et al. (2010) artificially polluted soils with filter dust from a non-ferrous metal smelter, studying changes in the metal fractionation in the soil after reforestation over 42 months. However, they found that the largest changes related to dissolution, adsorption of dissolved metals onto solid phases, and the formation of secondary phases occurred during the first 6 months of the experiment. Similarly, Ettler et al. (2012a, 2012b) observed rapid dissolution of Pb-smelter fly ash in an acidic soil during an initial pot experiment (504 h of monitoring), and conducted a 1-year *in situ* incubation experiment in both forest and grassland soils. They found that more than 60% of the fly ash was dissolved after 1 year of incubation, and the different releases and mobilities of contaminants (As, Cd, Pb, Sb, Zn) were mainly controlled by pH-dependent stabilities of the primary and newly formed phases (Ettler et al., 2012a,b).

The world production of Cu from the mining and processing of Cu ores attained 19.4 Mt in 2016 (USGS, 2017). Goonan (2005) evaluated the material flows in 30 Cu smelters around the world and found that their waste production varied in the range of 0.65–5.14 t for slag (weighed mean: 1.91 t), and in the range of 0.02–0.48 t for flue dust (weighed mean: 0.20 t) per 1 t of Cu produced. The problem of flue dust generation in the Cu industry has been aggravated in recent years due to increasing amounts of deleterious impurities in some Cu ores (e.g., Arndt et al., 2017; Chen et al., 2016; Schlesinger et al., 2011). During the pyrometallurgical processing, these impurities (As, Sb, Bi, and Pb) primarily concentrate in the flue dust. As a result, this material can hardly be recirculated back into the smelting and converting process, or used for hydrometallurgical recovery; they must be stabilized and/or stockpiled in waste disposal sites (Jarošíková et al., 2018; Nazari et al., 2017). The transport of these flue dust particles from undisclosed disposal sites (Shibayama et al., 2010), including wind erosion as well as direct emissions from Cu smelters (Kříbek et al., 2016) can be important sources of pollution to soil systems. Particles emitted from smelter operations are generally smaller in size than those that become windblown from disposal sites (e.g., Csavina et al., 2012). However, recent investigations have indicated that dust particles trapped by filters in flue-gas cleaning systems in smelters are chemically and mineralogically similar to the aerosol particles collected in their chimneys (Arndt et al., 2016), and thus they can be used as a proxy material for investigation of the fate of smelter emissions in environmental systems.

With these basic facts in mind, the aim of this paper was to investigate the long-term transformation of a copper smelter flue dust, particularly rich in As (>50 wt%), in different types of soils, with differing pH and vegetation covers. We performed a two year *in situ* incubation study in order to understand the processes affecting the release and subsequent mobility/attenuation of the

inorganic contaminants, especially As, in such environmental settings.

2. Materials and methods

2.1. Smelter flue dust

The flue dust used originated from baghouse filtering units in a copper smelter, where Cu-bearing sulphide concentrates, composed mainly of Cu-pyrite (FeS₂), chalcopyrite (CuFeS₂), and Cu-As sulphosalts such as enargite (Cu₃AsS₄) and/or tennantite (Cu₁₂As₄S₁₃) were processed in Ausmelt and reverberatory furnaces to produce blister copper. A previous investigation, based on a detailed multi-method characterization, indicated that the smelter dust consists predominantly of arsenolite (As₂O₃), with a moderate amount of gypsum (CaSO₄·2H₂O), as well as minor amounts of claudetite (As₂O₃), quartz (SiO₂), galena (PbS), and covellite (CuS) (Table S1 in the Supplementary Material; Jarošíková et al., 2018). Additionally, other trace constituents such as sphalerite (ZnS), enargite (Cu₃AsS₄), Bi-Te alloys (Bi-Te-Pb), metals (Bi, Se), Fe oxides (maghemite, Fe₂O₃, magnetite, Fe₃O₄), Ca arsenates (As apatites), other complex metal arsenates, and slag particles have been detected by a combination of electron microscopy, electron microprobe, and Raman microspectrometry (Jarošíková et al., 2018). The smelter dust was highly enriched in As (53.3 wt%), and also contained high levels of other contaminants (in wt%): Bi 0.80, Cu 1.07, Pb 3.41, Sb 1.26, and Zn 1.41 (Table S1).

2.2. In situ experiment

2.2.1. Soils

The long-term field-testing of smelter dust stability was initiated in October 2013, and was based on an experimental protocol previously described by Ettler et al. (2012a, 2012b). The following four soils with differing properties (pH, CEC - cation exchange capacity, organic matter content) were selected for this *in situ* incubation experiment due to the fact that the leaching of As and other contaminants from the smelter dust was highly pH-dependent (Jarošíková et al., 2018; Fig. S1):

- (i) Dystric Cambisol developed under beech (*Fagus sylvatica*) forest (pH 3.4–3.8);
- (ii) Dystric Cambisol developed under spruce (*Picea abies*) forest (pH 3.2–3.9);
- (iii) Haplic Cambisol, permanent grassland (pH 6.2–6.3);
- (iv) Haplic Chernozem, permanent grassland (pH 7.3–8.0).

The soil horizons were described according to the Guidelines for Soil Description (FAO, 2006), and the individual soil profiles were classified according to the WRB classification (IUSS Working Group WRB, 2014) (Fig. S2). To obtain reference samples, the uncontaminated soils were collected vertically as 5-cm thick segments with soil sample rings (5 cm diameter, volume 100 cm³; Eijkelkamp, The Netherlands) (Fig. S3). The soil parameters (pH, CEC) were determined using standard procedures (Pansu and Gautheyrou, 2006). Particle size distribution (fractions of clay, silt and sand) was obtained by the hydrometer method (Gee and Or, 2002). Total organic carbon (C_{org}) in the soil samples was determined using a combination of ELTRA CS 530 and CS 500 elemental analysers (ELTRA, Germany). Extraction of amorphous Fe oxyhydroxides was performed with ascorbic acid solution according to ISO 12782-1 (ISO, 2012). Table 1 provides a summary of the soils' properties.

2.2.2. Experimental setup

The flue dust (1 ± 0.0005 g) was inserted into double

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