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## Review

# Soil contamination near non-ferrous metal smelters: A review



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## ABSTRACT

This review summarizes over 160 studies focused on soil contamination near non-ferrous metal smelters. The methods of these investigations were examined with an emphasis on the combinations of traditional (geo)chemical approaches with various mineralogical and metal isotope techniques that are particularly helpful for depicting the fate of smelter-derived contamination in the soil. Differences in the distributions and binding of metal(loid)s in smelter-affected soils from temperate and (sub)tropical climatic zones indicate the greater vulnerability of the latter. Prevailing wind direction is a key factor affecting the dispersion of smelter emissions and their subsequent deposition into the soils, with greater importance found especially in arid areas. Whereas the greatest contamination is generally observed in the surface soil layers, downward migration of metal(loid)s in the soil profiles has been documented at numerous sites. Contamination of smelter soils significantly affects both plants and soil organisms, but suitable remediation techniques (such as chemical stabilization of soils by amendments) can be used for reducing the bioavailability of contaminants.

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## 1. Introduction

The mining and smelting of metal ores are one of the important sources of environmental pollution by metals and metalloids (Nriagu, 1996). According to a global inventory by Nriagu and

Pacyna (1988), in the late 1980s, about  $356\text{--}857 \times 10^6$  kg Pb, and  $557\text{--}1360 \times 10^6$  kg Zn were released into the environment annually through mining and smelting activities. More recently, Pirrone et al. (2010) estimated that ore mining and processing is responsible for 13% of global Hg emissions. Despite the fact that Hg, Pb, and Cd emissions from the non-ferrous metal industry decreased in Europe over the last 50 years due to the installation of efficient flue gas cleaning systems (Pacyna et al., 2009), the increasing industrial

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activities on other continents (Asia, Africa) could significantly affect the global emissions of metals (e.g., Pirrone et al., 2010; Zhang et al., 2011). For example, Zhang et al. (2011) estimated that up to 2007 cumulative emissions from mining, ore dressing, and smelting activities in China were about 1.62 Mt Pb and 3.32 Mt Zn, with the contribution of the smelting processes accounting for 19% and 27%, respectively. It is known that large-scale non-ferrous metal smelters are important local-to-regional sources of pollution. For instance, Li et al. (2011) reported that the largest Pb/Zn smelter in China, located in Zhuzhou (Hunan), emitted 77.82 tonnes of Cd into the atmosphere in the period 1991–2000, accounting for 95% of total emissions from the city.

Soils represent direct sinks for contaminants emitted to the atmosphere by smelters. Contaminants associated with particulates emitted from mining operations are usually concentrated in the fine fraction (<2  $\mu\text{m}$ ), and those from smelting even concentrated in the ultrafine particle fraction (<0.5  $\mu\text{m}$ ), which may travel greater distances into the environment (Ettler et al., 2005a; Uzu et al., 2011; Csavina et al., 2011, 2012, 2014; Sorooshian et al., 2012). This was perfectly demonstrated by Hou et al. (2006), who studied Pb concentrations and isotope compositions in soils affected by the Horne copper smelter (Rouyn-Noranda, Canada), and found that the signature of the smelter's emissions was to be found as far as 116 km downwind. However, highly volatile contaminants such as Hg can be deposited in soils to lesser extent. Wu et al. (2014) calculated that a large-scale Pb/Zn smelter in Zhuzhou (China) emitted 105 t of Hg during the period 1960–2011, with only 14% of this amount deposited locally in the soil, with the remainder emitted into the global pool. Historic smelting activities were often responsible for extensive soil contamination having persisted through to modern times. Baron et al. (2006) studied medieval metallurgical sites at the Mont-Lozère Massif (southern France), and estimated from the mass balances and isotope compositions that 95% of Pb in the soils originated from the medieval metallurgical workshops, rendering later pollution sources negligible. Similarly, Kierczak et al. (2013) found that soils in the areas around historic smelters, which were active between the 14th and 16th centuries, are still highly polluted with metal(loid)s (up to 4000 mg/kg Cu, 1500 mg/kg Zn, 300 mg/kg As, and 200 mg/kg Pb) due especially to the centuries-long dissolution of smelter wastes into the soils. They concluded that the legacy of old smelting sites, even those which have not been operational for centuries, must still be considered as a serious environmental problem today; these sites should be properly investigated before any decisions regarding remediation strategies are made (Kierczak et al., 2013).

This review's aim is to summarize the relevant studies (primarily those published in the last 15 years) devoted to the pollution of soils in the vicinity of non-ferrous metal smelters (with the exception of alluvial soils and peats), with a special focus on isotope techniques and advanced mineralogical approaches, which are extremely powerful in tracing pollution, especially in areas where mining and smelting operations are geographically close and standard geochemical approaches are unable to distinguish between these two sources of pollution. Moreover, those smelter sites, which heretofore had been overlooked (e.g., in Africa or China), have begun to be investigated in the last decade, in order to understand not only the extent of the pollution, but also the potential impacts on biota. I am following in the footsteps of an older review paper by Rieuwerts and Farago (1995) dedicated to Pb contamination in smelting and mining environments. Here, I especially emphasize the methodological advances, which have enabled the deciphering of geochemical processes in smelter-contaminated soils. Rieuwerts and Farago (1995) concluded that for polluted dusts and soils, Pb absorption by the human body is apparently lower in mining areas than in smelter areas, probably

due to differences in chemical and mineralogical forms of Pb. These facts were later confirmed by comparative studies assessing oral bioaccessibility of contaminants from mining- and smelter-impacted soils (e.g., Davis et al., 1996; Rieuwerts et al., 2000; Ettler et al., 2012a). Along with the consumption of contaminated food and water, which has greater significance for less developed areas where the population is dependent on local food and water sources, it has been suggested that the ingestion/inhalation of dust re-suspended from contaminated soils as well as small-size aerosols from smelting operations are among the major routes of human exposures to metal(loid)s, resulting in elevated contaminant concentrations in the blood or urine (Banza et al., 2009; Cheyens et al., 2014; Csavina et al., 2014). Despite the increasing number of investigations focused on potential contaminant bio-accessibilities from smelter soils (e.g., Carrizales et al., 2006; Romero et al., 2008; Roussel et al., 2010; Ettler et al., 2012a; Pelfrène et al., 2011, 2015), this subject remains beyond the scope of the present paper.

## 2. Methods of investigation

### 2.1. Screening geochemical studies

The spatial distribution of contaminants in soils near non-ferrous metal smelters depends on: (i) wind direction (hotspots are commonly elongated according to the prevailing wind direction) (Křibek et al., 2010; Stafilov et al., 2010; Ettler et al., 2011, 2014; Šajin et al., 2013, Fig. 1), (ii) the size of particulates emitted by the smelter (smaller particles can travel longer distances) (Csavina et al., 2011, 2012, 2014 and references therein), and (iii) the chemical and mineralogical composition of the particulates (if soluble forms are present in the dusts, greater downward leaching of contaminants can occur in the soil profiles) (Ettler et al., 2012b).

The highest concentrations of contaminants in soils near smelters occur in the uppermost horizons (e.g., Sterckeman et al., 2000; Ettler et al., 2004; Cecchi et al., 2008). For this reason, the

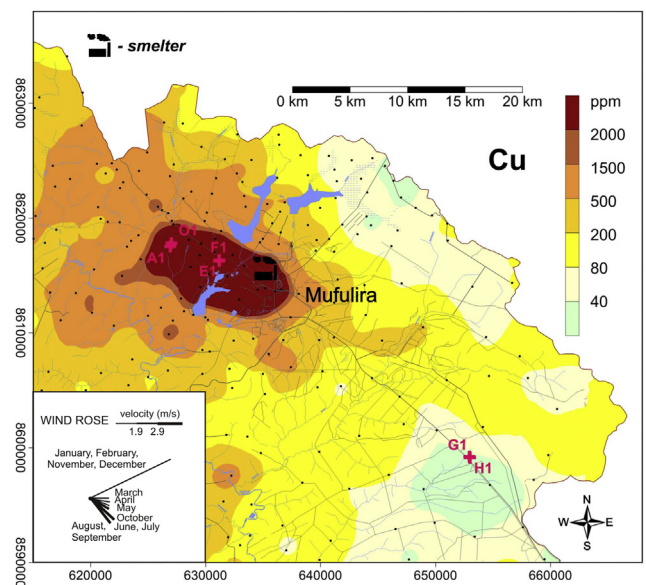


Fig. 1. The spatial distribution of Cu in topsoils near a Mufulira copper smelter, Zambian Copperbelt (modified from Křibek et al. (2010) and Ettler et al. (2014a)). Dots represent the topsoil sampling points, and red crosses the localization of the deep soil pits.

strategies of sampling for determination of the spatial distribution of contaminants in soils are either based on: (i) topsoils collected in the grid to construct distribution maps of elements (Křibek et al., 2010; Stafilov et al., 2010, Fig. 1), or (ii) topsoils collected in transects in different geographical or wind directions (Tembo et al., 2006; Hou et al., 2006). For topsoils, composite samples are generally prepared: for instance, Křibek et al. (2010) combined samples from the edges as well as from the central point of a 25 m × 25 m square; whereas Sterckeman et al. (2002) obtained a representative topsoil sample at each point by the mixing of twenty topsoil sub-samples collected within a circle of approximately 20 m in diameter. To assess the spatial distribution of contaminants in soils around a smelter, tens to hundreds of samples should be collected, analysed, and statistically evaluated before being plotted. However, inconsistencies in the definition of “topsoil” still occur in the literature. While only the few uppermost centimetres have been collected in some studies (0–5 cm; Rieuwerts et al., 1996b; Martley et al., 2004a; Stafilov et al., 2010; Křibek et al., 2010), other investigations were based on a ploughed layer corresponding to a depth of 0–20 or 0–25 cm (Adamo et al., 1996; Sterckeman et al., 2002; Douay et al., 2007; Li et al., 2011; Qasim et al., 2015). Moreover, the topsoil sampling is often done irrespective of the natural development of the soil horizons; thus, the final sample can be a mixture of different soil materials. For the screening studies, it is convenient to compare topsoil concentrations with regional or local background concentration levels. Based on the large scale investigation in the Zambian Copperbelt, Křibek et al. (2010) did not only collect topsoils, but also subsurface soil samples from a depth of 80–90 cm using a soil probe; by a comparative approach, these authors were able to discriminate concentration hotspots related to mining and smelting activities, and also natural enrichments derived from the bedrock, and transferred into the overlying mineral soil by weathering.

Another sampling strategy is based on the collection of soil profiles at various distances from the smelter stack and positioned according to the prevailing wind direction (upwind vs. downwind). The advantage of this approach is that samples collected in the soil pits can be fully described and characterized according to soil taxonomies (Soil Survey Staff, 2014; IUSS Working Group WRB, 2014). Two approaches are generally adopted: (i) soil sampling according to nominally selected depths (0–5 cm, 5–10 cm, 10–20 cm, etc.) (Dumat et al., 2001; Martley et al., 2004b; Křibek et al., 2010), or (ii) soil sampling according to naturally developed horizons down to the bedrock, which is generally preferred because different biogeochemical processes can occur in the individual soil horizons (it is recommended to divide thicker horizons into smaller subsamples; Ettler et al., 2005b; van Oort et al., 2006; Ettler et al., 2011). Finer-scale sampling (0.5–5 cm segments) was also adopted in some cases to describe fine vertical variations in contaminant concentrations in soil profiles (Fernandez et al., 2008; Klaminder et al., 2008; Ettler et al., 2011, 2014a). Moreover, sampling of soil profiles in different landscape settings (agricultural vs. forest; permanent pasture vs. arable land) provides very useful information on the effects of land use on the processes influencing variability in the contaminant distribution and mobility (Ettler et al., 2005b, 2014a; van Oort et al., 2006; Fernandez et al., 2007, 2010; Chrastný et al., 2012a; Vaněk et al., 2013).

Total contaminant concentrations in soils are generally determined after digestion in mineral acids. Whereas numerous authors use *aqua regia* “pseudo-total” extraction (Martley et al., 2004b; Křibek et al., 2010; Šajn et al., 2013); it has been found that especially for tropical soils this extraction might be insufficient, and total digestion in perfluoric (HF) and perchloric (HClO<sub>4</sub>) is preferred, as was recently demonstrated on Pb from smelter-affected Oxisols (Ettler et al., 2011).

## 2.2. Chemical extractions and soil mineralogy

A large number of single extractions simulating the “plant-available” or “labile” fraction of metal(loid)s in soils have been proposed and used for smelter-affected soils. The 0.01 M CaCl<sub>2</sub> extraction, simulating soil pore water (Dumat et al., 2001; Ettler et al., 2007c; Qasim et al., 2015), and the 0.05 M EDTA extraction simulating the plant-available fraction (Komárek et al., 2006; Chrastný et al., 2012a; Popescu et al., 2013; Ettler et al., 2014a) have been the most frequently used for metallic contaminants. The popularity of these extraction methods lies in their simplicity, extraction rapidity, comparability with other studies, as well as the availability of soil reference materials with certified (or at least indicative) concentration values for the major metallic contaminants such as Cd, Cr, Cu, Ni, Pb, and Zn (CRM 483 – sewage sludge amended soil, certified by European Community Bureau of Reference [BCR], Standard, Measurements and Testing Programme). In contrast, simple deionized water and 0.1 M Na<sub>2</sub>HPO<sub>4</sub> extractions have been suggested for quick estimates of easily exchangeable and specifically sorbed fractions of anionic contaminants (As, Sb) (Ettler et al., 2007b).

Various schemes for sequential extraction procedures (SEP) have also been applied to smelter-affected soils, in order to assess the chemical fractionation of metals (Adamo et al., 1996; Kabala and Singh, 2001; Burt et al., 2003; Ettler et al., 2005b; Knight and Henderson, 2006; Cecchi et al., 2008) and metalloids (Ettler et al., 2010). In the last decade, BCR SEP based on the work of Rauret et al. (1999) has frequently been used, especially due to its simplicity (a 3-step extraction) and the possibility of accuracy checking using two BCR certified reference materials (CRM 483 – sewage sludge amended soil, and CRM 701 – freshwater sediment) (Yang et al., 2010; Ettler et al., 2011; Chrastný et al., 2012a; Qasim et al., 2015).

Selective extractions, alone, can only hardly predict the binding of contaminants to soil constituents. For this purpose, their combination with mineralogical investigations at various levels of concentration and scale is extremely useful. Basic phase composition obtained by X-ray diffraction (XRD) analysis is routinely used to determine the major soil minerals, including those which can potentially bind contaminants by sorption or co-precipitation (e.g., clay minerals, oxides, and hydroxides) (e.g., Chrastný et al., 2012a; Vaněk et al., 2013). At high contaminant concentrations in soils, even metal(loid)-bearing phases can be directly detected by XRD in bulk samples. Using this kind of analysis, Ettler et al. (2005b) found anglesite (PbSO<sub>4</sub>) derived from smelter emissions in the most polluted horizon of the forest soil at Příbram (Czech Republic) (total Pb: 35,300 mg/kg); and Burt et al. (2003) detected anglesite, plattnerite (PbO), galena (PbS), quenselite (PbMnO<sub>2</sub>(OH)), tennantite ((Cu,Fe)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>), arsenosulvanite (Cu<sub>3</sub>As<sub>4</sub>S<sub>4</sub>), and chalcopyrite (CuFeS<sub>2</sub>) in soils near the Anaconda copper smelter (Montana, USA) with 475 mg/kg Pb and 1270 mg/kg Cu.

Scanning electron microscopy (SEM) coupled with energy dispersion spectrometry (EDS) is a useful tool for the visualization and analysis of metal(loid)-bearing particles from bulk soil samples (Henderson et al., 1998; Leguëdois et al., 2004; Cabala and Teper, 2007) or from the dense soil fraction. The dense fraction is often separated by extraction in heavy liquids, such as bromoform or tetrabromomethane (densities of 2.89 g/cm<sup>3</sup> and 2.96 g/cm<sup>3</sup>, respectively) (Adamo et al., 1996; Morin et al., 1999; Chopin and Alloway, 2007; Ettler et al., 2011; Konečný et al., 2014), or with a magnet (Lanteigne et al., 2012). Subsequently, specimens can be prepared as individual grains separated under a binocular microscope and attached on double-sided carbon tape (Knight and Henderson, 2006; Chopin and Alloway, 2007; Cabala and Teper, 2007) or embedded in epoxy resin and prepared as polished (thin) sections

(Lanteigne et al., 2014; Ettler et al., 2014a; Konečný et al., 2014).

Smelter-derived particulates from soils are chemically and mineralogically complex materials. They contain: (i) spherically shaped particles representing melt relicts emitted from the smelting process – composed of sulphides, oxides (spinel), or slag-like phases (glass and silicates); and (ii) irregular particles derived from materials not heated up to melting temperatures, which may correspond to unmelting ore, unreacted flux, or fuel materials (Fig. 2) (Adamo et al., 1996; Henderson et al., 1998; Gregurek et al., 1999; Cabala and Teper, 2007; Ettler et al., 2014a; Konečný et al., 2014). Moreover, as smelters are often located close to mining operations, the contamination may be mixed, and angular grains of metal-bearing particles windblown from mine tailing disposal sites are often found in the soil dense fraction (Fig. 2). Additional methods such as Raman spectroscopy, Mössbauer spectroscopy (Lanteigne et al., 2012), or trace element analysis by laser ablation ICP-MS (Lanteigne et al., 2014) can be used for further investigations of the soil particles. At some smelting sites it has been shown that the smelter slag particles are wind-dispersed from the slag dumps and directly deposited into the soils. The SEM/EDS investigations of slag fragments, weathered in soils, have indicated that metallic/sulphide inclusions and glass are the most susceptible to weathering, and could be responsible for the release of metals into soils; nevertheless, this process remains limited to the vicinity of slag disposal sites, and due to the larger sizes of slag particles (>1 mm) does not represent a significant risk for the broader environment (Sobanska et al., 2000; Kierczak et al., 2009; Chopin and Alloway, 2007). Compared to SEM, higher resolution microscopic methods such as transmission electron microscopy (TEM) coupled to EDS only rarely have been used for visualization and

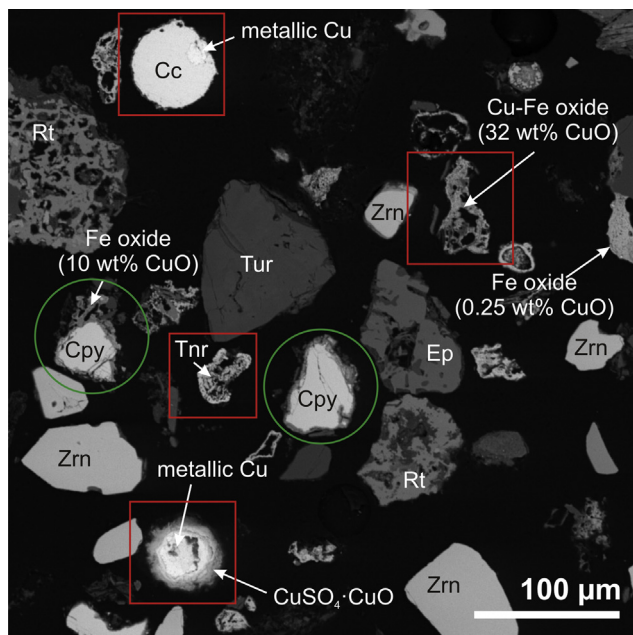
analysis of metal-bearing particles from smelter-affected soils, this probably due to the difficulties with specimen preparation (Buatier et al., 2001).

So far, relatively few studies have applied synchrotron-based methods to investigate the solid speciation of contaminants in smelter-contaminated soils. In the pioneering work by Morin et al. (1999), extended X-ray absorption fine structure (EXAFS) spectroscopy on soil samples from the vicinity of Pb/Zn smelters in northern France was used to quantitatively distinguish between Pb binding to humic substances (predominant in wooded soils) and Pb absorption to Fe- and Mn-oxides (predominant in tilled soils). In near-neutral Zn-polluted soils from the same area, EXAFS spectroscopy indicated that the Zn was mainly bound in the clay fraction (<2 μm) either as Zn/Al hydroxalite ([Zn,Al](OH)<sub>2</sub>(CO<sub>3</sub>)<sub>0.2</sub>·nH<sub>2</sub>O), a layered double hydroxide mineral (Juillot et al., 2003) or as dioctahedral ferruginous smectites (Vespa et al., 2010). In contrast, Roberts et al. (2002) showed by a combination of EXAFS with other mineralogical techniques that in more acidic smelter-impacted soils, the Zn was mainly bound in franklinite (ZnFe<sub>2</sub>O<sub>4</sub>) and sphalerite (ZnS), both emitted during the smelting process, and a minor proportion of Zn was adsorbed by Fe- and Mn-oxides. Nachtegaal et al. (2005) used μ-EXAFS spectroscopy, and confirmed that 10 years after the remediation of a soil polluted by a Belgian Zn-smelter (soil was treated by amendment with cyclonic ash, beringite, compost, and subsequent revegetation) about 50–70% of Zn was mainly bound to phyllosilicates. Other techniques such as synchrotron based X-ray microfluorescence (μ-SXRF) imaging were applied to visualize the distributions of contaminants in particles extracted from smelter-affected soils and to find correlations with other elements (Juillot et al., 2003; Nachtegaal et al., 2005; van Oort et al., 2006). Takaoka et al. (2005) used X-ray absorption near edge structure (XANES) to determine the redox speciation of Sb in smelter soils, and found that Sb occurred exclusively as Sb(V) compounds suggesting that metallic Sb and Sb<sub>2</sub>O<sub>3</sub> species, presumably emitted by the smelter, were fully oxidized after their deposition in soils.

### 2.3. Applications of isotopes

With the increasing use of metal isotopes in environmental geochemistry, as well as advances in isotope measurements using multi-collector ICP-MS, numerous metal isotope systems have become useful for the tracing of contamination sources. Since the review by Rieuwerts and Farago (1995), the development of isotope techniques became one of the major advances in investigation of the origin and fate of contaminants near non-ferrous metal smelters.

It has been demonstrated that Pb isotopes are not fractionated during the smelting process, and variations in Pb isotope compositions of the smelter effluents (slag, fly ash, emissions) can only be attributed to mixing of the Pb sources (ores, recycled Pb) in the smelting furnace charge (Rabinowitz, 2005; Shiel et al., 2010). Lead isotopes have thus been used to trace the extent of smelter contamination, which can be recognized at large distances, commonly tens of kilometres from the source (e.g., Hou et al., 2006; Ettler et al., 2011). Lead isotopes can also be used to differentiate between the smelter fingerprint and other potential sources (e.g., petrol combustion, other industrial processes, geogenic sources) (Ketterer et al., 2001; Bacon and Dinev, 2005; Fernandez et al., 2008; Tyzaska et al., 2012; Wen et al., 2015; Mihaljevič et al., 2011, 2015; Félix et al., 2015); however, changes in the smelting technology, the isotope compositions of the smelted ores, or the isotope composition of other pollution sources can complicate the situation. An interesting application of Pb isotopes was recently demonstrated by Klaminder et al. (2008), who found that O-



**Fig. 2.** Back-scattered electron (BSE) microphotograph of particles from the dense fraction of the highly polluted soil located 3.6 km downwind from the Mufulira copper smelter, Zambian Copperbelt (total Cu: 8980 mg/kg). Particles derived from smelter dusts are indicated by red squares, green circles indicate particles originating from mine tailings, other particles have a geogenic origin. Abbreviations: Cc – chalcocite (Cu<sub>2</sub>S); Cpy – chalcopyrite (CuFeS<sub>2</sub>); Cu–Fe oxide with 32 wt% CuO closely corresponding to delafossite (CuFeO<sub>2</sub>); Ep – epidote (Ca<sub>2</sub>Al<sub>2</sub>(Fe,Al)(SiO<sub>4</sub>)(Si<sub>2</sub>O<sub>7</sub>)O(OH)); Rt – rutile (TiO<sub>2</sub>); Tnr – tenorite (CuO); Tur – tourmaline (mainly schorl: NaFe<sub>3</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>4</sub>); Zrn – zircon (ZrSiO<sub>4</sub>) (modified from Konečný et al., 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

horizons of boreal forest soils collected near a copper smelter (Rönnskär, Sweden), and subsampled to 0.5-cm thick segments, can be successfully used as a semi-archive for the temporal reconstruction of smelter emissions. If the past atmospheric input recorded in the O-horizons were compensated to leaching losses, the Pb isotope and concentration patterns closely correlated with a similar record in peatbog profiles (Klaminder et al., 2008). A few studies also used Pb isotopes to calculate the downward penetration rate of smelter-derived Pb in the soil profiles. The length of time of the smelter's operation must be known. The fact that soils near smelters are often developed on a mineralized background, and the isotope signature of the processed ore is thus similar to that of the bedrock must also be taken into account for these calculations (Ettler et al., 2004; Prapaipong et al., 2008; Ettler et al., 2011). Ettler et al. (2004) took advantage of the historical change in smelting technology, where the primary Pb smelting (ore processing) was substituted by the secondary Pb smelting (car battery processing), and calculated, on the basis of changes in Pb isotope compositions of soils and smelter wastes, that the downward penetration rate of Pb, which corresponded to emissions from car battery processing, ranged from 0.3 to 0.36 cm/year. Chrastný et al. (2014) recently verified this hypothesis by incubation and laboratory experiments, and found that such high mobility of Pb can primarily occur in the forest litter. Even higher penetration rates attaining ~1 cm/year were calculated by Prapaipong et al. (2008) for soils near a Pb smelter in Missouri (USA). The Pb isotope compositions of different fractions obtained by selective leaching can show which part of smelter-derived Pb can be mobile. For instance, Ettler et al. (2011) found that in highly polluted Oxisol near a Cu smelter in the Zambian Copperbelt, the "labile" fraction, corresponding to ~1.5% of total Pb, and exhibited a downward migration at the rate of 1.36 cm/year.

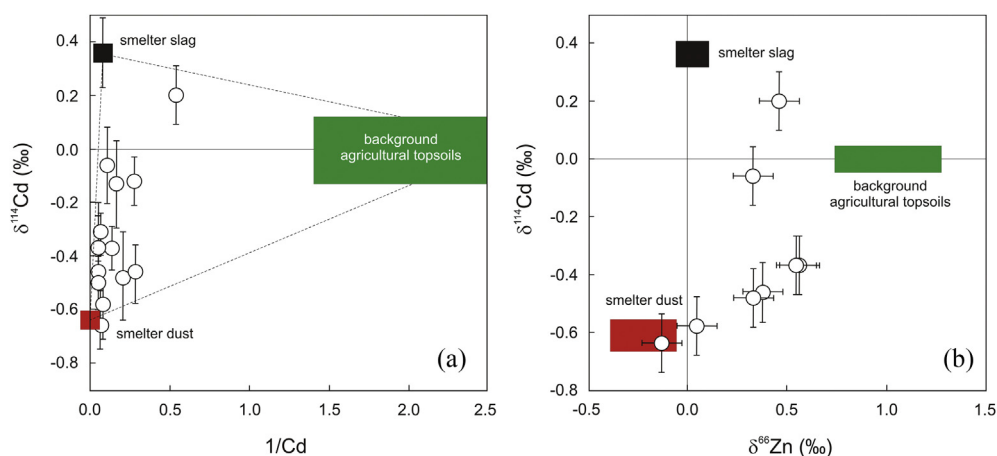
In contrast to Pb, isotope fractionation during the smelting process, leading to isotopically lighter emissions and isotopically heavier slag residues, has been suggested for other metals despite the fact that contradictory results have been reported in the literature. Whereas for Cd, Cloquet et al. (2006), and Shiel et al. (2010) found that smelter emissions were isotopically lighter compared to slag, more recently Chrastný et al. (2015) did not observe any Cd fractionation during the smelting process itself, but suggested that the interaction of Cd with solid soil components after its deposition in soil could be responsible for the variations found in different horizons of forest soils. Similar variable results were observed for Zn isotopes. The first detailed investigations by Mattioli et al. (2009) indicated that significant fractionation occurred in the smelting and refining processes in Pb/Zn smelters in the North of France, progressing from the  $\delta^{66}\text{Zn}$  value of sphalerite ore (from +0.88‰ to +0.16‰), to negative values in emissions from the blast furnace (−0.37‰ to −0.66‰) and distillation (−0.35‰). Slag-like particulates collected in proximity to the smelter exhibited positive  $\delta^{66}\text{Zn}$  values (+0.02‰ to +0.19‰), and the authors hypothesized that these were derived from the re-suspension of the slag heaps. In contrast, distant aerosols (PM<sub>10</sub>) that had negative values (−0.52‰ to −0.02‰) corresponded well to the isotopic signature of the smelter emissions (Mattioli et al., 2009). Similarly, at a Cu smelting site in Slovakia, Bigalke et al. (2010) found that Zn was isotopically lighter in smelter ash (−0.41‰) and in the organic soil horizons near the smelting facility (−0.85‰ to −0.47‰), whereas slag exhibited an isotopically heavier value (+0.18‰). In contrast to these studies, Shiel et al. (2010) reported that Zn isotope fractionation in the Trail Pb–Zn smelting complex (Canada) did not occur to such a large extent; surprisingly, the effluent of the hydrometallurgical process and the fumes were even heavier isotopically ( $\delta^{66}\text{Zn}$  from +0.41‰ to +0.51‰) than the Zn ore concentrate (0.09‰–0.17‰). Relatively little information is known about Cu

isotope fractionation in the smelting process. Bigalke et al. (2010) found that  $\delta^{65}\text{Cu}$  values varied little in the wastes and soils near a Cu smelting site, and no source identification was possible. All these observations clearly indicate that isotope fractionation is probably site- and/or technology-specific, and other biogeochemical processes (sorption, biological cycling) may be responsible for the isotope fractionation directly in the soil. In addition, the origin of ore concentrates processed in a smelter may be rather variable over time, and can also be responsible for changes in isotope signatures of the emissions despite the fact that, for example, Zn isotope compositions of sphalerite ores of various origins were found to be remarkably homogeneous with a mean  $\delta^{66}\text{Zn}$  value of  $+0.16 \pm 0.20\text{‰}$  (Sonke et al., 2008). The applications of diagrams in which isotope signatures of the soils and smelter-derived materials (feed, wastes) are plotted against inverse metal concentration are extremely useful to discern mixing between background and potential pollution sources (Fig. 3a). Moreover, it seems that the multi-isotopic approach, with at least two isotopic systems applied to the feed and effluents from smelting processes and environmental samples (soils, aerosols), will be more extensively used in the future for tracing the contamination near smelters as has recently been successfully demonstrated by Cloquet et al. (2008), Bigalke et al. (2010), and Wen et al. (2015) (Fig. 3b).

#### 2.4. Laboratory and field experiments

Laboratory and field (*in situ*) experiments are suitable tools for understanding the processes of contaminant release from smelter particulates after their deposition into soils. For instance, Cornu et al. (2007) used a laboratory pot experiment to study how redox changes influence Cd dynamics, in a re-wetted to 90% water-holding capacity (WHC) agricultural soil, contaminated by smelter fallout. As Cd is generally presumed to be more mobile in polluted soils, compared to other metals, this experiment confirmed a relatively high release of Cd during the initial stages of soil incubation, followed by a progressive decrease related to the establishment of reducing conditions, leading to precipitation of Cd sulphide in the soil (Cornu et al., 2007). Despite the fact that extraction methods have frequently been used to simulate soil solutions and to estimate the "labile" or "easily-extractable" pool of metal(loid)s in contaminated soils, it is always convenient to compare these extraction results with real pore water samples collected in the field. Clemente et al. (2008) sampled pore waters in soils near a former Cu refinery 20 years after cessation of the pollution source's activity, and found contrasting concentrations and mobility for the studied contaminants. Whereas Cu and As concentrations in the soil pore water were much higher closer to the soil surface, elevated concentrations of Zn and Cd were found in the deeper soil layers, indicating their potential vertical mobility in the soil profiles. In contrast, the mobility and concentrations of Pb and Sb in soil pore waters were rather low, even in the uppermost soil horizons, where the highest concentrations of these elements were observed (Clemente et al., 2008). Denaix et al. (2001) found up to 11 mg/l Zn in pore water, collected by zero-tension lysimeters, under the surface soil horizon (11,995 mg/kg Zn) in a Pb/Zn smelter-polluted area. Whereas 95% of Zn and Cd were mainly present in the dissolved form and were highly mobile, 50% of Pb in soil pore water occurred as colloids (Denaix et al., 2001). Citeau et al. (2003) also demonstrated that the Pb colloidal fraction was important, primarily in agricultural and grassland soils; however, the proportion of the colloidal fraction for all three studied contaminants (Pb, Zn, Cd) in a forest soil (podzol) was <10%.

Whereas particulates emitted by the smelter stacks are often composed of highly soluble phases, the slag-like fragments deposited into the soil by wind dispersion are generally less soluble



**Fig. 3.** (a) Cadmium isotopic compositions ( $\delta^{114}\text{Cd}$ ) as a function of inverse Cd concentrations (mg/kg) in soils, and Pb/Zn smelter-derived waste materials from Noyelles-Godault (northern France) with estimated compositions for: reference topsoils at 0‰ (green rectangular), polluted topsoils (open circles), dust (red symbol) and slag from a Pb/Zn smelter (black symbol). (b) Cd and Zn isotope compositions ( $\delta^{114}\text{Cd}$  vs.  $\delta^{66}\text{Zn}$ ) in soils, smelter slag and dust, and theoretical mixing curves calculated according to compositions of three end members (isotopically light smelter dust, isotopically heavy smelter slag, and uncontaminated soils) (redrawn after Cloquet et al., 2006, 2008). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(e.g., Ettler et al., 2005a; Knight and Henderson, 2006; Uzu et al., 2011; Ettler et al., 2014b). Ettler et al. (2012b,c, 2015a) recently used laboratory pot experiments with re-wetted acidic soils, where porous polyamide experimental bags (1- $\mu\text{m}$  mesh) filled with Pb smelter fly ash were incubated for 21 days. This approach has been found very useful for the calculation of mass balances and fluxes of individual contaminants released from fly ash into the soil, as well as for possible investigation of mineralogical changes of the fly ash after incubation using XRD, SEM, or TEM. Whereas As, Cd, and Zn were rapidly released from the fly ash into the soils and soil pore water, Pb and Sb were relatively efficiently retained due to formation of less soluble secondary phases, observed by TEM, within the weathered fly ash material (anglesite,  $\text{PbSO}_4$ ; and bindheimite,  $\text{Pb}_2(\text{Sb},\text{Sn})_2\text{O}_6(\text{O},\text{OH})$ , respectively) (Ettler et al., 2012b,c). Chrástný et al. (2012b) incubated mixtures of a similar Pb smelter fly ash with litter/humus, and also found that Cd and Zn were mobilized to a higher extent than Pb. The leaching and downward migration of contaminants is even more pronounced in tropical soils, as has recently been demonstrated by laboratory incubation of Cu smelter fly ash in an Oxisol (Ettler et al., 2015a).

A limited number of long-term field investigations of smelter fly ash reactivity in soils exist in the literature. They are generally based on three experimental setups, represented by the following examples:

- (i) Copper slag particles attached to a polymethylmethacrylate (PMMA) polymer support were exposed in acidic forest soils over the period of 18 months, and their weathering has been studied by X-ray fluorescence analysis (XRF) and SEM/EDS (Birkefeld et al., 2006). Despite the fact that Cu slag particles were found to be relatively resistant to weathering compared to other materials investigated (PbO and Cu concentrate), comparison with the results of laboratory leaching tests indicated that the faster dissolution rates observed in the field are probably caused by more intensive biological activity (effects of exudates from plant roots and fungi) (Birkefeld et al., 2006).
- (ii) Ettler et al. (2012b) carried out *in situ* incubations of Pb smelter fly ash in acidic forests and grassland soils using an experimental bag technique (described above). Their results indicated that up to 66% of fly ash dissolved after 1 year of incubation in soils, and newly formed phases efficiently

controlled the release of Pb, which was significantly less leached than other contaminants. In addition, the release of Pb was dependent on soil pH; whereas Cd and Zn were leached to a greater extent irrespective of soil pH, and partitioned more easily into the “labile” soil fractions (Ettler et al., 2012b).

- (iii) Yet another type of long-term experiment was conducted by Nowack et al. (2010), who used an artificial contamination approach. They manually introduced a filter dust from a non-ferrous metal smelter into the topsoil, equipped the experimental site with field lysimeters to collect soil water, and planted the site with trees. They investigated changes in chemical fractionation of contaminants in soils as a function of time (up to 42 months). The authors found that the largest changes in speciation, expressed as the redistribution between the fractions of the sequential extraction, occurred within the first 6 months. Moreover, plant activity kept the metals in a more soluble form, whereas at those experimental plots with no vegetation, a much higher proportion of metals were present in more refractory phases (Nowack et al., 2010).

### 3. Distribution and mobility of contaminants in smelter soils

An overview of those studies dealing with soils polluted by non-ferrous metal smelters in temperate climatic zones; plus those in tropical, subtropical, and arid areas is given in Tables 1 and 2, respectively. These tables clearly show that several sites have been extensively studied by numerous authors, having unravelled various aspects of the distribution, binding, and (bio)availability of contaminants in soils (Noyelles-Godault/Auby and Mortagne du Nord in northern France, Příbram in the Czech Republic, sites in the African Copperbelt, and a few localities in Canada and Poland). Moreover, a significantly lower numbers of studies have been conducted in (sub)tropical and dry areas, despite the fact that these soils are generally more vulnerable to metal(loid) pollution, because they generally exhibit a low soil organic matter (SOM) content, as well as containing low-activity clays (kaolinite) and less reactive Fe-oxides (hematite), leading to greater mobility of the contaminants (Rieuwerts, 2007). Maximum contaminant concentrations in these soils often exceed regional screening levels (RSLs) of chemical contaminants for residential soils, and in some cases

**Table 1**  
Examples of studies devoted to smelter-affected temperate soils.

Country	Locality	Smelting operation	Contaminants (maximum concentrations in mg/kg)	Spatial distribution	Soil profiles	Mineralogy	Extractions	Isotopes	Bioavailability	Reference	
France	Noyelles-Godault/ Auby	Pb/Zn smelters	Pb (1900)		*(Topsoils)	*				Morin et al. (1999)	
			Pb (4890), Zn (2685), Cd (61.7)		*					Sterckeman et al. (2000)	
			Pb (4264), Cu (127), Cd (39.9)		*			*			Dumat et al. (2001)
			Pb (4480), Zn (11,995), Cd (169)		*		*	(Colloids)			Denaix et al. (2001)
			Pb (2670), Zn (1865)		*		*				Buatier et al. (2001)
			Zn (1378), Pb (1132), Cd (21) and 15 other elements	*							Sterckeman et al. (2002)
			Zn (4391)		*	*	*				Juillot et al. (2003)
			Pb (1132), Cd (21)		*(Topsoils)					*(Pb, Cd)	Cloquet et al. (2006)
			Cd (21), Zn (n.a.)		*(Topsoils)					*(Cd, Zn)	Cloquet et al. (2008)
			Pb (1815), Cd (11.8)		*(Topsoils)						*(Vegetables)
	Zn (6908), Pb (3711), Cd (31.4) and 15 other elements	*			*					Douay et al. (2008a)	
	Pb (821), Cd (14.5)				*(Topsoils)				*(Wheat)	Douay et al. (2008b)	
	Pb (41,959), Zn (38,763), Cd (2402)	*					*			Douay et al. (2009)	
	Zn (1215), Pb (1058), Cd (14.9)				*(Topsoils)			*	*(Herbs)	Bidar et al. (2009)	
	Zn (6908), Pb (3026), Cd (31.4)		*(Topsoils)				*		*(Bioaccessibility)	Roussel et al. (2010)	
	Zn (2550)					*				Vespa et al. (2010)	
	Zn (1250), Pb (824), Cd (13)		*(Topsoils)				*		*(Bioaccessibility)	Pelfrène et al. (2011)	
	Zn (10,606), Pb (364), Cd (70)				*(Litter)				*(Soil macrofauna)	Godet et al. (2011)	
	Zn (7726), Pb (3551), Cd (72)				*(Topsoils)		*		*(bean)	Qasim et al. (2015)	
	Zn (7263), Pb (6002), Cd (62.7)		*(Topsoils)						*(Bioaccessibility)	Pelfrène et al. (2015)	
Zn (19,000)		*						*(Soil macrofauna)	Nahmani and Lavelle (2002)		
Mortagne-du-Nord	Pb/Zn smelters	Zn (17,956), Pb (4720), Cd (109)			*		*(Colloids)			Citeau et al. (2003)	
		Zn (2635), Pb (517), Cu (113), Cd (3.39)			*	*			Leguédois et al. (2004)		
		Zn (2635), Pb (517), Cu (113), Cd (3.39)			*	*				van Oort et al. (2006)	
		Zn (110), Pb (59.7)			*	*				Fernandez et al. (2007)	
		Pb (69.9)			*			*	*(Pb)	Fernandez et al. (2008)	
		Zn (109), Pb (61.5)			*			*		Fernandez et al. (2010)	
		Pb (1932), As (28), Sb (67) and other 5 elements			*	*	*			Cecchi et al. (2008)	
		Pb (37,300), Zn (27,600), Cu (715), Cd (48), As (1640), Sb (980)		*(Transect)							Rieuwerts and Farago (1996a)
		Hg (2.32)		*(Transect)							Rieuwerts and Farago (1996)
		Pb (58,500), Zn (21,900), Cu (2440), Cd (96)		*(Topsoils)							Rieuwerts et al. (1999)
Pb (4660), Zn (5740), Cu (146), Cd (43.5), As (204), Sb (167)		*(Garden topsoils)			*	*		*(Bioaccessibility)	Rieuwerts et al. (2000)		
Pb (81,041), Zn (1868), Cu (1097), Cd (46.63) and 32 other elements		*(Humus)							Suchara and Sucharová (2004)		
Pb (35,300)				*			*	*(Pb)	Ettler et al. (2004)		
Pb (35,300)				*	*	*			Ettler et al. (2005b)		
Pb (17,000)				*		*		*(Pb)	Komárek et al. (2006)		
Pb (36,234), Zn (519), Cu (488), Cd (11.9), As (120), Ag (25.1), Se (5.88)				*		*	*	*(Pb)	Komárek et al. (2007a)		
Hg (6.49)				*					Ettler et al. (2007a)		
Sb (705), As (336)				*		*			Ettler et al. (2007b)		
Pb (7331), Cd (98)				*		*		*(Maize)	Komárek et al. (2009)		
Sb (2058), As (447)				*		*			Ettler et al. (2010)		
Pb (57,100)				*			*	*(Pb)	Chrastný et al. (2014)		
Canada		Cu/Ni smelters	Ni (2149), Cu (1891)	*(Topsoil)		*	*			Adamo et al. (1996)	

	Sudbury (Ontario)		Ni (2150), Cu (1890), Zn (146) and other 5 elements	* (Topsoil)	*	*		Adamo et al. (2002)
			Cu (321), Ni (234), Zn (67.5), Pb (56.0), As (20.0)	* (Transect)			* (Microbes)	Anand et al. (2003)
			Cu (391), Pb (81.7), Ni (38.5) and other 7 elements	*			* (Spruce)	Nkongolo et al. (2008)
			n.a.		*			Lanteigne et al. (2012)
			n.a.		*			Lanteigne et al. (2014)
			Ni (1600), Cu (1330), Pb (176) and other 8 elements	*				Narendrula et al. (2012)
			Ni (1600), Cu (1330), Pb (176) and other 8 elements	*			* (Spruce)	Narendrula et al. (2013)
	Rouyn-Noranda (Québec)	Cu smelter	n.a.	* (Transect, humus)	*			Knight and Henderson (2006)
			Pb (869)		* (Transect)		* (Pb)	Hou et al. (2006)
	Flin Flon (Manitoba)	Cu/Zn smelter	Zn (7428), Cu (2670), Pb (1692), As (558), Cd (39), Hg (10) and other 2 el.	* (Transects)	*	*		Henderson et al. (1998)
Poland	Olkusz	Zn/Pb smelter	Pb (147,700), Zn (83,400), Cd (428), Tl (139)	* (Topsoil)	*			Cabala and Teper (2007)
			Zn (9630), Pb (1595), Cd (82.9), Cu (48.1)		* (Transect)			Tozsa et al. (2010)
			Zn (>3000), Pb (>1000), Cd (>20)		*	*		Chrastný et al. (2012a)
			Tl (30.1)		*	*		Vaněk et al. (2013)
			Cd (153)		*		* (Cd)	Chrastný et al. (2015)
	Legnica and Glogow	Cu smelters	Cu (1710), Pb (460)		*	*		Karczewska et al. (1996)
			Cu (426), Pb (130), Zn (92.3)		*	*		Kabala and Singh (2001)
			Cu (4500), Pb (2146), Zn (1222), As (90)		*	*	* (Pb)	Tyszkla et al. (2012)
	Bukowno Rudawy Janowickie	Pb/Zn smelter	Zn (12,400), Pb (3570), Cd (73.2)		*	*		Verner et al. (1996)
		Cu smelter (medieval)	Cu (4011), Zn (1503), As (333), Pb (200)		*	*	* (Pb)	Kierczak et al. (2013)
USA	Palmerton (Pennsylvania)	Zn smelter	Zn (32,500), Pb (3600), Cd (780), Cu (700) <sup>a</sup>		*		* (Pb)	Ketterer et al. (2001)
			Zn (6200)		*	*		Roberts et al. (2002)
	Glover (Missouri)	Pb smelter	Pb (1439)		*		* (Pb)	Prapaipong et al. (2008)
	Anaconda (Montana)	Cu smelter	Cu (1270), Zn (849), Pb (474.5)		*	*		Burt et al. (2003)
		Pb smelters (secondary)	Pb (2550)		* (Topsoils)			Eckel et al. (2002)
UK	Avonmouth	Pb/Zn smelter	Zn (3630), Pb (1740), Cu (161), Cd (54.5)		* (Topsoils)		* (Earthworms)	Nahmani et al. (2007)
	Prescot	Cu smelter	Cu (677), Pb (809), As (143), Zn (176)		*	*		Clemente et al. (2008)
South Korea	Janghang	Cu/Pb/Zn smelter	As (907), Pb (590), Cu (441), Zn (61)		* (Topsoils)	*	* (Earthworms)	Bade et al. (2012a)
			As (145)		*	*	* (Bacteria)	Shagol et al. (2014)
			Pb (219), Cu (122), As (18), Zn (67)		* (Topsoils)		* (Fungi)	Krishnamoorthy et al. (2015)
Finland	Harjavalta	Cu/Ni smelter	Cu (2304), Ni (161)		*			Derome and Lidroos (1998)
			Cu (2900), Ni (460)		* (Topsoils)		* (Worms)	Salminen and Haimi (1999)
Japan	Shiga	Sb smelter	Sb (2100)		*	*		Takaoka et al. (2005)
Sweden	Rönnskär	Cu smelter	Pb (9700), Hg (1.5)		* (Transect)		* (Pb)	Klaminder et al. (2008)
Belgium	Lommel	Zn smelter	Zn (20,476), Pb (2996), Cu (2132), Hg (737) As (312) and other 3 elements		* (Topsoils)	*		Nachtegaal et al. (2005)
Slovakia	Krompachy	Cu smelter	Cu (8087), Zn (2084)		* (Transect)		* (Cu, Zn)	Bigalke et al. (2010)
Bulgaria	Kuklen	Pb/Zn smelter	Zn (5231), Pb (4196), Cu (432), Ni (303), Cr (193), Cd (87)		* (Topsoils)		* (Pb)	Bacon and Dinev (2005)
Kosovo	Kosovska Mitrovica	Pb/Zn smelter			* (Topsoils)			Šajn et al. (2013)

(continued on next page)



Table 1 (continued)

Country	Locality	Smelting operation	Contaminants (maximum concentrations in mg/kg)	Spatial distribution	Soil profiles	Mineralogy	Extractions	Isotopes	Bioavailability	Reference
Macedonia	Veles	Pb/Zn smelter	Pb (35,000), Zn (12,000), As (3900), Cu (1600), Sb (1400) and other 31 elements Zn (27,000), Pb (15,000), Cu (1700), Cd (600) and other 38 elements							Staflov et al. (2010)

n.a. – not available.

USEPA (2015) selected screening levels for residential/industrial soils, respectively (in mg/kg): As (0.67/3.0), Cd (7.0/98), Cu (310/4700), Hg (0.94/4), Ni-soluble salts (150/2200), Ni – refinery dust (82/1100), Pb (400/800), Sb (3.1/47), Zn (2300/35,000).

CCME (2007) quality guidelines for agricultural/residential/industrial soils, respectively (in mg/kg): As (12/12/12), Cd (1.4/10/22), Co (40/50/300), Cu (63/63/91), Hg (6.6/6.6/50), Ni (50/50/50), Pb (70/140/600), Sb (20/20/40), Zn (200/200/360).

<sup>a</sup> Estimated from figures.

also industrial soils, as proposed by the USEPA (2015): As (0.67 and 3.0 mg/kg), Cd (7.0 and 98 mg/kg), Co (2.3 and 35 mg/kg), Cu (310 and 4700 mg/kg), Hg (elemental – 0.94 and 4 mg/kg), Pb (400 and 800 mg/kg), and Zn (2300 and 35,000 mg/kg), respectively. Canadian soil quality guidelines for the protection of environmental and human health (CCME, 2007) have often been used for polluted tropical soils. For example, Křibek et al. (2010) in their screening study, based on 719 topsoil samples across the Zambian Copperbelt, found that 91.23% of soils exceeded the Cu concentration guideline for agricultural/residential soils (63 mg/kg), and that 85.26% of soils exceeded the guideline for commercial/industrial soils (91 mg/kg).

The highest levels of metal(loid)s were generally found in the surface soil horizons, but comparisons of the soil horizons with the bottom layers of the soil pits, bedrock, or local-to-regional background have often indicated that the smelter-derived contamination can, to some extent, move downwards in the soil profiles (Derome and Lindroos, 1998; Sterckeman et al., 2000; Kabala and Singh, 2001; Burt et al., 2003; Ettler et al., 2004; Martley et al., 2004b; Ettler et al., 2005b, 2007a; Neaman et al., 2009; Křibek et al., 2010; Li et al., 2011; Chrastný et al., 2012a; Vaněk et al., 2013; Podolský et al., 2015). However, contrasting vertical distribution patterns, with higher concentrations of metal(loid)s in the deeper horizons, have also occasionally been observed; particularly at old (medieval) smelting sites, where slag waste dumps were revegetated, leading to the formation of a thin soil layer, as recently reported from a site near a former Cu smelting factory in Poland (Kierczak et al., 2013).

Surprisingly consistent data on metal speciation and mobility in Pb/Zn smelter-affected soil profiles were reported from various localities, indicating that Cd and Zn generally seem to be more mobile than Pb; and that the proportion of contaminants in the “labile” fractions of SEP, and subsequent vertical mobility, is generally higher for forest soils than for agricultural soils (e.g., Ettler et al., 2005b; van Oort et al., 2006; Douay et al., 2009; Chrastný et al., 2012a). The downward movement of contaminants can occur via leaching (Dumat et al., 2001; Fernandez et al., 2007), the movement of metal-bearing colloids (Denaix et al., 2001; Citeau et al., 2003), mechanical perturbation by ploughing (Rieuwerts and Farago, 1996a; Ettler et al., 2005b), or biological activity (e.g., earthworms; Sterckeman et al., 2000; Fernandez et al., 2010). Sequential extraction results as well as EXAFS investigations have indicated that the role of organic matter was crucial in the binding of Pb in forest soils; whereas in tilled soils, Pb was predominantly bound to Fe-oxides (Morin et al., 1999; Dumat et al., 2001; Ettler et al., 2005b; van Oort et al., 2006). Despite the fact that Pb is generally less mobile than other contaminants, the calculations based on isotope fingerprinting have indicated that the downward penetration rate of Pb can be remarkably fast, and varies in the range of 0.3–1 cm/year (Ettler et al., 2004, 2011; Prapaipong et al., 2008). It has been suggested that this phenomenon may be directly related to the mineralogical composition of the atmospheric fallout. Whereas particulates from primary Pb smelters are composed of relatively insoluble phases (PbSO<sub>4</sub>, PbSO<sub>4</sub>·PbO, PbS) (Sobanska et al., 1999), much higher solubility was observed for secondary Pb smelter particulates, composed of Pb-bearing chlorides (e.g., PbCl<sub>2</sub>, KPb<sub>2</sub>Cl<sub>5</sub> or Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl), whose higher solubility is probably the main reason for the higher downward leaching of Pb in the soil profiles (Ettler et al., 2005a,b; 2012a).

Spherical particles of variable compositions, up to tens of μm in size, were commonly found in the dense fraction separated from topsoils at numerous smelting sites (Adamo et al., 1996; Henderson et al., 1998; Knight and Henderson, 2006; Cabala and Teper, 2007; Ettler et al., 2014a; Konečný et al., 2014). Apart from relatively stable slag-like particles (composed of glass, magnetite, silicates) (Knight and Henderson, 2006; Chopin and Alloway, 2007), more

**Table 2**  
Examples of studies devoted to smelter-affected soils from (sub)tropical or arid areas.

Country	Locality	Smelting operation	Contaminants (maximum concentrations in mg/kg)	Spatial distribution	Soil profiles	Mineralogy	Extractions	Isotopes	Bioavailability	Reference
Zambia	Central-northern Copperbelt	Cu smelters	Cu (41,900), Co (606), Pb (503), Zn (450), As (255) and other 5 elements	*(Topsoils)	*					Křibek et al. (2010)
			Cu (3067), Zn (280), Co (84.2), Pb (50.0), As (3.81)		*(Topsoils)				*(Cassava)	Křibek et al. (2014)
	Kitwe (Copperbelt)	Cu smelter	Cu (37,770), Co (676), Zn (549), Pb (419), As (85.2)	*(Topsoils)	*	*	*			Ettler et al. (2011)
			Cu (27,410), Co (606), Pb (480), Zn (450), As (255)	*(Topsoils)					*(Bioaccessibility)	Ettler et al. (2012a)
			Cu (37,770), Co (676), Zn (549), Pb (419), As (85.2)		*			*(Pb)	*(Tree biomass)	Mihaljević et al. (2011)
	Mufulira (Copperbelt)	Cu smelter	Cu (8980), Zn (83), Pb (42), Co (46)		*	*	*		*(Worms)	Konečný et al. (2014)
	Kitwe and Mufulira (Copperbelt)	Cu smelter	Cu (8980), Zn (97), Pb (42), Co (46)	*(Topsoils)	*	*	*			Ettler et al. (2014a)
	Kabwe (Zambia)	Pb smelter	Hg (0.39) and other 7 elements							Podolský et al. (2015)
DR Congo	Lubumbashi (Katanga, Copperbelt)	Cu smelters	Pb (759), Zn (106), Cu (58.2), Cd (22.3)	*(Topsoil, transects)						Tembo et al. (2006)
			Cu (14,200), Co (6150), Zn (1250), Pb (809) and other 7 elements	*						Narendrula et al. (2012)
			Cu (14,200), Co (6150), Zn (1250), Pb (809) and other 7 elements	*			*			Narendrula et al. (2013)
			Cu (8957), Co (145), Zn (622)	*(Topsoil)						Pourret et al. (2015)
		Cu (11,110), Co (152) <sup>a</sup>	*(Topsoils)						*(Metallophytes)	Lange et al. (2014)
		Cu (150) (mean value)	*(Topsoils)						*(Bioaccessibility)	Cheyne et al. (2014)
China	Zhuzhou (Hunan)	Pb/Zn smelter	Zn (3349), Pb (1197), Cu (157), As (93), Cd (41.1), Hg (2.89)	*(Topsoils)	*					Li et al. (2011)
			Ag (3.71), Bi (21.4), Co (30), Cr (199) and other 6 elements	*(Topsoils)	*					Li et al. (2014)
	Hangzhou (Zhejiang)	Cu smelter	Zn (11,840), Cu (716), Cd (8.67)		*		*			Liu et al. (2010)
	Huludao (Lianing)	Zn smelter	Hg (3.80)		*(Topsoils)				*(Crops)	Zheng et al. (2007)
	Xikuangshan (Hunan)	Sb smelter	Sb (5045), As (205)		*(Topsoils)		*		*(Radish)	He (2007)
	Fuyang (Zhejiang)	Cu smelter (secondary)	Hg (15)	*(Topsoils)	*					Yin et al. (2009)
	Magu (Guizhou)	Zn smelter	Pb (37,770), Zn (31,625), Cd (131)		*(Topsoils)	*	*		*(Pb,S)	Yang et al. (2010)
Nanning (Guangxi)	Pb/Sb smelter	Pb (992), Zn (597), Cu (39), Cd (22) [geometric means]	*(Topsoils)					*(Vegetables)	Cui et al. (2004)	
Mexico	Zhujiawu (Zhejiang)	Cu/zn smelter	Zn (3219), Cu (658)	*(Topsoils, transect)					*(Microbes)	Wang et al. (2007)
		Pb smelter	Pb (111,000), Zn (51,500), As (20,400), Cu (594), Cd (573)	*(Topsoils)		*	*			Gutiérrez-Ruiz et al. (2005)
			Pb (31,410), Zn (12,280), As (10,330), Cu (400), Cd (20)	*(Topsoils)			*			Villalobos et al. (2010)
			Pb (31,420), Zn (12,280), As (6043), Cu (726), Sb (270), Cd (88)	*(Topsoils)		*	*			Gutiérrez-Ruiz et al. (2012)
	San Luis Potosí	Cu smelter	Pb (24,615), Cu (15,099), As (9340), Zn (5267), Cd (594)	*(Topsoils)		*	*			Gutiérrez-Ruiz et al. (2005)
		Pb (12,600), As (4424)	*(Topsoils)					*(Bioaccessibility)	Carrizales et al. (2006)	
		Pb (2532)		*(Topsoils)				*(Bioaccessibility)	Romero et al. (2008)	
		Pb (24,620), Cu (10,620), As (10,330), Zn (5080), Cd (680)	*(Topsoils)			*			Villalobos et al. (2010)	
Chile	Puchuncaví	Cu smelter	Cu (3718), Zn (174), Zn (105), Cd (1)	*(Topsoils)	*		*			Ginocchio et al. (2004)
			Cu (636)	*(Topsoils)			*			Neaman et al. (2009)
			Cu (4449), Zn (839), Pb (302) and other 18 elements	*(Topsoils)		*				Parra et al. (2014)
Australia	Port Kembla (New South Wales)	Cu smelter	Cu (1597), Pb (295), Zn (180), As (26)	*					Martley et al. (2004a)	
			Cu (1348), Zn (325), Pb (251), Cd (3.8)		*	*	*			Martley et al. (2004b)

(continued on next page)

Table 2 (continued)

Country	Locality	Smelting operation	Contaminants (maximum concentrations in mg/kg)	Spatial distribution	Soil profiles	Mineralogy	Extractions	Isotopes	Bioavailability	Reference
Namibia	Tsumeb	Cu/Pb smelters	Hg (4.39) and other 7 elements Zn (9740), Pb (8170), Cu (4970), As (2370), Cd (511)	*(Topsoils)	*	*		*(Pb)	*(Tree biomass)	Podolský et al. (2015) Mihaljević et al. (2015)
Spain	Tharsis, Riotinto and Huelva	Cu smelters	Pb (8306), As (3074), Cu (850), Zn (257)	*	*	*	*			Chopin and Alloway (2007)
Brazil	Santo Amaro (Bahia)	Pb smelter	Zn (95,940), Pb (37,460), Cu (3196), Cd (771)	*(Topsoils)					*(Earthworms)	Niemeyer et al. (2010)
USA	Hayden (Arizona)	Cu smelter	Pb (340), As (105), Cd (10) <sup>b</sup>	*	*			*(Pb)		Félix et al. (2015)

USEPA (2015) selected screening levels for residential/industrial soils, respectively (in mg/kg): As (0.67/3.0), Cd (7.0/98), Co (2.3/35), Cu (310/4700), Hg (0.94/4), Ni-soluble salts (150/2200), Ni – refinery dust (82/1100), Pb (400/800), Sb (3.1/47), Zn (2300/35,000).

CCME (2007) quality guidelines for agricultural/residential/industrial soils, respectively (in mg/kg): As (12/12/12), Cd (1.4/10/22), Co (40/50/300), Cu (63/63/91), Hg (6.6/6.6/50), Ni (50/50/50), Pb (70/140/600), Sb (20/20/40), Zn (200/200/360).

<sup>a</sup> Data provided by Olivier Pourret.

<sup>b</sup> Estimated from figures.

reactive metal-bearing sulphides, oxides, sulphates, and carbonates were also found. However, the contamination is often mixed, as smelters are commonly located near mining operations and the soil dense fraction not only contains spherical particles formed by condensation at high temperatures during the smelting process, but also wind-dispersed particles from mine tailing sites (Fig. 2). Upon weathering, these particles can release common metallic contaminants (Pb, Cu, Zn, Cd, Ni), and also other associated trace elements (Ti, Co, As, Se), as revealed by laser ablation ICP-MS investigations (Lanteigne et al., 2014) or SEM/EDS analysis (Cabala and Teper, 2007). Lanteigne et al. (2012) recently suggested a weathering sequence for rounded Cu/Ni smelter-derived particulates, exposed for decades in temperate topsoils near Sudbury: (i) sulphide inclusions are exposed to soil pore water through fractures within the surrounding slag-like matrix (glass, Fe-silicates, magnetite); (ii) oxidation and release of metals occurs, followed by their co-precipitation in newly formed Fe-oxides; and (iii) the silicate matrix of rounded inclusions is slowly dissolving for a longer period of time, while magnetite crystals remain unaltered, forming a collapsed skeleton of the original particle. Lanteigne et al. (2012) also found that Cu-bearing spinel (CuFe<sub>2</sub>O<sub>4</sub>) from deposited smelter emissions tended to dissolve more easily than a Ni-bearing one (trevorite, NiFe<sub>2</sub>O<sub>4</sub>), leading to preferential release of Cu and its partitioning into the “labile” fractions in the soil. The most dynamic mineralogical transformations of smelter particulates, which mainly include dissolution and precipitation of the newly formed phase, occur in the organic horizons due to the presence of organic ligands, and also due to generally more acidic conditions (e.g., Ettler et al., 2012a and references therein). Interestingly, Cabala and Teper (2007) found in rhizospheric soils polluted by smelter particulates that plant-root exudation not only enhances the dissolution of primary phases, but also the crystallization of secondary metal-ferrous solids (mainly carbonates, sulphosalts, and oxides), which precipitated directly on the plant root epidermis and fungal hyphae. The precipitation of secondary phases formed during the pedogenic processes in the form of Fe-, Mn-, or clay-rich coatings, or spherulites that are often difficult to characterize due to their size or chemical/mineralogical complexity, and which play a key role in the storage of contaminants in smelter-affected agricultural soils from temperate areas (Leguédouis et al., 2004; van Oort et al., 2006). Moreover, the natural precipitation of secondary phases directly in soil can immobilize contaminants, as recently demonstrated by Gutiérrez-Ruiz et al. (2012) in highly polluted soils near a Mexican Pb smelter, where insoluble Pb arsenates formed.

Sampling of soil profiles, from both wooded and non-wooded plots, at the same distance from the smelter indicated that much higher contaminant concentrations were observed in forest soils, especially in organic horizons (Rieuwerts and Farago, 1996a; Ettler et al., 2005b; Douay et al., 2009; Chrastný et al., 2012a; Vaněk et al., 2013). This has been explained by the higher interception of smelter emissions by tree canopies, leading to high levels of contaminants in the litter and in the humus layer (Rieuwerts and Farago, 1996a; Ettler et al., 2005b). It has also been suggested that lower concentrations of contaminants in tilled soils can reflect the effects of ploughing, and subsequent dilution in the topsoil layers (Rieuwerts and Farago, 1996a) or annual crop off-take (Ettler et al., 2005b). Ginocchio et al. (2004) at Cu smelter-affected sites in central Chile found that soils that developed below shrubs exhibited higher concentrations of metals than those that developed in open spaces; however, their bioavailability was much lower due to binding to SOM. Nonetheless, surprisingly contrasting metal distributions have recently been reported by Ettler et al. (2014a) in tropical soil profiles from forested and grassland areas near a Cu smelter in the Zambian Copperbelt. A higher proportion of metal-bearing particles and higher metal concentrations were found in

soils from unforested sites. It has been hypothesized that this phenomenon could be related to the more frequent and intense bushfires in the forested areas, leading to mobilization of pollutants contained in biomass-rich topsoils back into the atmosphere (Ettler et al., 2014a). This observation has also been supported by Pb isotope compositions in forest topsoils, which were free of anthropogenic Pb, in contrast to the youngest segments of tree rings from the same area (Mihaljević et al., 2011). Further research is needed to elucidate this hypothesis.

#### 4. Contaminant bioavailability in smelter soils

##### 4.1. Effects on plants and fungi

The accumulation of contaminants in plants grown on smelter-affected soils is either focused on cultivated crops, native species (including trees), or species used for the phytostabilization of smelter sites. Lange et al. (2014) found that Cu and Co accumulation in *Crepidodipalon tenuis*, which is a metallophyte species growing on Cu- and Co-rich soils, was much lower in Cu smelter-affected areas than naturally enriched soils in Katanga (DR Congo), indicating the relatively lower Cu and Co bioavailability. Nkongolo et al. (2008) studied black spruce (*Picea mariana*) and trees grown on soils near the Sudbury Cu/Ni smelters, and observed low metal contents in the tree biomass, far below the toxic levels for vegetation. In a later study, Narendrula et al. (2013) found that needles of white spruce (*Picea glauca*) trees from the Sudbury region did not exhibit any relationship between genetic variations and soil pollution by metal(loid)s. Tree ring studies at smelter-affected sites indicated that the transfer of contaminants into the wood is mainly determined by the above-ground uptake (dissolution of metal-bearing particles attached to needles, foliage, or bark) and that their transport from soils via the root system remains limited (Mihaljević et al., 2011, 2015).

Maize (*Zea mays*) grown in soil artificially contaminated by Pb smelter fly ash exhibited a decrease in biomass yield as a function of the amount of the spike, and showed an increase in the concentration of Cd and Pb in the biomass. If EDTA was added to promote the translocation of contaminants from a highly contaminated spiked soil (7331 mg/kg Pb, 98 mg/kg Cd), the plant showed symptoms of chlorosis and necrosis, and only produced a negligible amount of biomass (Komárek et al., 2009). The translocation of contaminants into the plant (lettuce, *Lactuca sativa*) has been found to be dependent on the size of industrial particles. Uzu et al. (2009) reported 20% greater Pb uptake by plants when soils were spiked with <2.5 µm smelter particulates compared to those spiked with coarser particulates. Nevertheless, grassland species are generally more tolerant to high levels of metals in soils. Bidar et al. (2009) studied seasonal and annual variations of metal uptake and toxicity in two grassland species (clover, *Trifolium repens*; and perennial rye-grass, *Lolium perenne*). Both plants accumulated metals, primarily in their roots, and their translocation to aerial parts of the plants remained limited over time. Both plant species seemed to tolerate high levels of contaminants in soils, and were found suitable for phytostabilization of the polluted site (Bidar et al., 2009).

Douay et al. (2008) investigated how a smelter closedown affected metal content in wheat (*Triticum aestivum*) cultivated in the area, and found that during the smelter activity up to 0.8 mg/kg Cd and 8 mg/kg Pb were in the grain, and for straw the maximum concentrations of Cd and Pb were 5 mg/kg and 114 mg/kg, respectively. After the smelter's closedown, a large decrease of Pb in the grain (82%) and in the straw (91%) occurred, whereas a smaller decrease was observed for Cd (none for the grain, 39% for the straw). Despite this improvement, 80% of samples remained

unacceptable for human consumption (Douay et al., 2008). Křibek et al. (2014) recently compared cassava (*Manihot esculenta*) grown on uncontaminated and contaminated soils in mining and smelting areas of the Zambian Copperbelt, and found that despite higher translocation of contaminants to tubers and leaves from soils in contaminated areas, contaminants in leaves can be attributed to dust from smelting operations (Cu sulphides/sulphates and slag particles) as well as re-suspended dust from contaminated soils and mine tailings, which settle on the surface of leaves. Thus, it is important to stress that contaminated soil dust re-suspension can be responsible for high levels of contaminants in the above-ground parts of the vegetation even after the cessation of industrial activities. Cui et al. (2004) studied soil-to-vegetable transfer of contaminants near a Pb smelter in China, and found highly contrasting bioaccumulations in vegetables, even in those of the same genus. For instance, whereas *Brassica juncea* exhibited high Pb levels, *Brassica campestris* had low Pb accumulation; the authors concluded that by selecting particular vegetables, it would be possible to reduce the risk of human exposure.

Compared to plants, fungi are more effective in the leaching, translocation, and bioconcentration of metal(loid)s in polluted areas due to extensive mycelium growth in the soils. The investigation of arbuscular mycorrhizal fungi (AMF) structure, abundance, and species richness in smelter-impacted soils indicated that some of the species (e.g. *Funneliformis* spp.) were very sensitive to high concentrations of metals and metalloids; whereas richness and diversity of *Glomeraceae* family increased with increasing As, Cd, and Zn concentrations in soils. The authors concluded that such tolerance could be used in plant growth promotion and subsequent phytoremediation process in smelter-affected environments (Krishnamoorthy et al., 2015). Cornejo et al. (2008) found a strong relationship between the amount of glomalin-related soil protein (produced by AMF in soils) and the Cu and Zn contents in copper smelter-affected soils, suggesting that AFM can mitigate metal-related stress in highly polluted soils. Surprisingly, relatively few studies had combined the investigation of contaminant concentrations in edible parts of mushrooms and corresponding soils near non-ferrous metal smelters. For example, Komárek et al. (2007a) studying three different edible species grown in forest soil near a Pb smelter found high levels of Pb (up to 165 mg/kg) and Cd (up to 55 mg/kg) in mushrooms; using Pb isotopic tracing they demonstrated that the “labile” fraction of Pb in the soils was related to contamination from secondary Pb smelting process, and is taken up by the fruiting bodies of mushrooms.

##### 4.2. Effects on soil organisms

At metallurgical sites, it has been found that high concentrations of metals in soils can affect microbial activity (expressed as various parameters such as enzyme activity, biomass carbon, or phospholipid fatty acid profile) as well as viable population size and structure (Kelly and Tate, 1998; Kelly et al., 2003; Wang et al., 2007). For example, a good correlation was observed between the soil enzyme activity and distance from the smelter (Wang et al., 2007). Metal- or metalloid-tolerant bacteria can be helpful in the mitigation of contaminants in smelter soils. Very recently As-tolerant bacteria were isolated from smelter soils in South Korea and it was evident that these microbes positively affect plant growth during phytoremediation (Shagol et al., 2014).

High levels of contaminants in smelter soils can reduce the overall density of earthworms and other macrofaunal population, but no simple relationship between the total metal concentration and species richness can be resolved, and it is highly site-specific (Kelly and Tate, 1998; Nahmani and Lavelle, 2002). Thus, some studies also found that earthworms (*Eisenia fetida*) or enchytraeid

worms (*Cognettia sphagnetorum*) did not exhibit any response to smelter-contaminated soils (Nahmani et al., 2007; Salminen and Haimi, 1999); furthermore, increasing distance from the smelting operations did not correlate well with increasing microorganism population, diversity, and dynamics (Anand et al., 2003). In contrast, Tozsa et al. (2010) found along with a pollution gradient in the vicinity of Pb/Zn smelter at Olkusz (southern Poland) that the dominating enchytraeid *C. sphagnetorum* and other species (*Enchytraeus*, *Fridericia*, *Henlea*) exhibited a much lower density in the polluted sites. Nevertheless, the authors admitted that the biodiversity of the enchytraeid community was affected by other environmental factors (pH) rather than by metal concentrations. The enchytraeid reproduction test (ERT) with *Enchytraeus crypticus* or *E. albidus* is used within the OECD ecotoxicological testing programme, and is recommended for the toxicity testing of soils. However, only a limited number of studies have been specifically devoted to toxicity testing of smelter soils. For instance, Konečný et al. (2014) studied a set of Cu smelter-affected tropical soils from the Zambian Copperbelt, which exhibited a significant pollution gradient. They found that the number of reproduced enchytraeids negatively correlated with total Cu and Co concentrations and EDTA-extractable Cu; whereas other soil parameters had no effects. No reproduction was possible in soils with Cu levels >5000 mg/kg, and the calculated median effect concentration (EC50) for Cu in soil corresponded to 351 mg/kg. Single chemical extractions are often used as surrogate measures for the determination of the “bioavailable” portion of metal(loid)s from a polluted soil. Conder et al. (2001) compared several chemical extractions and earthworm bioassays, and found that  $\text{Ca}(\text{NO}_3)_2$ -extractable metal concentrations were good predictors of metal bioavailability from Zn smelter-affected soils. Bade et al. (2012a) used diffusive gradients in thin films (DGT), an *in situ* method measuring the flux of “labile” contaminants from the soil, plus an *Eisenia foetida* earthworm uptake experiment, and concluded that DGT can be used as a biomimic surrogate for the earthworm uptake of metals (Cu, Pb, Zn) from smelter soils.

Among soil invertebrates, woodlice (*Porcellio scaber*) play an important role in litter decomposition processes, and may be used as a sensitive organism to assess the toxicity of polluted forest soils. For example, Godet et al. (2011) used woodlice for toxicity testing of wooded areas near Pb/Zn smelters in northern France, and found that compared to control sites they exhibited higher mortality, smaller weight gain, and high accumulation of Cd, which was probably related to the Cd/Zn ratio in the food.

## 5. Potential remediation techniques

Whereas traditional soil “clean-up” strategies are either based on the simple disposal or isolation of contaminated soil, sustainable soils remediation approaches, based on mineralogical and geochemical knowledge, are needed for the future (Hodson, 2010). While numerous soil remediation studies are available for mining-contaminated areas, there have been relatively few investigations solely on the remediation of smelter soils (Table 3 provides some examples).

The simplest means of soil remediation (but often not the cheapest one) is the replacement of contaminated soil, which is dug up, removed from the site, and stored elsewhere (Hodson, 2010), followed by the topsoil layer being substituted by uncontaminated soil. This approach has been applied in areas near Pb/Zn smelters in northern France, where communities cultivated home-grown vegetables (e.g., lettuce, radish, carrots), and had become exposed to high levels of metals *via* their diet (Douay et al., 2008c). A 3-year study indicated a clear improvement in the quality of the vegetables, with 17% of them still exceeding EU limits for foodstuffs; the

authors suggested that this was due to foliar contamination by re-suspended dust fallout coming from the closed smelter site and the adjacent polluted soils (Douay et al., 2008c).

Soil decontamination by leaching, with solutions containing EDTA as a chelating agent in laboratory columns, has been found to be relatively efficient in the elution of Pb and Cd (Kedziorek and Bourg, 2000), but it has never been adopted in the field for remediation of soils near smelters.

Assisted (or enhanced) phytoextraction, where chelating agents are also used, has been applied as a cost-effective remediation method at numerous contaminated sites, but the currently achieved contaminant removal rates from soil to plants are not adequate for phytoextraction to be a fast and efficient clean-up technology (Tack and Meers, 2010). Vysloužilová et al. (2003) compared Cd and Zn phytoextraction potential for seven clones of willow (*Salix* sp.) planted on smelter-affected soils with 4.73 mg/kg Cd and 180 mg/kg Zn, and found remediation factors of 20% for Cd, but only 4% for Zn. On soils from the same area containing up to 1360 mg/kg Pb, Komárek et al. (2007b) found that the application of EDTA was more efficient than that of ethylenediaminedisuccinic acid (EDDS), removing up to 60% of the total Pb concentration in the soil. In addition, maize (*Z. mays*) exhibited better results than poplar (*Populus* sp.) when extracting Pb from a more acidic (pH 4.8) smelter-polluted soil than from a mining soil (pH 6.6) (Komárek et al., 2007b). In a subsequent study, Komárek et al. (2008) used poplar for an EDTA- and chloride-enhanced phytoextraction experiment, and found that phytoextraction efficiencies after 2 vegetation periods were comparable, but were relatively low for Cd (<1.27%) and Zn (<0.33%), and extremely low for Pb (<0.04%) and Cu (<0.05%). Moreover, due to low biomass yields, poplars were found to be unsuitable for the phytoextraction of metals from severely contaminated agricultural soils. Many sites are contaminated with more than one element. The distribution of contaminants is highly heterogeneous and phytoextraction targets contaminants, which mainly occur in the plant-available fraction. This bioavailable pool in the soil may decrease over time, and thus the long-term performance of phytoextraction might be limited (Tack and Meers, 2010). Moreover, unwanted leaching of metal-chelant complexes was nevertheless detected, and may lead to groundwater pollution (Komárek et al., 2007b; Tack and Meers, 2010 and references therein).

Various amendments are either used to immobilize contaminants by sorption/ion exchange, encapsulation and/or neo-formation of solids, or to improve physicochemical conditions (pH, organic matter content), which are necessary for the stabilization process (O'Day and Vlassopoulos, 2010 and references therein). Phosphoric acid, diammonium phosphate (DAP) or hydroxyapatite have been used with success to immobilize Pb in smelter soil *via* the *in situ* formation of sparingly soluble pyromorphite [ $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ] (Basta et al., 2001; McGowen et al., 2001; Ryan et al., 2001; Yang et al., 2001; Basta and McGowen, 2004). Lime or limestone amendments reduce metal solubility by increasing soil pH, which leads to increased sorption to soil particles and formation of less soluble precipitates; nevertheless, the remediation efficiency is highly variable, with better performance for lime due to cementation reactions such as the formation of calcium-silicate-hydrates (CSH) or calcium-aluminate-hydrates (CAH) (Basta and McGowen, 2004; Bade et al., 2012b). Interestingly, Basta and McGowen (2004) found that treatment with DAP was highly effective not only for Pb (98.9% reduction compared to control), but also for Cd (94.6%) and Zn (95.8%). Limestone, although moderately effective for reducing Cd (55%) and Pb (45.2%) was a poor performer for Zn (21.9%); as a result, co-application of amendments for the remediation of smelter soils was suggested. Iron and manganese oxides with a high potential for adsorption of metal(loid)s are often used

**Table 3**

Selected studies on remediation of smelter-polluted soils.

Country	Locality	Smelting operation	Contaminants	Remediation technique	Reference
Czech Republic	Příbram	Pb smelter	Zn, Cd	Phytoextraction (willow)	Vyslouzilová et al. (2003)
			Pb	Phytoextraction (maize, poplar)	Komárek et al. (2007b)
			Pb, Zn, Cd	Phytoextraction (maize, poplar)	Komárek et al. (2007c)
			Pb, Zn, Cd, Cu	Phytoextraction (poplar)	Komárek et al. (2008)
			Pb, Cu, Cd	Amendment (amorphous Mn oxide, maghemite, nano-magnetite)	Michálková et al. (2014)
France	Noyelles-Godault/Auby	Pb/Zn smelters	Pb, Zn, As, Sb, Cu, Cd	Amendment (amorphous Mn oxide)	Ettler et al. (2015b)
			Pb, Cd	Extraction/washing by EDTA	Kedziorek and Bourg (2000)
	Site near Limoges	Pb/Zn smelters Cu smelter	Pb, Cd Cu, Pb, Zn, Cd	Soil replacement (vegetables) Amendment (amorphous Mn oxide, maghemite, nano-magnetite)	Douay et al. (2008c) Michálková et al. (2014)
Belgium	Lommel	Zn smelter	Zn, Pb, Cu, As, Hg	Amendment (cyclonic ash, beringite, organic compost), re-vegetation	Vangronsveld et al. (1995, 1996)
			Zn	Amendment (cyclonic ash, beringite, organic compost)	Nachtegaal et al. (2005)
			Zn, Pb, Cu, Cd	Amendment (cyclonic ash, Na silicate, lime, phosphoric acid)	Geebelen et al. (2006)
Austria	Arnoldstein	Pb/Zn smelter	Pb, Cd	15 amendments and accumulation study by barley	Friesl et al. (2006)
			Pb, Zn, Cd	Amendment (lime, red mud, gravel sludge)	Friesl-Hanl et al. (2009)
USA	Joplin (Missouri)	Pb smelter	Pb	Amendment (phosphate)	Yang et al. (2001)
	East Helena? (Montana)	Pb smelter	Pb	Amendment (phosphate)	Ryan et al. (2001)
	Palmerton (Pennsylvania)	Zn smelter	Zn	Amendment (sewage sludge, fly ash, limestone)	Kelly and Tate (1998), Kelly et al. (2003)
	Blackwell (Oklahoma)	Zn smelter	Zn	Amendment (lime-stabilized biosolids, rock phosphate)	Conder et al. (2001)
			Zn, Pb, Cd, As	Amendment (rock phosphate, diammonium phosphate, lime)	McGowen et al. (2001), Basta and McGowen (2004)
Bartleville, Blackwell, Henryetta (Oklahoma)	Zn/Pb smelters	Pb, Zn, Cd	Amendment (biosolids, rock phosphate)	Basta et al. (2001)	
South Korea	Janghang	Cu/Pb/Zn smelter	Pb, Zn, Cu, Cd, As	Amendment (lime)	Bade et al. (2012b)

as amendments. Recently, Michálková et al. (2014) compared the remediation potential of various Fe- and Mn-(nano)oxides in smelter-contaminated soils (amendments added at a concentration of 1 and 2% [w/w]), and found that treatment with an amorphous Mn oxide (AMO) resulted in >92% decrease in the exchangeable metal fraction, mainly due to the greater sorption capacity of AMO compared to that of nano-magnetite (Fe<sub>3</sub>O<sub>4</sub>) and nano-maghemite (Fe<sub>2</sub>O<sub>3</sub>). Similarly, AMO has been added at the concentration level of 2% (w/w) to a Pb smelter-affected agricultural soil, and the remediation potential has been evaluated by a pH-dependent leaching test after 6 months of incubation. The results indicated that the “labile” pool of As, Pb, and Sb significantly decreased in treatments with AMO; leaching of As, Cu, Pb, and Sb decreased down to 20%, 35%, 7%, and 11% of the control, respectively. In contrast, no effects were observed for Cd and Zn (Ettler et al., 2015b).

The efficiency of remediation with amendments (or the combination of various amendments) should be evaluated over longer time perspectives. However, relatively few long-term studies are available in the literature. Near a former Zn smelter in Lommel (Belgium), combinations of various amendments (beringite [modified aluminosilicate originating from fluidized bed burning of coalmine slag], cyclonic ash, lime, and phosphoric acid) have been used for highly polluted soils, and the remediation potential was evaluated over time (Vangronsveld et al., 1995, 1996; Nachtegaal et al., 2005; Geebelen et al., 2006). The reduction of phytotoxicity by addition of beringite was confirmed 15 months after treatment, and the water-extractable fraction of metals was up to 70 times lower compared to non-treated soils (Vangronsveld et al., 1995, 1996). A comparison of different treatments indicated that the metal immobilizing potential of Na-silicate additives was limited (due to reversible sorption of metals), while irreversible fixation at

constant pH was the major metal immobilization mechanism for other treatments (cyclonic ash, lime, and phosphoric acid) (Geebelen et al., 2006). Changes in Zn speciation were studied at soils from this site, collected 12 years after being remediated with cyclonic ash and compost. Surprisingly, the EXAFS spectroscopic data coupled to bioavailability tests indicated that Zn had similar solid speciation in both treated and non-treated soils (~8% of Zn was bioavailable); however, the incorporation of Zn into newly formed precipitates (Zn–Al layered double hydroxides and Zn-phyllsilicates) in both soil samples led to natural attenuation of the exchangeable Zn at near neutral pH (Nachtegaal et al., 2005). A similar long-term investigation of smelter soil remediation based on a laboratory batch leaching, a pot study and a pilot-scale testing was carried out near a former Pb/Zn smelter in Arnoldstein (Austria). Based on laboratory batch leaching tests, 5 treatments (combinations of gravel sludge, ferrihydrite, red mud, limestone and biocompost) were selected from 15 potential amendments and subsequently used for a pot experiment with barley (*Hordeum vulgare*). The results indicated that ferrihydrite-bearing amendments, especially in combination with sludge, were the most effective treatments for reducing Cd and Pb uptake, as well as transport in the plant (Friesl et al., 2006). However, a field experiment conducted during one vegetation season did not support the data from the pot trials, and the authors concluded that the application technique of amendments in the field has to be improved by deeper placement (Friesl et al., 2006). The evaluation of the treatments in a long-term perspective (5 years) indicated that the highest efficiency was for an amendment composed of gravel sludge and red mud (easily-extractable Cd, Pb, and Zn were reduced up to 99%); however, it was suggested to use this amendment in combination with metal-excluding cultivars (Friesl-Hanl et al., 2009).

## 6. Conclusions and perspectives

Soils near non-ferrous smelters are highly polluted by metal(-loid)s, whose concentrations often exceed limit values for residential and industrial soils as stipulated by national environmental agencies. Smelter-related soil contamination generally decreases with distance from the source. It is mostly bound in surface soil layers, follows the prevailing wind direction(s) in the area, and can often be recognized tens of km away from the source. Soils in smelter areas are also commonly connected to mines and/or are developed on mineralized backgrounds, and it is often difficult to differentiate between individual pollution sources by using standard geochemical approaches. To describe and depict the extent and fate of smelter-related contamination in soils, it is very useful to use metal isotope systems, for instance those where fractionation between the feed (ore) and emissions occurs during smelting (Zn, Cd), or those where no isotope fractionation has been reported, and changes in isotope compositions of the emissions reflect the isotope signature of the processed ore (Pb). Due to the fact that some results on isotope fractionation are still contradictory, and that chemical fractionation in the soil seems to complicate the source identification, a multi-isotopic approach is needed. Moreover, source tracing in the smelter-affected environmental systems is further complicated by the fact that the smelter feed used for metal production, over time, is chemically and isotopically variable. For this reason, investigations of the distributions of the so-far less-studied trace elements (Ag, Bi, In, Se, Tl, ...) could be another tool for multi-elemental tracing of smelter-derived contamination in soils (for this, there will be a need for new polluted soil CRMs in the future). The combination of traditional geochemical approaches, based on contaminant concentrations and extractabilities in soils, should be combined with detailed mineralogical investigations as well as applications of advanced techniques, such as synchrotron-based XAS, which are useful for the investigation of smelter-derived particulates and their weathering processes, determining the release of contaminants into the soil, and their subsequent binding to individual soil components. Still, relatively little is known about the fate of smelter-derived contamination in soils from tropical and arid areas, despite the fact that they are more vulnerable than are temperate soils. Given the fact that environmental measures are often less efficient in less developed countries where smelting industries are operating, there will be the need for future investigations of smelter-affected soils in the tropics.

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