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ORIGINAL ARTICLE

Chemical associations and sorption capacity of Pb and Zn: column experiments on a polluted soil from the Amizour mining district (Algeria)

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Abstract The column leaching behavior of lead and zinc is studied on a soil sample from the Amizour-Bejaia mining region, which is one of Algeria's largest natural reserves for Pb and Zn ores. The maximum amount of metal bound to the soil sample after column leaching by a mono-metal solution at pH 7 is 7.0 and 11.3 g/kg for Zn and Pb, respectively. These values exceed the maximum loading capacities derived from previous batch experiments conducted under similar conditions. The studied soil sample displays a stronger affinity for Pb than Zn under the study conditions. These two metals are associated with various chemical fractions of the mine soil sample, as revealed by a five-step, operationally defined sequential chemical extraction procedure (with fractions categorized as: exchangeable, acid extractable, reducible, oxidizable, and residual) following column leaching. After metal addition and sorption, carbonates (i.e. the extractable fraction) and Fe- and/or Mn-(oxy)(hydr)oxide phases (reducible fraction) in the soil sample dominate for both Pb and Zn. The extractable fraction is mainly reserved for the purpose of zinc retention; moreover, the stabilization with Fe–Mn (oxy)(hydr)oxide phases serves as a major carrier for Pb.

Keywords Mine soil · Sequential extraction · Trace metals · Column experiments

Introduction

Pollution caused by metal elements in soils constitutes a threat to both the environment and human health. Such pollution may originate from various industrial activities (Loska et al. 2004; Wei and Yang 2010). Mining activities have been reported to cause metal contamination in soil over a localized area (Webber 1981; Freedman and Hutchinson 1981). Metalliferous mine spoils result from the disposal of metal-rich overburden and excavation wastes. Polluted soil can thus contain metal concentrations 100–1000 times greater than their background levels (Elliott et al. 1986; Siegel 2002; Jiang et al. 2004). During the mining and smelting processes, wastewater and dust containing potentially toxic metals are discharged into the environment, and these metals are transferred into surface water, groundwater, agricultural soils and living organisms. The impacts of metal accumulation in soil can therefore create ecological risks for plants and other organisms growing in such soil and, consequently, risks to human health throughout the food chain (Nagajyoti et al. 2010). As a major biogeochemical sink for contaminants, agricultural soils close to non-ferrous metal mines are often contaminated by metal elements due to irrigation and flooding (Cheng et al. 2011). Once agricultural soil has been contaminated, the metals accumulate in the crops and are then transferred by various routes to the human body (Mench et al. 1994; Cheng et al. 2011; Liu et al. 2011;

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Yang et al. 2013). Due to toxicity, persistence and bioaccumulation, metal elements can lead to adverse effects on both animals and humans (Dong et al. 2010; El Hamiani et al. 2010).

The transfer of metals into soils and their behavior in the natural environment have been increasingly investigated (Christensen 1984, 1987; Lin et al. 2000; Sterckeman et al. 2000; Boularbah et al. 2006; Mouni et al. 2009, 2013; Rodríguez et al. 2009; Pelfrêne et al. 2012). While zinc is considered to be an essential trace element, in offering a variety of useful physiological and biochemical functions, other metal(loid) elements (such as arsenic, cadmium, chromium, lead, manganese or mercury, among others) are potentially toxic even in small amounts (Zabetoglou et al. 2003; Järup 2003; Coelho et al. 2014). They can cause debilitating disease in humans and animals due to irreversible changes in the body, especially the central nervous system, leading to psychotic disorders and other ailments (Coen et al. 2001; Dolk and Vrijheid 2003; Parajuli et al. 2013; Neal and Guilarte 2013). Soils have a finite capacity to attenuate trace metal concentrations through their multiple reactive mineral and organic components, which are involved in metal retention through forming inner and outer-sphere complexes (Evans 1989). Clay minerals, metal (hydr)oxides and organic matter are key constituents of soil particle surfaces and contain distinct metal retention sites; consequently, metals may be found in various forms within the solid soil phase, namely: (a) on non-specific ion exchange sites; (b) on functional groups of organic matter and metal oxides; and (c) in the structure of primary and secondary minerals (Bradl 2004). The metal sorption–desorption process in both natural soils and different model minerals plays a significant role in controlling the aqueous concentrations of metal species in soils. Metal sorption is typically described in terms of two basic mechanisms: specific sorption, e.g. surface complexation; and non-specific sorption such as ion exchange.

The chemistry of Pb and Zn in soils is affected by three main factors: specific sorption to various solid phases, precipitation of highly stable compounds, and formation of relatively stable complexes with soil components (Evans 1989; Duquette and Hendershot 1990). In recent years, many studies have focused on the sorption–desorption of lead and zinc ions onto different soil materials, with large numbers of experimental and modeling studies reporting their findings (Abd-Elfattah and Wada 1981; Martínez and McBride 1998; Trivedi et al. 2003). These studies have shown that the sorption of metal cations is often pH-dependent, whereas Fe and Mn oxide and hydroxide minerals, as well as humic substances, dominate (Pelfrêne et al. 2012). Factors such as pH and organic matter content in a contaminated soil can be correlated to metal solubility (Sauvé et al. 2000; Rodrigues et al. 2010a, b). Moreover, geochemical models are frequently used to describe and predict sorption and mobility in soils and sediments (Voegelin et al. 2001; Mallmann et al. 2012). Since total metal content in soils only provides limited (and sometimes misleading) information regarding environmental effects, the chemical fractionation must be taken into account during pollution studies (Li and Thornton 2001).

The present paper aims to study the column leaching behavior of lead and zinc onto a soil sample from the Amizour-Bejaia mining region (Algeria). The Oued Amizour deposit is one of the most valuable natural reserves for Pb and Zn ores in the whole of Algeria, and a mining project is currently being planned to operate using this deposit. The results of the present study may be helpful in predicting metal ion transport and evaluating the impact of lead and zinc discharges on soil quality, on the basis of the results of the column experiments, which closely resemble real-world environmental conditions.

Materials and methods

Soil characterization

A composite soil sample (approx. 20 kg) was prepared by collecting 1–2 kg of loose surface soil at a depth of 0–30 cm by hand digging at 15 points on a brownfield site located in the Amizour-Bejaia region (eastern Algeria). This material was homogenized, air-dried and sieved through ASTM standard sieves. Soil particles finer than 2 mm were used for the present studies. A number of selected soil sample properties, as previously determined by Mouni et al. (2009) on the composite soil sample, are detailed in Table 1. In order to know the overall concentration of Pb and Zn, bulk soil samples from the Amizour mining site were analyzed with a SPECTRO iQ II energy dispersive X-ray fluorescence (XRF) spectrometer.

Table 1 Chemical and physical properties of Amizour soil

Particle size		Metals	
Clay (%)	39.7	Fe_2O_3 (%)	3.4
Silt (%)	20.6	CaO (%)	2.6
Sand (%)	39.5	Pb (mg kg^{-1})	472
Surface area (m^2 g^{-1})	29.4	Zn (mg kg^{-1})	630
pH	6.9	Cu (mg kg^{-1})	452
CEC (cmol kg^{-1})	17.8	Cd (mg kg^{-1})	1.2
OM (g kg^{-1})	1.7	Mn (mg kg^{-1})	2.7
Total N (g kg^{-1})	2.6	Ni (mg kg^{-1})	202
$CaCO_3$ (%)	1.4		

Sequential extractions

The soil samples were pre-washed and freeze-dried before all experiments. In order to investigate the solid fractionation of the target metals, we applied the five-step, operationally defined sequential extraction protocol, as set forth by Delmas et al. (2002). The association of each chemical element with different fractions in the soil has been identified through several dissolution steps: (f1) exchangeable fraction ($MgCl_2$-displaceable); (f2) carbonate-bound (acid extractable) fraction; (f3) Fe/Mn oxide-bound (reducible) fraction; (f4) organic matter and sulfide-bound (oxidizable) fraction; and (f5) residual non-silicate-bound (mineralized) fraction. The extracts from each step were filtered through a 0.45-μm filter, acidified and analyzed by means of atomic absorption spectroscopy (AAS) (Shimadzu AA6500). The sum of metal concentrations from the five extractions was compared with the total soil concentration as determined by total acid digestion in a microwave oven. For soil samples derived from column experiments, the recovery rates were 94 % for Pb and 92 % for Zn; this is an acceptable accuracy for this sequential extraction protocol, as it has typically been observed (Fonseca and Martin 1986; Davidson et al. 1998; Patinha et al. 2015).

Column experiments

Column experiments were conducted to compare differences in Zn and Pb fraction distribution before and after leaching, analogous to a short-term hydrodynamic situation such as precipitation events. Continuous-flow column experiments were conducted to investigate metal transport through the mine soil; these experiments complemented our previous batch-type experiments (Mouni et al. 2009) and provided a better approximation to field conditions.

The metal solutions were prepared using lead nitrate $Pb(NO_3)_2$ (purchased from Panreac) and zinc nitrate $Zn(NO_3)_2$, $4H_2O$ (from Merck). All solutions were prepared in demineralized water and adjusted to pH 7 and 0.1 M ionic strength with sodium nitrate in order to limit colloid formation and filter blocking (Jiang et al. 2004). Each experiment was repeated twice to verify reproducibility; the results output represent mean values (standard deviation <10 %). The column experiments were all performed at room temperature (25 ± 2 °C). A series of cylindrical, high-density polyethylene columns with a 1.8-cm inner diameter were dry-packed with approx. 42.5 g of raw mine soil for a 10-cm height, yielding a bulk density of approx. 1.67 g/cm^3. The columns were then leached downwards from the top using a continuous leaching solution flow of 0.25 mL min^{-1}, introduced by a peristaltic pump (model BT300-2J, from Thermoline Scientific). A total 8-h pulse of 20 mg L^{-1} Pb or Zn solution was applied, with each pulse being followed by a deionized water (pH 7) flush for a duration of 30 h. Effluent samples were collected using a fraction collector (Frac-920 model, from GE Healthcare) and analyzed for pH and metal concentrations using AAS (Shimadzu AA6500). To determine the hydraulic characteristics of these soil columns and the retardation factor of each metal within the column, a separate experiment was run according to the procedures for metal solutions as regards flow rate, with a 10 mg L^{-1} solution of $NaNO_3$ as a non-reactive solute tracer and a 30-min pulse. The tracer elution was monitored by a UV–visible spectrometer (Libra s32 model, from Biochrom) at a 225-nm wavelength.

Results are presented with respect to V/V_p, where V denotes the volume of the cumulative leachate and V_p the pore volume of the column ($V_p = 19$ mL), as calculated from data with the tracer included.

Results and discussion

Soil properties

From the data in Table 1, this soil sample is a neutral clay loam (USDA 1987) with low organic matter (OM) content, a moderate cation exchange capacity and a relatively limited specific surface area. From X-ray fluorescence measurements, the bulk soil sample studied contains ca. 4.78 % Zn and ca. 0.57 % Pb.

Located some 10 km from the Algerian seaport of Bejaia, the Oued Amizour region is a geological anomaly as regards both zinc and lead (Fig. 1). Likely ore reserves amount to 38.1 million metric tons at 4.78 % zinc and 1.36 % lead and are to be mined using the block-cave mining method. The polymetallic mineralization contains disseminated sphalerite, galena and pyrite in addition to lodes with the same minerals within a calcite/gypsum/anhydrite gangue (Benali 2007). This Amizour mineralization can be characterized as volcanogenic massive sulfides (VMS). The supergene period corresponds to the neo-formation of certain Fe (oxy)(hydr)oxides, such as haematite and goethite, and Cu hydroxycarbonates such as malachite and azurite.

At a site contaminated to this extent, the soil can assimilate a pool of metal elements, which then act as a potential secondary source of environmental contamination (Denaix et al. 2001; Ettler et al. 2005).

Column leaching experiments

Prior to metal transport experiments, non-reactive tracer (nitrate) tests were conducted in order to characterize the hydrodynamic properties of the soil column. The results of these experiments are presented in Fig. 2. Under saturated,

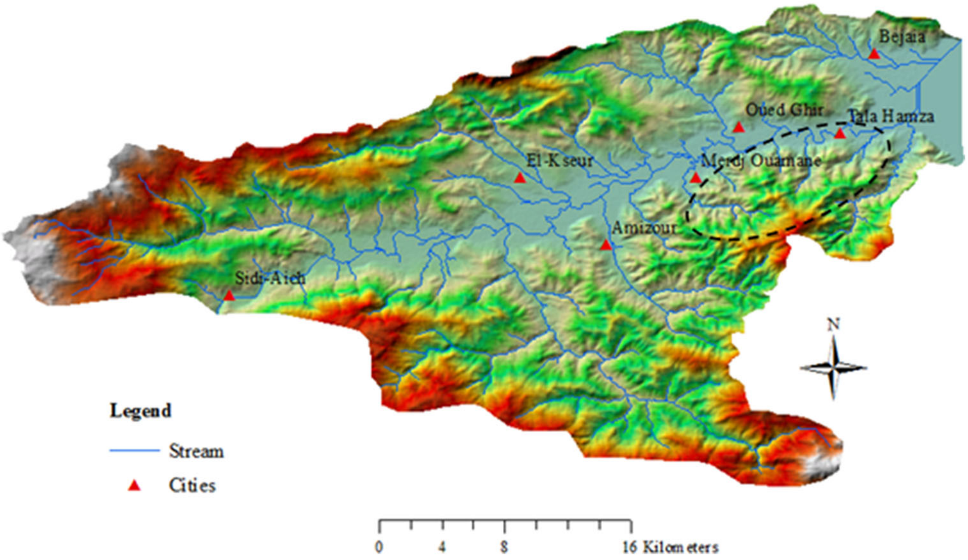

Fig. 1 Map of study area showing the sampling location

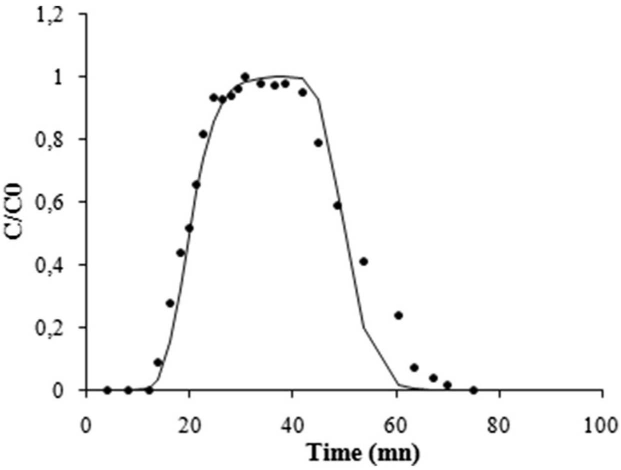

Fig. 2 Experimental breakthrough curve of nitrate (*filled circle*) and modeling (*line*)

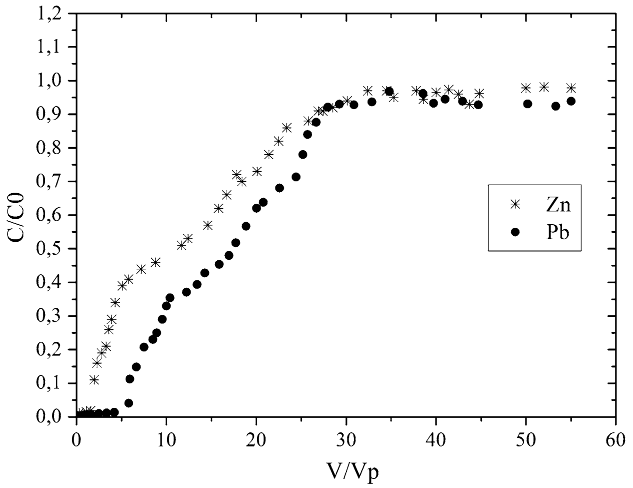

Fig. 3 Experimental breakthrough curves obtained for Pb^{2+} (*filled circle*) and Zn^{+2} (*asterisks*) in soil column

steady-state flow conditions, the breakthrough curve (BTC) of nitrate was almost symmetrical, thus indicating limited preferential transport path behavior within the soil column. From a simulation run using the SOLUTE code (Banton and Bangoy 1997), the following parameters can be estimated: dynamic rate = 0.53 cm/min; dispersion coefficient = 0.15; and retardation factor = 1. This last value is well correlated with a non-reactive tracer.

The experiments with Pb or Zn solutions, followed by water at pH 7, were undertaken to simulate the progressive migration of metals leached by rainwater through the soil column (Fig. 3). Replicate experiments provided comparable results (agreement to within 10 %); for the sake of clarity, only the mean results are shown.

In the first six pore volumes of percolated Pb solution injected from the column top, all of the metal was retained by the soil, and its concentration in the eluate was less than 0.3 mg/L. This total concentration corresponds to 6360 mg/kg of Pb retained by the soil, i.e. sorbed to the matrix. Furthermore, Zn was only retained in the first three pore volumes of injected solution. The average concentrations of Zn and Pb in the soil following sorption in dynamic column experiments are approx. 6990 and 11,300 mg/kg, respectively, which exceed the maximum sorption amounts evaluated in batch studies, i.e.: Zn $q_{\max} = 1937$ mg/kg, Pb $q_{\max} = 7140$ mg/kg (Mouni et al. 2009). Column experiments therefore allow for molecular diffusion phenomena to occur in the matrix, which actually increases the sorption capacity of the two metals onto the soil sample.

Moreover, Zn and Pb concentrations decreased along the column. A large amount of each metal is retained in the column top. At between 2–4 and 4–6 cm from the column

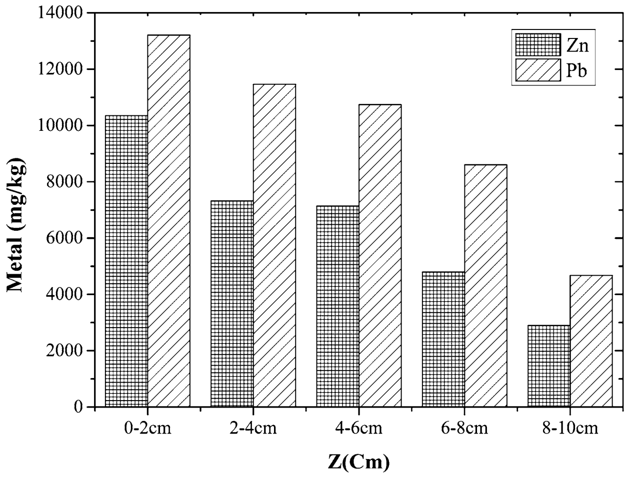

Fig. 4 Evolution of Pb (*hatched*) and Zn (*grey*) concentrations along the column height Z

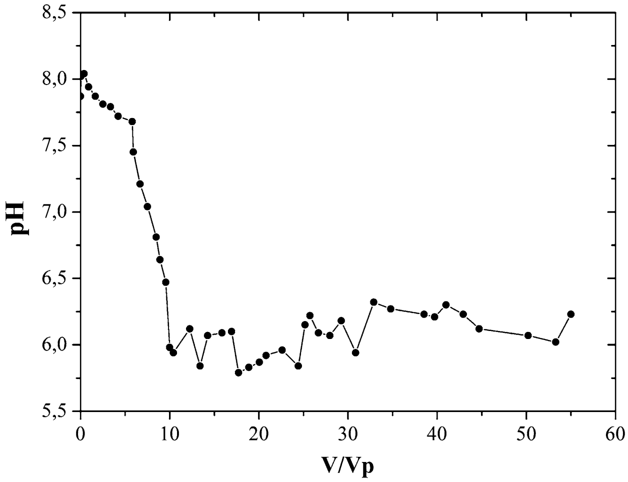

Fig. 5 pH evolution during column elution (case of Zn)

top, the Zn and Pb concentrations remained constant, i.e. at around 7300 and 11,000 mg/kg respectively (Fig. 4). Both these concentration values match the average column content, as measured with respect to the Zn and Pb used to percolate three pore volumes for Zn and six pore volumes for Pb.

In contrast, the significant decrease in pH from 7.7 to 5.9 during experiments, associated with a runoff volume of between five and ten pore volumes (Fig. 5), indicates the competition generated at the exchange sites by metal cations: H^+ ions are substituted by cations and released into solution, which is responsible for producing this pH drop. The value of pH subsequently stabilized at 6.0 ± 0.3 during the leaching experiment.

Despite the numerous batch sorption studies available, column transport and sorption experiments with polluted soil samples and metal solutions are rather scarce. Reference can, however, be made to a study on the dynamic sorption of Zn onto a sandy loam soil column (Miretzky et al. 2006) and its leaching with various solutions, including complexing agents like low molecular-weight organic acids and EDTA. More detailed studies have focused on the competitive sorption and transport of single, binary and multi-metal solutions (containing Pb^{2+}, Zn^{2+}, Ni^{2+} and/or Mn^{2+}) onto a lateritic soil sample at pH 5 (Chotpantarat et al. 2011, 2012). From these column experiments and the modeling of metal transport data, the higher sorption capacity of Pb can be deduced, along with a possible competitive behavior in binary or multi-metal systems.

Sequential extractions

The solid fractionation of both Pb and Zn in the soil sample was significantly modified after contact with fresh metal solutions and then with water at pH 7 (Fig. 6).

Although Pb was initially mainly present in the f3 (reducible) fraction (62.7 %), after column leaching it was found in both the f2 (extractable) and f3 (reducible)

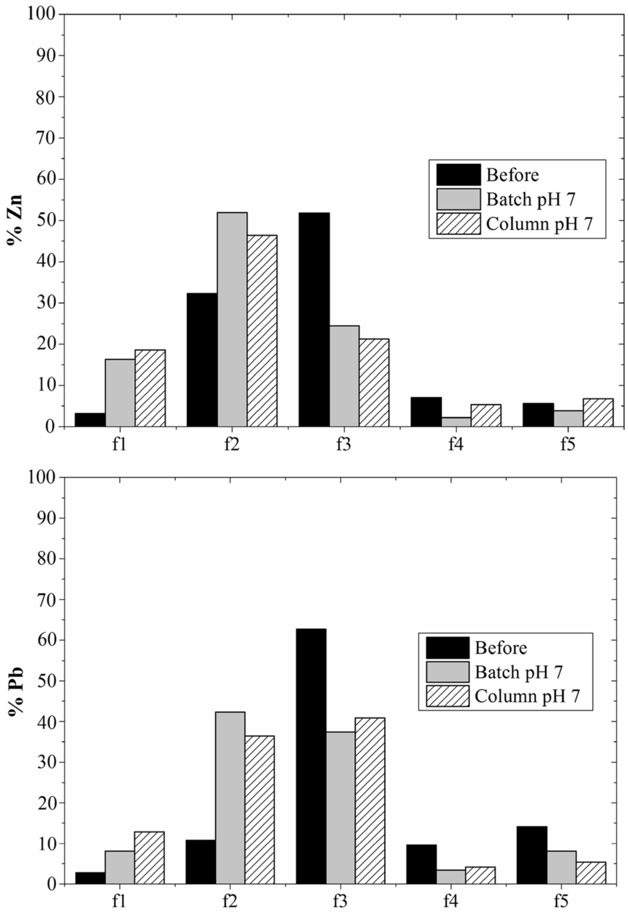

Fig. 6 Fractionation of Pb and Zn in soil sample before and after batch or column sorption experiments at pH 7

fractions (at 36.4 and 40.9 %, respectively). The increases in f1 (from 2.8 to 12.9 %) and f2 (10.8 to 36.4 %) are easily understood, due to the absence of aging in recent spikes; and the slight decrease in f3 (62.7 to 40.9 %) can be explained by a stabilization of metal injected onto Fe- and/or Mn-(oxy)(hydr)oxides (Komárek et al. 2013), resulting in low f4 and f5 fractions.

In the case of Zn, the main fraction after column leaching is f2 (46.4 %), followed by f3 and f1 (21.3 and 18.6 %, respectively). We once again observed a net increase relative to the initial soil sample fractionation for both f1 (from 3.2 to 18.6 %) and f2 (from 32.3–46.4 %), while f4 and f5 remained nearly constant and f3 decreased (from 51.8–21.3 %).

In Fig. 6, we compare these column data against those obtained during batch sorption experiments at the same pH 7 (Mouni et al. 2009). In the present case, these results are similar for batch and column studies under the same experimental conditions, thus indicating the usefulness of batch experiments in predicting the realistic field behavior of metal emissions from a polluting site.

When studying soil samples from around an old Pb/Zn mine, Rodríguez et al. (2009) similarly observed that Pb was mainly present in reducible form, meaning that it can be released for example during high flooding events. Zn was associated with the acid-extractable form, thus enhancing mobility into ecosystems. These results are the same for urban topsoil (kitchen garden and lawn) in the vicinity of two Pb and Zn smelters in operation for long periods, where Pb is present at 70–90 % in the reducible fraction and Zn at approx. 40 % in both the exchangeable and reducible fractions (Waterlot et al. 2013). In the case of waste on acidic bedrock from a former Pb/Zn/Ag mine, metals were mainly concentrated in the residual fraction: 40–70 % for Pb, and 75–98 % for Zn, depending on the sampling site (Pascaud et al. 2014). In dredged sediments near a Pb/Zn mine, Pb was mainly in the reducible fraction; the Zn location varied but stayed primarily in the oxidizable fraction (Cappuyns et al. 2007).

Moreira et al. (2001) conducted a series of sequential extractions on four different agricultural soil samples after mono-metal spiking. For the two soil samples with low carbonate content ($C_{\mathrm{inorg}} = 2$ or 7 g/kg), Zn remained mainly in the exchangeable fraction (65 or 76 %, resp.), while Pb was distributed between the exchangeable (41 or 37 %, resp.) and carbonate-bound (27 or 31 %, resp.) fractions. Metal behavior is quite different in the case of the two soil samples with higher carbonate content ($C_{\mathrm{inorg}} = 23$ or 51 g/kg), where the oxidizable fraction predominates for Zn (i.e. organic matter bound, 66 or 76 %, resp.), whereas Pb is found in both the reducible (57 or 50 %, resp.) and oxidizable (30 or 43 %, resp.) fractions.

In another detailed study, Fonseca and Martin (1986) first verified the selectivity of a six-step procedure for kinetic sequential chemical extractions, using a series of Pb- and Zn-bearing minerals. They then applied this extraction protocol to two distinct soil samples: one as a carbonate, the other an aluminosilicate. These authors concluded that such a technique may be applied to geochemical exploration at a given metal-containing site.

At an abandoned mining site on a silt-loam carbonated soil, with as high as 13 g/kg Pb and 189 g/kg Zn, Iavazzo et al. (2012) obtained the following data from a five-step extraction scheme devoted to differentiate the CO_3-bound fraction: Pb is mainly associated with Fe/Mn oxides and with carbonates (41 and 29 %, resp.), although Zn is essentially associated with Fe/Mn oxides (42.8 %), then with the oxidizable (25.6 %) and carbonate (23.5 %) fractions; and the residual fractions are 17 % for Pb and 8 % for Zn, respectively.

Arenas-Lago et al. (2014) carried out a six-step extraction scheme in order to discriminate the role of Mn oxides, and amorphous vs. crystalline Fe oxides, from an abandoned Pb/Zn mine site on a carbonated soil area. The two metals of interest were present in concentrations of 6.8 g/kg Pb and 32.3 g/kg Zn; they mainly appeared in the residual fraction (43 and 42 % for Pb and Zn, respectively), and in association with amorphous Fe oxides (58.8 and 28.6 %, resp.), with a notable contribution of Mn oxides phases for Zn (25.5 %).

Operating with the BCR four-step method on topsoils sampled near an active Pb/Zn smelter, Wang et al. (2015) claimed that Zn (total concentration = 102.6 mg/kg) is mainly blocked in the residual fraction (79 %), although Pb (total = 41.3 mg/kg) is distributed between the reducible and residual fractions (42 and 40 %, resp.). Thus, if the mobile fractions accounted for only ca. 20 % for Zn, the pollution risks were higher for Pb (ca. 60 % mobile phases).

Patinha et al. (2015) applied a slightly different seven-step sequential extraction protocol to a number of urban dust samples from a city exposed to various industrial factory emissions. They observed that the majority of Pb and Zn was extracted in their first three fractions (i.e. exchangeable + acid soluble + bound to Mn oxyhydroxides), which correspond in large part to anthropogenic sources. On the other hand, they traced relationships between the oral bioavailability of metals and the solid mineral phases in the dusts studied. In similar studies [Howard et al. (2013) for Pb; Molina et al. (2013) for Zn] sequential extractions have also been compared with metal bioavailability from both selected mineral phases and soil samples.

From this brief survey of the literature, we can thus infer some general trends for Pb and Zn chemical association to solid phases in soil samples affected by nearby (former) mines and/or smelters.

Conclusion

Our column experiments have indicated that soil samples from this mining district display a stronger affinity for Pb than for Zn, whenever these metal elements were introduced as salt solutions. After adding metals into the soil column, the fact that Pb and Zn in the soil sample associated with various solid chemical fractions has provided further insight into their behavior during leaching under field conditions.

After column leaching, Pb is distributed in both f2 (extractable) and f3 (reducible) fractions (at 36.4 and 40.9 %, respectively). For Zn, however, the main fraction after column leaching is f2 (46.4 %), followed by f3 and f1 (21.3 and 18.6 %, resp.).

The importance of the Fe/Mn (oxy)hydroxide phases for Pb and of the carbonate phases for Zn should be taken into consideration when such sites are designated to change activities or when rehabilitation processes require examination.

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