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In situ investigation of dissolution of heavy metal containing mineral particles in an acidic forest soil

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Abstract

We report the application of an in situ method to obtain field dissolution rates of fine mineral particles in soils. Samples with different metal-containing mineral and slag particles (lead oxide, copper concentrate and copper slag) from the mining and smelting industry were buried in the topsoil of an acidic forest soil for up to 18 months. In addition we studied the dissolution of these particles in samples of the same soil, in a sand matrix and in acid solution under constant temperature and moisture conditions in the laboratory. Under field conditions the PbO particles dissolved quite rapidly ($2.4 \pm 0.7 \times 10^{-10}$ mol Pb m^{-2} s^{-1}), whereas the copper concentrate ($<1 \times 10^{-11}$ mol Cu m^{-2} s^{-1}) and the copper slag particles ($4.3 \pm 0.8 \times 10^{-11}$ mol Cu m^{-2} s^{-1}) proved to be more resistant to weathering. In addition to qualitative information on dissolution features (SEM), the method yielded quantitative data on in situ dissolution rates. The dissolution rates followed the order: sand with acid percolation (pH 3.5; lab) < soil (lab) < soil (field) < acid solution (pH 3.5; lab). Dissolution rates in soil were found to be lower under laboratory than under field conditions. The faster field rates may in part be attributed to the higher biological activity in the field soil compared to the same soil in the laboratory.
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1. Introduction

Considerable areas surrounding industrial and mining sites are polluted by metal containing dusts emitted from these sources. The release of heavy metals into soil solution due to weathering of these particles can seriously reduce soil fertility, adversely affect the quality of surface and ground waters and lead to health risks for the consumers of crops produced on such soils. Metal mines are one of the major industries producing metal containing dusts and slags (Porter and Bleiwas, 2002). In the process of crushing, milling and concentrating, large quantities of waste particles are generated (∼8000 Mt solid waste in 1999) (Lottermoser, 2003). While they can vary considerably in composition, these wastes usually contain high concentrations of hazardous metals. Over the centuries worldwide mining and smelting activities have led to the accumulation of mining wastes deposited in the environment (Martin et al., 2002). In the past, several disastrous mining accidents have resulted in the release of large amounts of these wastes into the environment and contaminated wide areas (Penman, 2001; Riba et al., 2004). The possibility to study the transformation behavior of potential hazardous particles under individual field conditions contributes important data for environmental risk assessment studies.

In order to assess the risks arising from such contamination it is important to know the weathering kinetics of these particles in soils and sediments (Alloway and Ayres, 1997). The dissolution of (toxic) mineral particles has been investigated in many laboratory (Casey et al., 1993; Strömberg and Banwart, 1999b; Ettler et al., 2002), lysimeter (Schnoor, 1990; Velbel, 1990; Swoboda-Colberg and Drever, 1993) and field studies (Vidal et al., 1999; White and Brantley, 2003). These studies were primarily interested in weathering as a process of soil formation whereas the question of weathering as a potential environmental risk was neglected. Several of the studies (Schnoor, 1990; Casey et al., 1993;

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Swoboda-Colberg and Drever, 1993; White and Brantley, 2003) reported a discrepancy between dissolution rates in the laboratory and in field experiments. Schnoor (1990) found that dissolution rates of aluminosilicate minerals were one to two orders of magnitude lower in field than in laboratory experiments. Velbel (1990) found that dissolution rates of feldspars differed between field and laboratory experiments by orders of magnitude in favor for the laboratory. Casey et al. (1993) investigated the weathering of olivine minerals and also reported differences by orders of magnitude between field and laboratory conditions. All of these authors attributed these discrepancies to differences in moisture and temperature conditions between laboratory and field. All the laboratory experiments were conducted under controlled conditions in batch reactors, fluidized bed reactors or saturated columns (lysimeters), whereas the field experiments have to deal with seasonal fluctuations and spatial heterogeneities (mineralogy, soil types and biological activity) that are difficult to control.

A difference in weathering conditions between laboratory and field, which is of particular importance, is the activity of organisms. Microorganisms, fungi and plants accelerate mineral weathering through biomechanical and biochemical attack (Banfield et al., 1999; Burford et al., 2003). Mycorrhizal fungi are especially effective agents of bioweathering in dissolving minerals (Jongmans et al., 1997) and solubilizing heavy metals (Martino et al., 2003). The soil in the immediate vicinity of plant roots (rhizosphere) has chemical, physical and biological properties that are substantially different from those of the bulk soil. For example, Hinsinger et al. (1993) observed increased mobilization of metals and transformation of minerals with decreasing pH in the rhizosphere of *Brassica napus*. The exudation of organic substances is another mechanism by which plant roots can mobilize metal ions (Dakora and Phillips, 2002). In particular, organic ligands such as citrate, oxalate and phenolic acids as well as siderophores were all found to increase mineral weathering rates (Pohlman and McColl, 1986; Jones, 1998; Zhang and Bloom, 1999; Liermann et al., 2000; Kraemer, 2004). Dissolved organic substances leached from plant litter have the ability to mobilize mineral-bound metals (Pohlman and McColl, 1988). Banks et al. (1994) found that the rate of Zn leaching from soil contaminated by mine-tailing material was lowest in the absence of plants, intermediate in the presence of plants and microorganisms and highest if only plants and no microorganisms were present. Augusto et al. (2000) observed that feldspar minerals did weather at various rates under different tree species.

The difficulty to reproduce field weathering conditions in the laboratory has led to an intensive search for methods to study the dissolution of mineral particles in situ under field conditions. Various approaches have been taken. One is the study of weathering in lysimeters experiments in which dissolution rates are determined from the analysis of solution and discharge samples (Swo-boda-Colberg and Drever, 1993). Another approach employed bags filled with test minerals which are inserted into soils and recovered after some time (months to years) and then analyzed by various techniques for differences in mineral composition (Hatton et al., 1987; Augusto et al., 2000). Bag methods have the disadvantage that the particles are not in direct contact with the matrix in which they are buried as they are separated from it by the bag material. In addition placing a bag into the soil disturbs the soil structure. Bennet and co-workers (Bennet et al., 1996; Rogers et al., 1998) and Maurice et al. (2002) inserted perforated polyethylene bottles ("microcosms") filled with silicate test minerals into groundwater wells, stream sediments, and soils determined dissolution rates from microscopic analysis of recovered samples. This method is perfectly suited to study mineral dissolution under saturated conditions with sufficient flow through the perforated containers, providing a constant contact of the test particles with the sediment/soil solution. This method has also been applied to follow the dissolution of feldspars in soils (Nugent et al., 1998). However, burying relatively large bottles (8–10 ml volume) in soils disturbs soil structure and local hydrology considerably.

To improve the methodology for in situ studies we developed an adapted technique which provides direct contact of test particles with the adjacent matrix (Birkefeld et al., 2005). In this method, the particles of interest are fixed by a thin film of epoxy resin to acrylic glass polymer supports. Apart from the area in contact with the epoxy resin, the particle surfaces are exposed to the surrounding soil without interference of any barrier. The method does not work for particles smaller than 20 μm because they are completely covered by resin. The support material and the fixation are very resistant to mechanical and chemical stress so that the sample can be incubated in soils under field conditions for periods of months to years. As they are flat and can be made very small in size, their placement into soil can be achieved with less disturbance than that of bags or microcosms but the soil structure is still disturbed locally. The supports can be recovered easily and the remaining metals can be quantified and the particles can be examined using optical and electron microscopic methods.

In this study, we show the potential of the new method to determine dissolution rates of metal-containing mineral and slag particles in soils under field conditions. This is the first investigation on the dissolution kinetics of heavy metal containing waste particles emitted from mining and smelting industries in acidic forest soils. We also performed control experiments in which we incubated particles under constant temperature and moisture conditions in samples of the same soil as used in the field and for comparison also in acidic quartz sand and solution environments. Based on the results reported in the literature introduced above, we expected to observe much higher dissolution rates in the laboratory than in the field.

2. Methods and materials

2.1. Sample preparation

Particle supports were made from polymethylmethacrylate (PMMA) polymer (Plexiglas®/Acrylite®). Pre-cut plates of (2 cm × 2 cm) were weighed with an accuracy of 0.1 mg by means of an analytical balance (Mettler Toledo AT 261, Switzerland). The weight of each plate was carved into its back side. Then the plates were covered with a thin adhesive film of a two-component epoxy resin (Bisphenol A resin—Suter, Switzerland) using a micro-foam paint roll. For this purpose, a set of 10 weighed and marked supports was placed in two rows in a frame holder. Finally, the selected particles were applied onto the support surfaces by using a downsized copy of a commercial available dust spray gun. Particles were applied onto the supports, holding the spray gun perpendicular in a distance of 1.5 m to frame holder. Gentle moving of the dust spray gun during application (30 s) produced a relatively homogenous distribution of the particle on the supports. For a more detailed description of method the reader is referred to Birkefeld et al. (2005).

2.1.1. Pre-experimental analysis

For this study different sample plates were prepared with three types of particles: lead oxide which was obtained from a commercial manufacturer (Pennaroya Oxide Ltd., Germany), copper concentrate which came from the mining industry (Chile) and copper smelting slag from a smelter facility in northern Chile. Lead oxide particles are a typical component of metal refining industry emissions. Copper concentrate and copper smelting slag particles are major components of mining industry emissions (including ore smelting). After hardening of the epoxy resin (12 h) the polymer plates were analyzed by energy dispersive X-ray fluorescence analysis (XRF) (Spectro X-Lab 2000, Germany) to determine the elemental composition of the mineral particles fixed to the supports. Stereo microscopy was used to assess the coating quality. A custom calibration was used for each particle type to convert the XRF counts into concentrations. For this purpose a sample set with different particle concentrations was first analyzed by XRF and afterwards completely dissolved and analyzed by atomic absorption spectroscopy (Varian SpectrAA 220, Australia).

The elemental composition, main mineralogical phases, and specific surface areas of the three particle types are given in Table 1.

2.2. Experiments

2.2.1. Field experiments

The topsoil of an acidic dystic Cambisol under a mixed oak-beech forest near Zurich (Switzerland) was chosen for the field test ($pH_{0.01MCaCl_2}$ 3.8, C_{org} 2.5%). The texture of the topsoil was a silty loam (clay/silt/sand 21/50/29%). The site was situated at 520 m a.s.l. The total precipitation over the 18 months of the experiment was 1200 mm. The mean temperature over the 18 months was 8.9 °C (Fig. 1). In order to insert the particle-coated polymer supports into the soil small slits were opened in the soil matrix from the surface by means of a sharpened stainless steel lancet (3 cm width; 0.5 cm thickness; 40 cm length). A small nylon thread attached on the non-coated side of the support protruding from the soil surface marked the exact location for later recovery. Ten supports of each
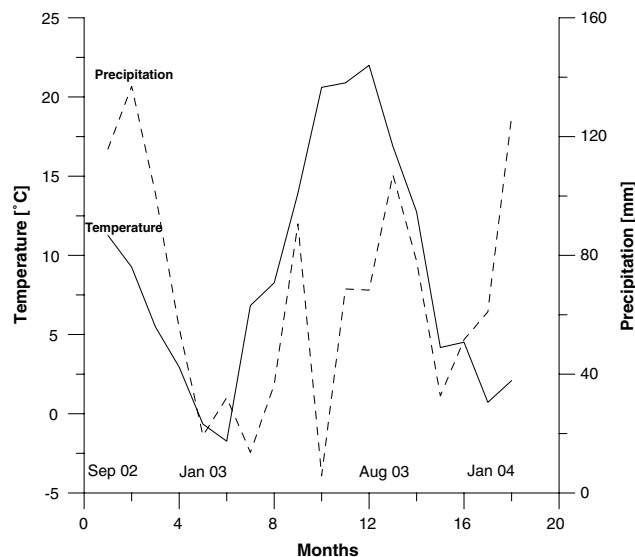

Fig. 1. Climate data (temperature and precipitation, monthly average) during the experimental time – Data taken from weather recording station Hönggerberg of the Institute of Atmospheric and Climate Sciences (IAC*ETH*) of ETH Zurich at a distance of about 500 m from our field site.

Table 1
Properties of the mineral particles used in this study (minor mineral phases in italics)

Phase	Mineral name	Chemical formula	Particle size (μm)	N$_2$-BET surface (m^2 g^{-1})	Origin
Lead oxide	Massicot	PbO	20–100	0.11	Pennaroya Oxide Ltd., Germany
	Litharge	PbO			
Copper concentrate	Chalcopyrite	CuFeS$_2$	20–100	1.27	Copper Mine, Chile
	Pyrite	FeS$_2$			
	Nantokite	*CuCl*			
	Roxbyite	*Cu$_7$S$_4$*			
	Molybdenite	*MoS$_2$*			
Copper slag	Fayalite	Fe$_2$SiO$_4$	20–100	0.41	Copper Smelter, Chile
	Magnetite	Fe$_3$O$_4$			

particle type were implanted at a depth of 15 cm in a row, separated by distances of 10 cm from each other. Samples were left up to 18 months in the soil, including two winters and one summer. The samples were inserted into the soil in the beginning of September, 2002.

Recovered samples were put into small labeled polyethylene bags to keep them field-moist and transferred to the laboratory. Here they were immersed in a distilled water bath for about 5 min to soften residual soil particles, which were then removed from the support surface using a small soft brush. Afterwards the samples were let to dry under ambient air over night.

2.2.2. Laboratory experiments

For the laboratory experiments three dark polypropylene pots were filled with topsoil collected from the field site and two polypropylene pots were filled with acid washed clean quartz sand. Plates coated with lead oxide, copper concentrate and copper slag were inserted into the pots in the same way as in the field. The pots containing acidic forest soil were irrigated with synthetic rain solution (made from p.a. grade chemicals, Fluka Chemicals, Switzerland and Merck Chemicals, Germany) which had the following composition: N 3.5 mg L^{-1}; Cl 0.6 mg L^{-1}; Ca 0.2 mg L^{-1}; K 0.3 mg L^{-1}; SO_4 0.3 mg L^{-1}; Na 0.1 mg L^{-1}; P 0.1 mg L^{-1}; Mg 0.03 mg L^{-1}; Zn 0.01 mg L^{-1}; pH 5.5. The pots with quartz sand were irrigated with a HNO_3 solution of pH 3.5. Irrigation was provided from two glass bottles using a multi-channel peristaltic pump (Ismatec BVP-12, Switzerland) and distributed through perforated PE tubing at a rate of 75 ml per day per pot corresponding to a precipitation of 1100 mm per year. The same peristaltic pump was also used to collect the drainage water. The experiment was run for 3 months at room temperature (20 °C). Samples were retrieved every 2–4 weeks and processed using the same procedure outlined for the field samples. In an additional experiment, plates with lead oxide were incubated in a 5 L polyethylene tank filled with a HNO_3 solution which had a pH of 3.5. The solution was slowly stirred with a magnetic stirrer (Heidolph MR 3004, Germany). As in the other experiments, samples were recovered at regular intervals (weeks) and analyzed over a period of 3 months.

2.3. Sample analysis

Field and laboratory samples were analyzed in the same way. The cleaned and dried samples were inspected under a stereomicroscope for damages and then analyzed by XRF spectroscopy (Spectro X-Lab 2000, Germany) to establish the loss of concentration during the experiment. In addition, a selection of samples was sputter coated with gold and analyzed by scanning electron microscopy (SEM) (Obducat CamScan CS44, Sweden) for morphological changes, in particular for features of dissolution on the particle surfaces and for growth of new phases. The SEM instrument was equipped with an energy dispersive X-ray detector (EDX) (EDAX Econ, USA), allowing to make a qualitative elemental analysis of small areas (∼20 nm).

Dissolution rates were calculated from the decrease in heavy metal contents of the samples (XRF before and after the experiment), divided by the BET surface area of the particles.

3. Results

3.1. Particle characterization

The X-ray diffraction (XRD) analysis of the lead oxide particles revealed the presence of the two PbO polymorphs, massicot and litharge (Table 1). Particle sizes ranged from 20 to 100 μm. The N_2-BET surface area was 0.11 $m^2 g^{-1}$. X-ray fluorescence (XRF) analysis revealed Cu and Zn as minor constituents of the lead oxide particles (Table 2). The copper concentrate particles were a conglomerate of typical minerals from a porphyric deposit, containing chalcopyrite ($CuFeS_2$) as the most abundant mineral phase and roxbyite and nantokite as minor copper phases (Table 1). The Cu concentrate had a copper content of 26% (Table 2) and a specific surface area of 1.27 $m^2 g^{-1}$.

The mineral composition of the copper smelting slag was typical for smelter slags (Imris et al., 2000). Magnetite and fayalite were the main phases (Table 1). These iron bearing minerals are secondary minerals that are generated during the ore smelting process after iron oxide is added as a flux substance (Gee et al., 1997). The surface area of the slag particles was 0.41 $m^2 g^{-1}$ and the residual copper concentration was 0.6% (Table 2). Such a low copper content is typical for slags cleaned in electric furnaces by the procedure described by Mechev (1997). According to Warczok et al. (2002) slags cleaned by this procedure also contain elevated magnetite contents. The occurrence of a fayalite phase was also reported for copper slags analyzed by Imris et al. (2000). We conclude from the XRF and XRD analysis that about half of the Fe in the slag material used in this

Table 2
Concentrations of selected elements in the particles used in this study

Element	PbO	Unit	Cu concentrate	Unit	Cu slag	Unit
Cu	100	mg kg^{-1}	268	g kg^{-1}	6000	mg kg^{-1}
Zn	130	mg kg^{-1}	1560	mg kg^{-1}	2025	mg kg^{-1}
Pb	800	g kg^{-1}	120	mg kg^{-1}	345	mg kg^{-1}
Fe	<1	g kg^{-1}	112	g kg^{-1}	366	g kg^{-1}
Si	<1	g kg^{-1}	80	g kg^{-1}	45	g kg^{-1}

study was present in the fayalite phase and the other half in the magnetite phase.

3.2. Dissolution under field conditions

Fig. 2 shows the recovery of particles bound on the retrieved samples after various exposure times as a percentage of the initial metal mass on the respective sample. The lead oxide particles lost about 40% of the initial Pb content during the 18 months of the experiment. SEM
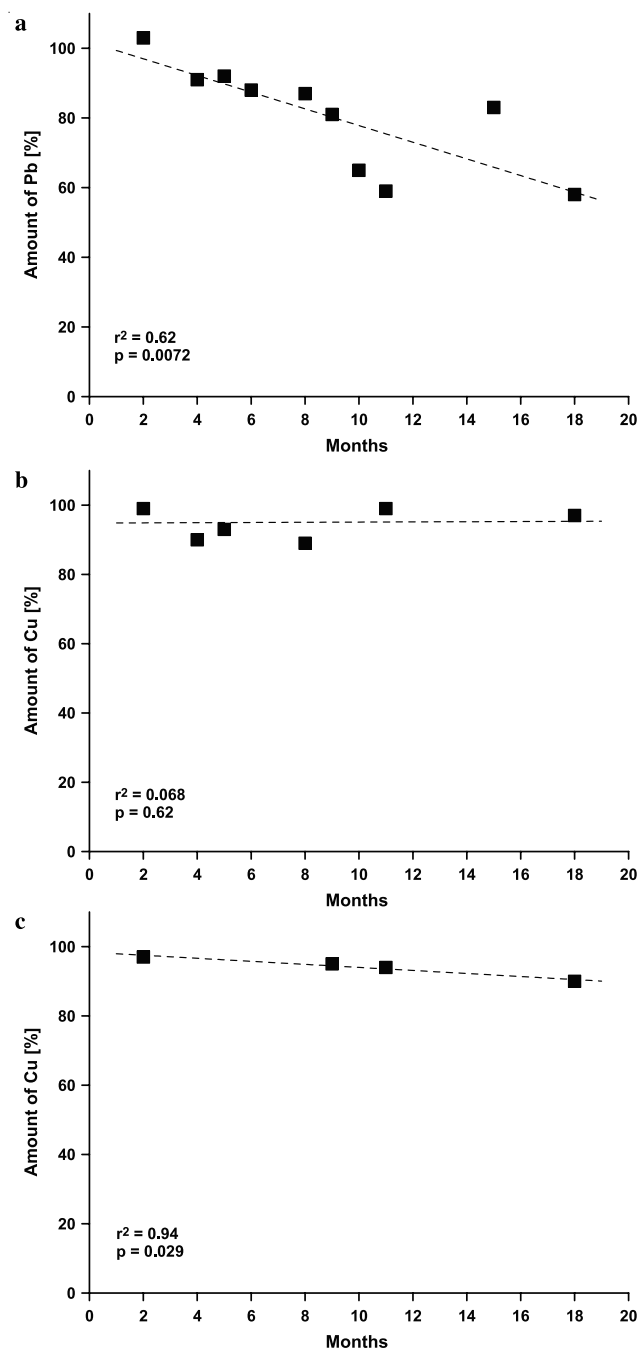

Fig. 2. Dissolution of lead oxide (a) copper concentrate, (b) and copper slag particles, (c) in acidic forest soil under field conditions for 18 months, expressed as mass of metal recovered in percent initial mass of metal (determined by XRF).

images show typical morphological features of the progressive dissolution of the lead oxide particles (Fig. 3). First the top layer is dissolved, then cavities and holes appear which grow and form a cellular structure. The average dissolution rate calculated from the best-fit line in Fig. 2 is 2.4×10^{-10} mol Pb $m^{-2}\,s^{-1}$ (Table 3).

The Cu content of the copper concentrate varied in the samples recovered over the 18 months of the field experiment, but did not show a significant trend (Fig. 2b). Also the SEM microphotographs do not show definitive features of weathering (Fig. 4). The calculated dissolution rate was $<1 \times 10^{-11}$ mol Cu $m^{-2}\,s^{-1}$.

The concentration of Cu in the copper smelting slag decreased to 90% (0.15 mg Cu sample^{-1}) of the initial value over 18 months (Fig. 2c). The SEM pictures showed approximately 10, quite distinct minor dissolution features on each particle (insets Fig. 5). An average dissolution rate of 4.3×10^{-11} mol Cu $m^{-2}\,s^{-1}$ is calculated (Table 3).

3.3. Dissolution under laboratory conditions

Fig. 6 shows the loss of metal content of the particles in the laboratory experiment. The average dissolution rate was 1.9×10^{-10} mol Pb $m^{-2}\,s^{-1}$. The lead oxide particles incubated in the acidified sand were dissolved at a rate of 7.7×10^{-11} mol Pb $m^{-2}\,s^{-1}$ and showed less morphological signs of dissolution than the particles incubated in the forest soil (Fig. 7). The most rapid dissolution is calculated in the case of the lead oxide samples incubated in the stirred acidic solution at pH 3.5 (9.5×10^{-9} mol Pb $m^{-2}\,s^{-1}$) (Table 3). At the termination of the experiment almost all particles had been completely dissolved. All dissolution rates from the field and laboratory experiments are summarized in Table 3. The copper concentrate particles showed almost identical dissolution rates in the soil and in the sand (1.1×10^{-10} mol Cu $m^{-2}\,s^{-1}$ and 9.5×10^{-11} mol Cu $m^{-2}\,s^{-1}$, respectively). No distinct dissolution features were recognized in SEM images of either case (Fig. 4). The dissolution rates of copper slag particles differed between soil and sand. The dissolution rate of the slag particles is 5.9×10^{-11} mol Cu $m^{-2}\,s^{-1}$ in the soil pots and 1.1×10^{-11} mol Cu $m^{-2}\,s^{-1}$ in the sand pots (Table 3).

4. Discussion

4.1. Applicability of the new in situ technique

The new in situ technique proved its general applicability for field and laboratory studies for extended times. The presented results are the first data on the dissolution of fine grained mineral particles under in situ conditions in soils. The new in situ polymer support method is not limited to particles in the centimeter or millimeter-range, as other in situ methods (Ranger et al., 1991; Maurice et al., 2002) but can be applied to particle sizes down to ~20 μm. The particles are well attached to the support and particle loss during the experiment is negligible (Birkefeld et al.,
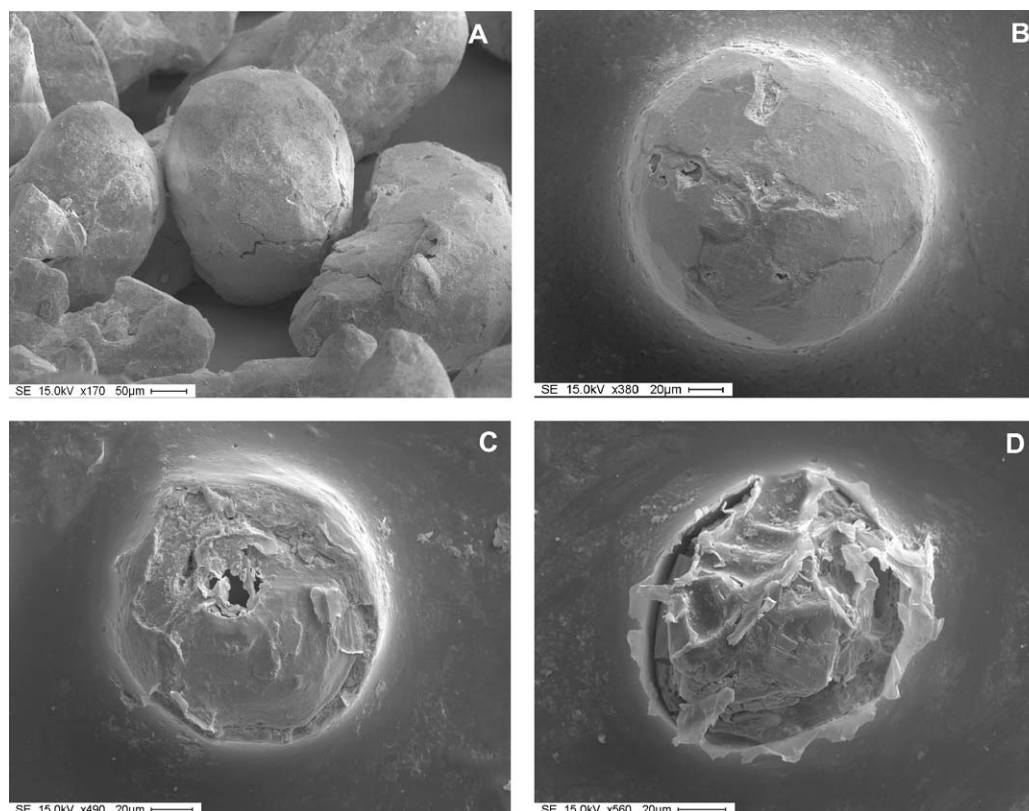
Fig. 3. SEM microphotographs of lead oxide particles after different reaction times in an acidic forest soil under field conditions. (A) Lead oxide particle appearance before the experiment, (B) after 6 months, (C) after 15 months, (D) after 18 months.

Table 3
Dissolution rates (±error) in mol m^{-2} s^{-1} for the PbO, Cu concentrate, and Cu slag in acidic forest soil in the field, in the same soil in the laboratory, in sand percolated with HNO$_3$ solution (pH 3.5) and in stirred HNO$_3$ solution of pH 3.5 (PbO only)

Type of particles	Experiment	Dissolution rate (mol Pb resp. Cu m^{-2} s^{-1})
PbO	Forest (field site)	$2.4 \pm 0.7 \times 10^{-10}$
PbO	Forest soil (lab)	$1.9 \pm 0.3 \times 10^{-10}$
PbO	Acidic sand (lab)	$7.7 \pm 1.0 \times 10^{-11}$
PbO	Acid solution (pH 3.5)	$9.5 \pm 0.6 \times 10^{-9}$
Cu concentrate	Forest (field site)	$<1 \times 10^{-11}$
Cu concentrate	Forest soil (lab)	$1.1 \pm 0.4 \times 10^{-11}$
Cu concentrate	Acidic sand (lab)	$1.0 \pm 0.2 \times 10^{-11}$
Cu slag	Forest (field site)	$4.3 \pm 0.8 \times 10^{-11}$
Cu slag	Forest soil (lab)	$5.9 \pm 2.2 \times 10^{-11}$
Cu slag	Acidic sand (lab)	$1.1 \pm 0.9 \times 10^{-11}$

2005). Only a small amount of the particle surface is in contact with the polymer support which exposes the majority (~85%) of the particle surface for reactions with the surrounding soil. The detection limit of the quantification method is predominantly based on the analysis of the concentration difference of particles on the support before and after exposure to the soil. A major advantage of the method is that the dissolution can be observed by microscopic investigation of the particles as well as by quantification of the mean dissolution rate. The method can therefore yield both quantitative as well as qualitative data.

4.2. Dissolution rates

Although dissolution rates had been measured for some of the components of the particles used in our study (e.g., fayalite, pyrite) (Siever and Woodford, 1979; Parsons et al., 2001), dissolution rates of composite mineral compounds consisting of these phases have never been determined before. The copper concentrate used in this study is composed of several different phases, in particular chalcopyrite and pyrite. We were unable to find data on dissolution rates for the composite particles, although these are the forms in which these minerals are actually released into the environment. However, dissolution rates have been measured for some of the components (pyrite, chalcopyrite) of these particles in acidic solutions (Abraitis et al., 2004). In a laboratory column experiment Nicholson et al. (1990) found significant surface alterations (cracks, surface spalling) on pyrite minerals after a period of several months. Nahon (1991) reported that sulfidic ore minerals generally begin to oxidize in <1 year. Williamson and Rimstidt (1994) observed dissolution rates of 8.8×10^{-9} mol Fe m^{-2} s^{-1} for pyrite in a laboratory batch experiment. Given these data, we expected a significant dissolution of the copper concentrate particles under the acidic soil conditions because pyrite was a major constituent of this material. However, the material proved to be stable for the investigated time period of 18 months because we observed neither dissolution
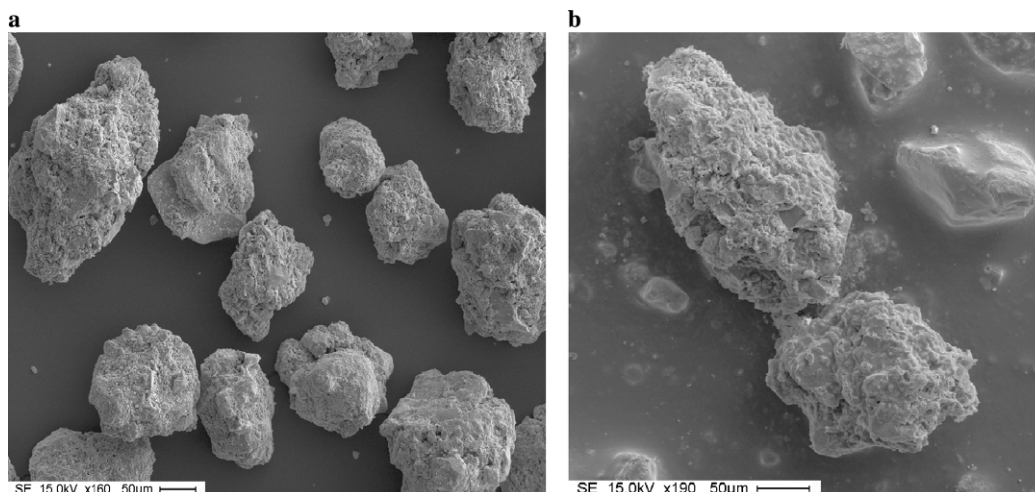
Fig. 4. SEM microphotographs of copper concentrate particles before the experiment (a) and after 8 months, (b) in the acidic forest soil under field conditions.
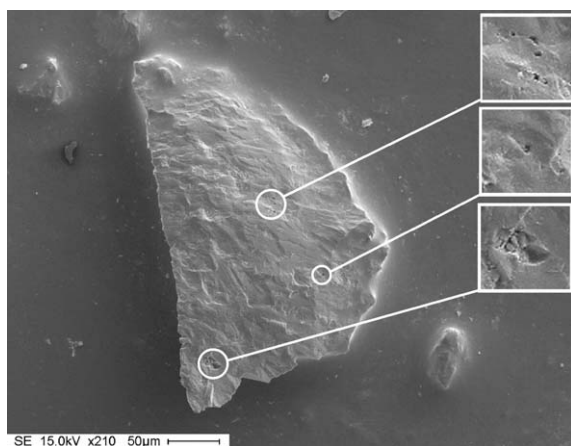

Fig. 5. SEM microphotograph of a copper slag particle after 15 months exposure to the acidic forest soil. Circles indicate minor dissolution features on the particle surface.

features nor a decrease in the Cu content of the material. Inhibition of pyrite oxidation by humic acid and oxalate (Belzile et al., 1996), silicate (Kargbo and Chatterjee, 2005) and metal cations (Bostick et al., 2000) has been reported. These compounds are all present in soil solution and may have retarded the dissolution to below our detection limit.

The copper slag was also a mixture of different phases, mainly fayalite and magnetite. The dissolution rates of copper concentrate and copper slag particles given here refer to the release of Cu and not of Fe. The slag had a molar Fe/Cu ratio of 68. If we assume that the ratio was the same in the component phases and that dissolution of fayalite and magnetite occurred at the same rate (see Table 4), then we can transform the dissolution rate to 2.9×10^{-9} mol Fe m^{-2} s^{-1}. Table 4 shows an overview of reported dissolution rates of slags or some of the components of the slag at pH values similar to our study. The used methods varied significantly between the different studies and no data are available for the behavior of these phases under natural conditions. The observed in situ value for the slag lies at

the upper end of the reported dissolution rates. It therefore seems that dissolution under field conditions is accelerated relative to laboratory-based studies. However, more studies with composite mineral phases under natural conditions are needed to understand the inhibition or enhancement of the dissolution of different composite mineral phases (e.g., Cu concentrate or slag) in the environment.

4.3. Comparison of in situ field with laboratory dissolution rates

The data obtained in the field soils (Fig. 2) show significantly more scatter than the laboratory data (Fig. 6), except for the copper slag particles. This indicates that conditions were more heterogeneous with respect to the local geochemistry or hydrology in the field than in the laboratory, although the soil material was the same. However, this is what we would expect since the laboratory soils were thoroughly homogenized and evenly irrigated.

The PbO particles buried in pots with the acidic forest soil in the laboratory showed the same dissolution features than the particles in the field experiment. Presumably similar processes are therefore responsible for the dissolution in both cases.

According to the literature dissolution usually occurs faster in the laboratory than in the field (Swoboda-Colberg and Drever, 1993; White and Brantley, 2003). Indeed, we also observed that dissolution of PbO was 40 times faster in the stirred solution than in the field. In most instances when dissolution rates have previously been compared between field and laboratory experiments, the laboratory rates originated from batch experiments, flow-through reactors, saturated columns or fluidized bed reactors (Wogelius and Walther, 1992; White et al., 1994; Strömberg and Banwart, 1999a; White and Brantley, 2003). Under these conditions the particles are continually flushed and reaction rates are not limited by lack of moisture or by the build-up of diffusion gradients.
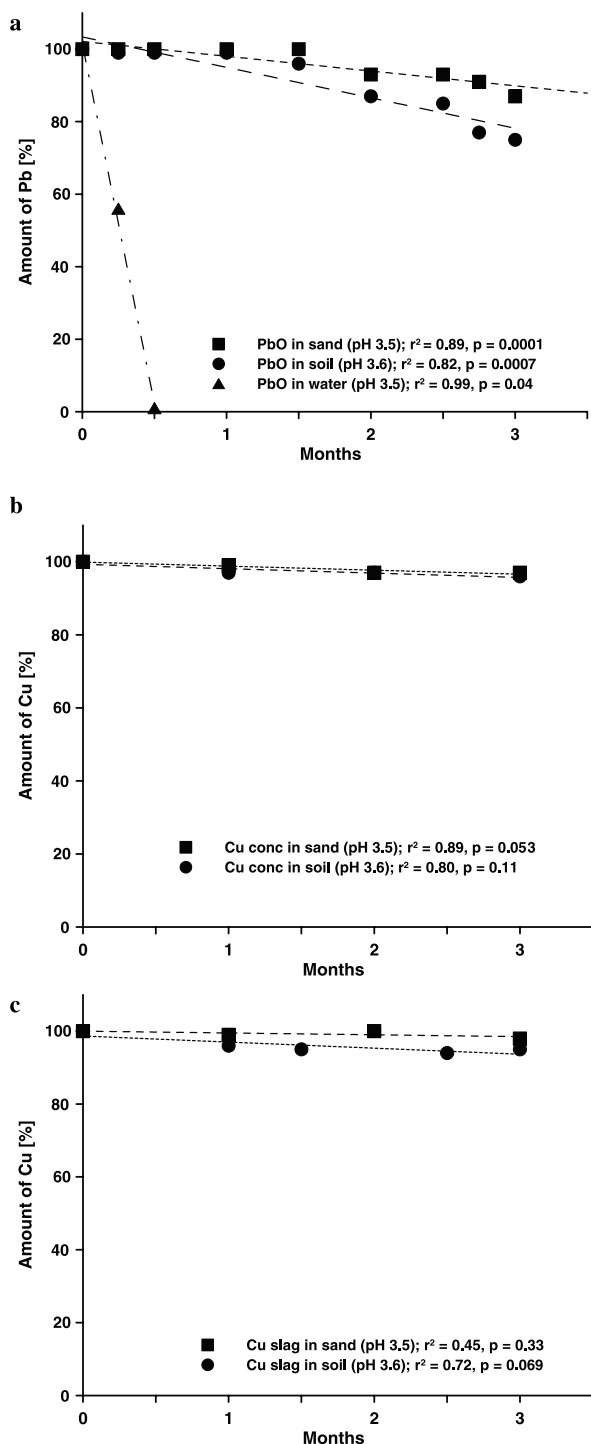
Fig. 6. Dissolution of lead oxide (a) copper concentrate, (b) and copper slag particles, (c) under laboratory conditions in acidic forest soils, sand percolated by HNO_3 solution with pH 3.5 and in stirred HNO_3 solution with pH 3.4 (only for PbO). The results are expressed as mass of metal recovered in percent initial mass of metal (determined by XRF).

The rates measured in the field were generally higher than the rates determined for soil or sand in the laboratory. The lead oxide dissolution rates followed the order sand (pH 3.5) < soil (laboratory) < soil (field) < solution (pH 3.5).

Dissolution of PbO was 1.3 times faster in the field than in the same soil in the laboratory. Dissolution in the acidified sand was 3 times slower than in the field at the same pH. The dissolution rate calculated for Cu smelting slag was 4 times faster in the field than in the acidified sand, but only 73% of the rate measured in the soil in the laboratory (Table 3). We used the identical test samples in all experiments and the same procedures in the field and in the laboratory to place them into the soil. The most obvious differences in the experimental conditions were the temperature, the moisture regime, the disturbed soil structure and the biological activity. The mean temperature in the field was 9 °C (Ø 18 months) while the laboratory temperature was around 20 °C. Therefore, we would anticipate that the higher temperature would result in accelerated dissolution rates in the laboratory.

Given that most dissolution reactions are pH-dependent (Furrer and Stumm, 1986; Wieland et al., 1988; Schnoor, 1990), variations in soil solution pH between laboratory and field exposure may also lead to different dissolution rates. The pH value of the used soil was measured in a soil slurry in 0.01 M $CaCl_2$. The pH in the quartz sand was established by percolating an acid solution with pH 3.5, resulting in a soil solution pH of about 3.5–3.9 at the depth where the supports were buried. While the average pH was therefore comparable in the field and in the laboratory, seasonal fluctuations in pH over time in the field may have affected the dissolution rate.

Another important factor is the moisture content of the soils. Due to the large variability in moisture conditions of field soils, Swoboda-Colberg and Drever (1993) consider this factor a major source of uncertainty in field weathering experiments. This uncertainty includes the potential influence of preferential flow events. Hornberger et al. (1990) discussed the possibility that preferential flow in soil could prevent infiltrating water from passing along the mineral surfaces of the matrix and thus slow down particle dissolution. The pots in the laboratory were watered regularly and the soils thus kept moist all the time. In the field, however, dry periods alternated with wet periods (Fig. 1). Lower moisture should have reduced dissolution. Therefore, the difference in moisture regime does not explain the higher dissolution rates in the field.

The lowest dissolution rates for PbO and Cu slag were found in the sand, which had no biological activity. In the forest soil the particles were under the influence of vegetation, root processes, root-associated fungi, bacteria and leaf litter leaching. Prior to the laboratory experiments the soil was dried and sieved through a 2 mm mesh. Thus most roots, litter and macro fauna were removed from the soil. Fig. 8 shows some fungal hyphae colonizing oxide particles recovered from the field, indicating the intricate relationship between the particles and their soil environment. No such hyphae were found in the laboratory samples. The importance of fungi for mineral weathering has been reported frequently (Pohlman and McColl, 1988; Hinsinger et al., 1993; Banfield et al., 1999; Burford et al., 2003), and the SEM pictures which could be obtained with our in situ technique gave direct morphological evidence of the close
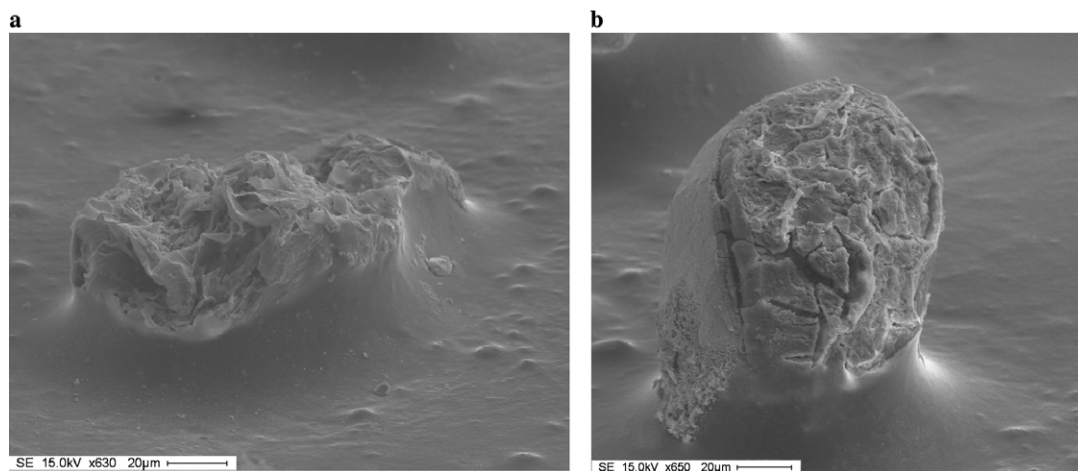
Fig. 7. SEM microphotographs of lead oxide particle dissolution in a laboratory pot experiment. (a) Dissolution after 3 months in an acidic forest soil, (b) dissolution after 3 months in a quartz sand irrigated with HNO_3 solution (pH 3.5).

Table 4
Dissolution rates in $mol\, m^{-2}\, s^{-1}$ reported for various mineral phases equivalent to those used in this study

| Phase	Conditions	Rate	Reference
Copper slag	Synthetic soil solution at pH 2–3	5.7×10^{-16} mol Fe $m^{-2}\, s^{-1}$	Ettler et al. (2002)
Base metal slag	TCLP leaching test at pH 3.6	4.7×10^{-10} mol $m^{-2}\, s^{-1}$	Parsons et al. (2001)
Fayalite	Fluidized bed reactor at pH 3.6	3.9×10^{-9} mol Fe $m^{-2}\, s^{-1}$	Wogelius and Walther (1992)
Fayalite	Batch reactor at pH 4.5	1.7×10^{-11} mol Fe $m^{-2}\, s^{-1}$	Siever and Woodford (1979)
Magnetite	Batch reactor at pH 3.6	1.6×10^{-11} mol Fe $m^{-2}\, s^{-1}$	White et al. (1994)
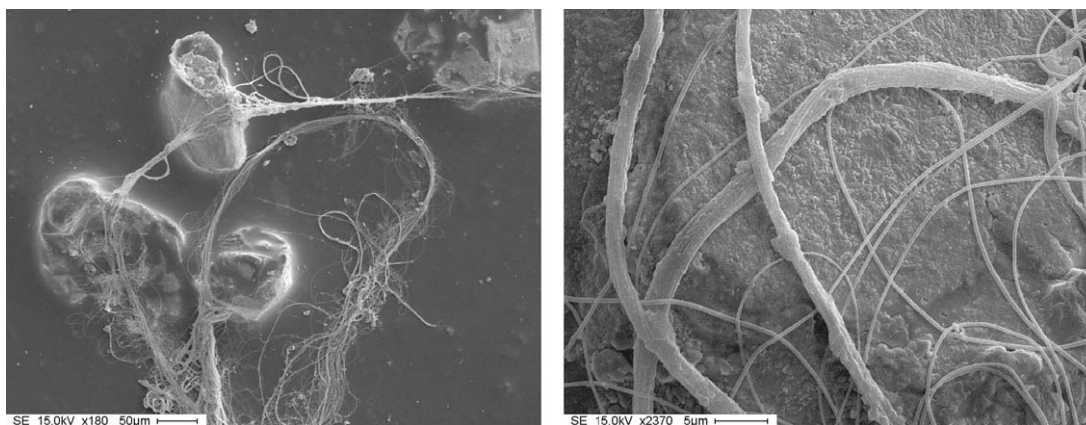
Fig. 8. Fungal hyphae on lead oxide particles recovered from the acidic forest soil.

interaction between fungi and the particles. The accelerated rates measured in the field compared to the same soil in the laboratory may point to a significant contribution of biological processes. Whereas the biological contribution to the weathering of minerals containing nutrients (e.g., phosphate or calcium) is well known (Ranger et al., 1991; Bennett et al., 1996; Jongmans et al., 1997; Rogers et al., 1998; Banfield et al., 1999; Burford et al., 2003), it is less understandable that potentially toxic minerals such as PbO which do not contain any nutrients are actively dissolved by biological processes. However, higher biological activity may also lead to higher concentrations of dissolved organic carbon (Kalbitz et al., 2000). Francis and Dodge (1986) showed that microbial activity and organic acids increased

the dissolution of PbO particles in comparison to pure inorganic acidified (HNO_3) solutions. The capacity of the dissolved organic carbon to solubilize metals is well known (Hering, 1995). The faster dissolution rate in the field soil compared to the laboratory soil or the quartz sand can therefore also be attributed to the presence of DOC in soil solution that accelerated the dissolution in addition to biological processes.

5. Conclusions

Three types of particles were used to study mineral dissolution in an acidic forest soil under field and laboratory conditions over a period of 18 months. Lead oxide particles

dissolved about 5 times faster than copper concentrate particles and copper smelter slag particles. The use of an in situ method allowed determining dissolution rates and micromorphological weathering features on the particles. To our knowledge this is the first time that dissolution of fine particles was analyzed quantitatively under in situ field conditions.

The experiments did not confirm the expectation of higher dissolution rates in the laboratory compared to the field. The higher average temperature and the higher average moisture content in the laboratory would have lead to an expected increase in the dissolution rate. However, rates measured in situ in the field showed a tendency to faster dissolution rates. This points to a significant contribution of the more intensive biological activity, e.g., from plant roots and fungi, under field conditions, and the coupled higher DOC concentrations.

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