

A New In Situ Method to Analyze Mineral Particle Reactions in Soils

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We developed a simple method to monitor the transformation of particles in soils under in situ conditions. The particles were fixed on small polymer supports (2 cm × 2 cm) with a thin film of epoxy resin. Attached to these carriers, the particles could be put into close contact with soil at a chosen site and easily recovered after extended periods of time. The method was tested with lead oxide and copper concentrate in the field. Quartz and copper oxide particles were used in preliminary laboratory experiments. The used particles sizes ranged from 20 to 200 μm. Laboratory and field experiments with acidic and calcareous soils showed that the PbO and Cu concentrate coated polymer supports were stable under field conditions for at least one year. Nondestructive X-ray fluorescence spectroscopy was used to quantify the metals before and after exposure. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy as well as micro-Raman spectroscopy was used to identify signs of dissolution and newly formed mineral phases. The mineral dissolution rate could be determined under field conditions. The new method has the potential to be used in other environmental media such as sediments or water to study the reactions of a variety of particles larger than 20 μm.

Introduction

Soils represent an important sink for heavy metals released by human activities into the environment (e.g., through industrial processing, mining, agricultural application of metal-containing products and wastes, or traffic emissions) (1). Abandoned mine sites, tailing dumps, or accidental spills (2) as well as metal smelters and waste incinerators are possible contamination sources of particulate metals. Large quantities of these particulate emissions end up in soils via atmospheric deposition (3). There, they are dissolved and transformed into new phases with time. As this may strongly affect the mobility, reactivity, and bioavailability of the polluting metals, knowledge about these phase transformation processes and their kinetics is crucial for the long-term site assessment of such particular pollution (4).

The dissolution and transformation of solid heavy metal phases in soil have frequently been studied in laboratory systems (5, 6). However, reaction rates measured under laboratory conditions can be very different from rates determined in situ in soils and sediments (7–9). The weathering kinetics of silica minerals, for example, was found to differ by some orders of magnitude between laboratory and field experiments (10–12). Reasons for this discrepancy were reported to be, for example, differences in thermody-

namic saturation conditions between column effluents and natural waters (12) as well as problems in defining and measuring surface areas of natural porous media or decreasing reactivity with time (13).

Some attempts have been made to study the reactions of heavy metal particles under field conditions. Test mineral particles were mixed into a topsoil horizon in the field (14). This experimental approach disturbed the soil system in a massive way by means of mixing the test particles with the previously undisturbed soil. This is a major drawback of the method while it provides direct soil–particle contact. The following analysis steps of the in situ reacted particles can be carried out by synchrotron based XAS techniques such as XANES or EXAFS and give detailed information about newly formed mineral phases in soils (15) as well as micro-XRD techniques (16).

Perforated (1 mm Ø) polypropylene bottles filled with minerals chips of a millimeter to centimeter scale (9, 17) have been used for mineral transformation studies in stream sediments and in groundwater (18). This method needs saturated conditions and has therefore the drawback that it cannot be used in unsaturated soils. Furthermore, the minerals are not in direct contact with the soil matrix.

The in situ behavior of minerals has been studied in soils under environmental conditions by means of placing small porous (20 μm Ø) bags filled with test particles into soils (19, 20). This technique ensures that at the end of the incubation time, the remaining minerals can be completely recovered and analyzed. The mineral grains, however, are not in direct contact with the surrounding soil. Microbial colonization, the interaction with roots and fungal hyphae, is excluded by the bag material. Furthermore, particles inside the bag are not in contact with soil solution but with a solution that has been altered by the large amount of particles present inside the bag. These methods cannot be applied to fine particles and dusts because of the potential loss of particles through the sample container perforations.

The sparse amount of available literature about the reactions of fine particles and nondefined phases indicates the methodical and analytical difficulties of determining the transformation of these mineral phases in soils under in situ conditions. To our understanding, an experimental in situ method applied to soils and sediments will always have to disturb the systems to place samples for reaction into the system. However, a new method should at least minimize this disturbance while maximizing the soil–mineral contact. Our objective therefore was to develop and test a simple method to monitor such transformations of fine particles in terrestrial systems. The general concept of the new method was to fix particles on polymer plates so that they can be put into direct contact with soil or another matrix and subsequently be recovered without losses other than by the weathering process to be investigated.

Materials and Methods

Polymer Supports. Poly(methyl methacrylate) (PMMA) polymer (Plexiglas/Acrylite) was used as the base material for the supports. PMMA is highly resistant against weathering and has excellent mechanical and chemical properties (21–23). The PMMA polymer supports can remain for long times (years) in field experiments under environmental conditions without decomposition (23). The material is environmentally inert and does not release or accumulate any chemical substances (21). PMMA is certified to be used

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TABLE 1. Origin, Particle Size Ranges, and Surface Areas of Particles Used in This Study

	unit	lead oxide (PbO)	copper oxide (CuO)	copper concentrate	quartz sand
supplier		Pennaroya Oxide, Germany	Merck, Germany	Mining Industry, Chile	Fluka, Switzerland
particle size	μm	20–100	80–200	20–100	100–200
BET surface	$\text{m}^2 \text{g}^{-1}$	0.11	2.67	1.27	0.08 ^a

^a Data taken from ref 30.

for food and medical applications. According to the European standard EEC 90/128 (24), it is physiological harmless, which emphasized its suitability for environmental studies. The supports were pre-cut and fine molded into squares of 2 cm \times 2 cm. The size was chosen to fit the sample holder of the X-ray fluorescence spectrometer, which was used for the analysis of the samples. Every support was cleaned with ethanol to remove any traces of the cooling fluid that had been used in the cutting process. Each plate was weighed with an analytical balance (Mettler AT 261, Switzerland) to an accuracy of 0.0001 g, and the individual weight was carved into the reverse side. The carving did not change the support mass, which was proved by a weighing test on $N = 10$ supports performed on the same analytical balance. The thickness of the supports was chosen to be 2 mm to avoid torsion and bending of the material during further processing.

Epoxy Resin. To fix the particles, a film of a two-component epoxy resin (Bisphenol A resin, Suter, Switzerland) was applied onto the polymer supports. A resin with relatively high dynamic viscosity (7000 mPa s) was used to minimize creeping onto the particles due to the capillarity effect. Hardened epoxy resin has excellent mechanical and chemical properties to withstand ambient conditions without losing its adhering characteristics (25, 26). The resin is certified to be used for shipbuilding (25), which makes it suitable to be used under environmental conditions in the presence of water.

Coating Process. A set of 10 weighed and marked supports was placed in two rows in a custom-made holder made of a PMMA plate (Plexiglas/Acrylite). The center part of the plate was countersunk to a depth of 2 mm to make the polymer support surfaces level with the holder. The supports were pressed against the outer frame by means of a pressure plate of 2 mm thickness, which pushed against the supports by means of two screws.

Five milliliters of well-mixed two-component epoxy resin was put in a paint tray. A commercially available micro-foam paint roller was wetted with resin by touching the resin surface. Then, to enhance permeation of the resin, the roller was rolled 10 times on the tray. This resulted in a homogeneous distribution of the resin in the paint roller. The resin-loaded roller was scrolled four times over the polymer supports, resulting in a thin epoxy resin layer. After a prereaction time of 10 min, the frame with the epoxy prepared supports was placed in a spray chamber of 2 m length, 1 m width, and 1 m height. The chamber was shielded with polyethylene sheets and connected to the laboratory air extraction system. Selected particles/minerals were applied onto the support surfaces by using a dust spray gun from a commercial hardware store. It was found that this dust spray gun had elevated particle consumption, so a downsized version was constructed (Figure 1S, Supporting Information). Reducing the size of the spray device allowed us to handle much smaller amounts of particles than with the original spray gun. Furthermore, we mounted the particle reservoir on the top of the spray gun instead of on the bottom. This allowed us to reduce the air flow as sufficient particles fell into the device by gravity.

Particles were applied from a distance of 1.5 m to the supports holding the spray gun perpendicular to the frame with the supports. Gentle movement of the dust spray gun

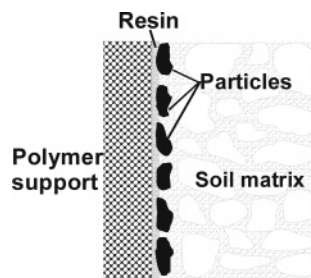


FIGURE 1. Schematic sketch of the particles attached to a polymer support through a thin resin layer. The particles' surface area, which is not covered by the epoxy resin, is in direct contact with the soil matrix and open for reactions.

during application (30 s) resulted in relatively homogeneous coverage. The supply of compressed air was adjusted to a working pressure of 0.15 Mpa, providing a smooth air flow with homogeneous particle distribution preventing particle damage upon epoxy resin impact. Directly after the application process, the supports were removed from the frame and placed on a tray for the hardening of the resin (hardening time according to the resin manufacturer) under ambient laboratory conditions. The particle mass on the supports was determined by subtracting the mass of applied resin and the mass of the support from the total weight of the coated support. Table 1 gives an overview of the selected particulate materials used in this study. Figure 1 shows a schematic sketch of the method. The drawing shows the polymer support as the carrier material with the thin film of epoxy resin. On the resin the particles are fixed, exposing their surfaces directly to the soil matrix. Unlike the previously presented methods, this approach ensures a close and direct contact of the test particles with the surrounding soil. Recovery of the exposed particles after incubation allows the determination of dissolution and transformation rates and the examination of the changes that occurred during exposure to the soil environment by a broad range of analytical techniques.

Insertion into Soil. Each polymer plate was analyzed by energy dispersed X-ray fluorescence analysis (XRF) (Spectro X-Lab 2000, Germany) for the initial amount of metals. A thin thread of nylon (fishing line) was attached to the backside of the supports with a small drop of epoxy resin as glue. Then, the polymer supports were implanted into field soils with the help of a small lancet made of stainless steel. The bottom of the lancet was flattened to facilitate penetration into soil. The implanting device was pushed into the soil to a depth of 20 cm and bent forward to open a small slit. The polymer support was inserted into this slit, and its particle-coated side was pressed against the soil. Then, the slit was closed again by inserting the lancet 5 cm away from the slit and bending it toward it. The thin nylon thread attached to the support marked the location where the support was buried (Figure 2S, Supporting Information). At the end of the chosen incubation time, the plates were removed from the soil by digging them out with the adhering soil. The recovered supports were immersed for some minutes into a distilled water bath to loosen attached soil particles, and this was supported by careful light strokes with a soft brush. Supports buried in sandy or loamy soils had only a small

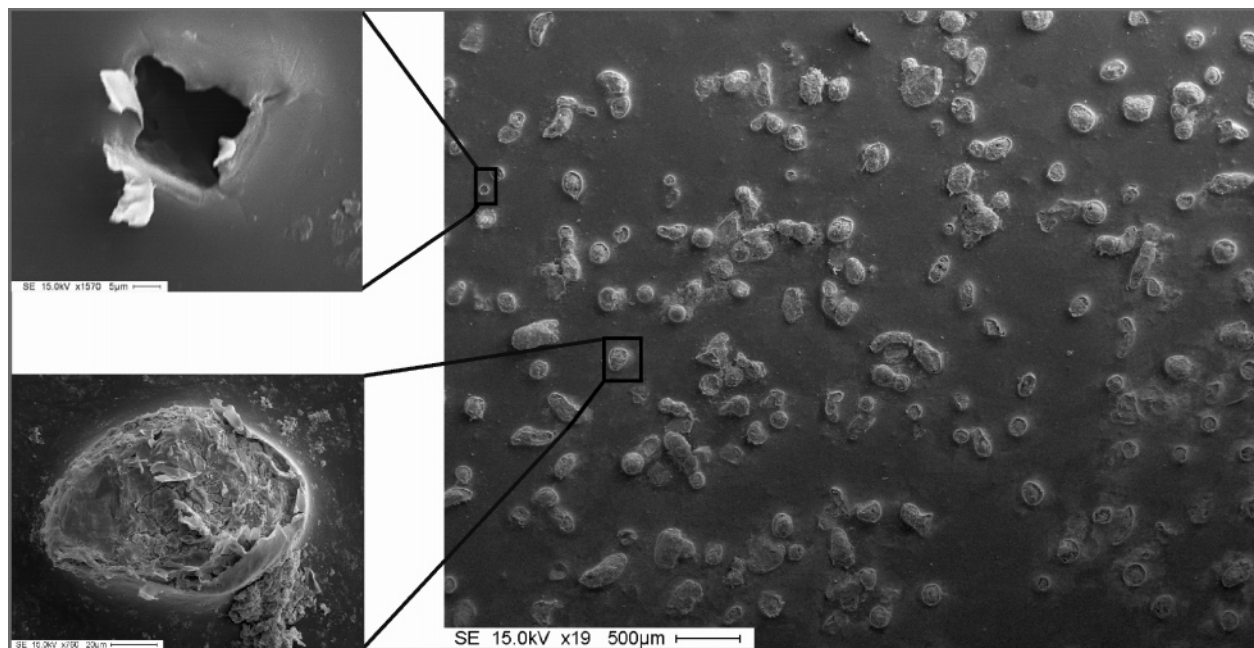


FIGURE 2. Support covered with PbO and buried in acidic soil for 18 months. Traces of a fallen off particle are shown in the top left picture. A partially dissolved particle is shown in the bottom left picture.

amount of attached particles that were very easy to remove. The samples were then left to dry at room temperature overnight. Stereomicroscopy was used to get a first overview of dissolution signs or newly formed mineral phases on the particle surface. Scanning electron microscopy, SEM (Obducat CamScan CS44, Sweden), in combination with a microscope attached EDX probe (Edax ECON) was used to analyze surface changes on the mineral particles as well as to identify the elemental composition of newly formed phases. Micro-Raman spectroscopy (Jobin Yvon Horiba LabRam HR, France) was used to analyze newly formed mineral phases.

Estimation of the Exposed Surface Area of Particles. The specific surface area of the mineral particles was determined in advance by BET analysis (Micromeritics Gemini 2360, Great Britain) using nitrogen gas as an adsorbant. A set of PMMA supports coated with copper oxide (Merck Chemicals, Germany) as a test substance was used to determine the free exposed surface of the particles. The exposed surface describes that part of the particle surface that is not in contact/covered by epoxy resin but in free contact with the soil (Figure 1). This surface part of the minerals can take place in potential phase transformation reactions. Phenylphosphonic acid (PPA) (Fluka Chemicals, Switzerland) was adsorbed on the copper oxide coated supports and on copper oxide in bulk suspension. PPA was used because phosphonic acids are known to strongly absorb onto almost all mineral surfaces (27). For the copper oxide supports, a concentration range of 5–60 μM PPA was used, and for the copper oxide in suspension, a range of 5–500 μM PPA was used. Pure PMMA supports and resin only covered supports without particles were used as control samples. The PPA solutions were buffered at pH of 7.1 with a 2 mM morpholinoethanesulfonic acid (MES) solution (Fluka Chemicals, Switzerland). The concentration measurements were carried out by ion chromatography (Dionex DX100).

Mechanical Stability. To test the stability of the particle coating, two separate experiments were carried out. The first experiment was intended to simulate the abrasion forces during the insertion process. Supports were coated with quartz sand to simulate particles, and then a semi-hard paintbrush was stroked about 10 times over the surface. The

loss of particles was determined as the difference between weights before and after the experiment. In addition, we examined the supports for traces of detached particles by means of optical and electron microscopy. The lost particles could be clearly noticed because they left behind empty cavities in the epoxy resin (Figure 2).

The second test was intended to simulate particle dissolution. Polymer supports were coated with lead oxide particles (approximately 50 mg support⁻¹) and then submerged for 12 h in a stirred 0.1 M EDTA (Merck Chemicals, Germany) solution at pH 5. Micro-photographs were taken before and after the incubation through a stereomicroscope (Zeiss Stemi 2000-C, Germany). In addition, SEM pictures were taken from parts of the incubated support where indications of particle dissolution were found in the stereomicroscope photographic pictures.

Calibration of XRF. XRF was used to quantify the metal content of the supports before and after recovery. A custom-made calibration was performed for all used particles. A set of 15 supports, coated with PbO, was incubated for various times (1–240 min) in a 0.1 M EDTA solution at pH 4.5 to obtain different concentrations of PbO and quantitatively analyzed by XRF. After the XRF analysis, the remaining particles of the supports were completely dissolved by microwave-assisted dissolution (Milestone ETHOS, Italy; 0.1 M EDTA, pH 4.4, 150 W, 60 min), and the dissolved Pb was quantitatively analyzed by flame-AAS. With the acquired calibration, it was then possible to obtain the actual elemental concentration on the individual support by means of the noninvasive XRF analysis.

Soil Experiments. The method was tested in pot experiments under laboratory conditions. PMMA support samples were buried at a depth of 5 cm in polypropylene pots filled with weakly acidic silty clay and acidic loam soil (Table 2). The pots were irrigated with synthetic rain (made from p.a. grade chemicals, Fluka Chemicals, Switzerland and Merck Chemicals, Germany) of the following composition: P 0.1 mg L⁻¹; Na 0.1 mg L⁻¹; K 0.3 mg L⁻¹; Ca 0.2 mg L⁻¹; Mg 0.03 mg L⁻¹; Zn 0.01 mg L⁻¹; Cl 0.6 mg L⁻¹; SO₄ 0.3 mg L⁻¹; and N 3.5 mg L⁻¹. The pH was adjusted to a value of 5.5 by HCl. The irrigation was applied with a multichannel peristaltic pump (Ismatec BVP-12, Switzerland) and distributed through

TABLE 2. Properties of the Test Soils

soil origin	loam forest	silty clay agriculture	calcareous loam pasture	calcareous sand Pleistocene sand deposit
pH (in 0.01M CaCl ₂)	3.8	6.6	7.5	8.1
carbonate content (%)	<0.4	<0.1	7.2	35.1
organic matter content (%)	2.5	1.5	3.1	0.1
grain size distribution (clay-silt-sand) (%)	21-50-29	36-49-15	25-40-35	5-7-88

perforated tubing, at a rate corresponding to the average precipitation of 1100 mm per year for Zurich. The same peristaltic pump was also used to collect the drainage water. The experiment was run for 4 months at 20 °C (room temperature).

In addition, field experiments were carried out where PbO and Cu concentrate-coated supports were placed for up to 18 months in a calcareous sandy soil (pH 8.1) and an acidic silty forest soil (pH 3.8). The supports were inserted at a depth of 10 cm. Soil properties are given in Table 2.

Results and Discussion

Durability of Supports. In contact with acidic (pH 3.8) and near neutral (pH 6.6) soil (Table 2) as well as in acidified water (pH 3.0), the polymer supports did not show any visible changes over the incubation period of 4 months in the laboratory pot experiments. Also in the field, where supports were incubated for periods of up to 18 months, we observed no changes in the PMMA support material. The weight carving on the backside of the support was not affected and clearly readable after these time spans. Also, the epoxy resin did not show any signs of degradation in the tests. Neither neutral or acidic conditions affected its structure.

Coating Process. In first trials, the spray device was used as obtained by the supplier. However, the material consumption rate was found to be too high (100 g of particles per 30 s spray time), making the use of small sample amounts impossible. Therefore, the device was downsized to a reasonable scale (Figure 1S, Supporting Information) with an optimal material consumption rate. The downsized dust spray gun enabled us to apply 15 g of particles per 30 s spray time. To ensure a consistent, gravity enhanced particle flow, the material reservoir was changed from the bottom to the top of the dust gun. The adjusted working air pressure for the spray device provided a gentle airflow transporting the particles homogeneously toward the supports. The viscosity of the applied epoxy resin attenuates the impact forces of the particles on the support surface preventing them from potential harm. Particle damage could be excluded by comparison of pure bulk particles with particles applied with the spray device onto the supports.

The average amount of epoxy resin on the support surface ($N = 30$) was 0.011 g with a standard deviation of 6.0%. The average mass of lead oxide particles fixed to the supports in one test experiment was 0.047 g ($N = 20$), with a coefficient of variation of 11.5%. Figure 3 shows that the particles were evenly distributed on the surface of the support in a monolayer. Only their rear side was covered by resin.

Preliminary tests showed that the application of particles by simple sprinkling with a brush or fine meshed sieve did not provide a homogeneous particle cover.

The homogeneity of the coating can be increased by narrowing down the width of the size distribution of the particles. Tests with epoxy resins of various viscosities showed that resin with low viscosity tended to creep onto the particles and sometimes completely covered them. This effect was particularly pronounced for relatively small particles. The use of a high viscosity resin reduced this effect, but for very small particles it was still a problem. Tests with a variety of different materials showed that the particles should have a minimum size of 20 μm diameter.

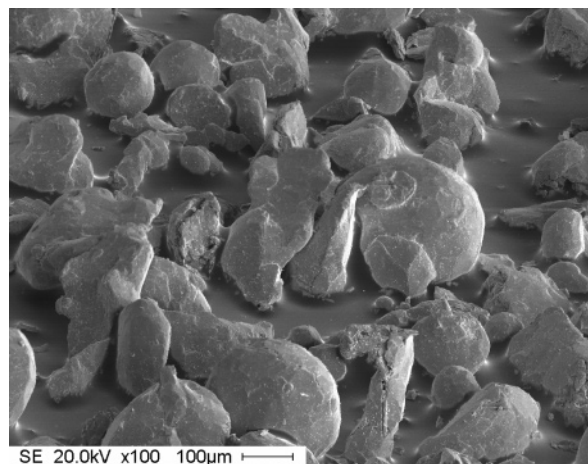


FIGURE 3. SEM microphotograph of initial PbO particles on the support.

Mechanical Stability. A major concern of the method is that particles could be lost from the support during exposure and analysis. The effect of sample handling was analyzed by means of an abrasive brush test. The test results confirmed the stability of the test coating on the PMMA supports. Only 0.0022% of the applied sand particle mass was lost on average ($30 \pm 14 \mu\text{g}$ from 0.048 g per support). Thus, particle losses due to abrasion during the handling, insertion, and recovery of the coated supports were considered to be negligible.

Also, potential weathering during exposure time did not weaken the adhesion of the particles to the resin. SEM pictures and stereomicroscope photographs showed only very few empty cavities in the resin surfaces or other signs that would have indicated that particles had fallen off. In Figure 2, both an empty cavity and a partially dissolved particle are shown and are distinguishable without problems. In all tests, particles were dissolved partially at their exposed surfaces but remained attached to the epoxy resin surface. Particle counts on recovered supports ($N = 8$), which had been buried up to 18 months in different soils, showed that a negligible amount of particles had fallen off the reacted support. Table 3 shows individual results for different soils from the particle counting. This confirmed that extended field incubation times (greater than one year) did not result in the loss of particles due to the insertion, recovery, and cleaning process. Neither the soil pH, the soil texture, or the changes between summer and winter with freezing and thawing and wet and dry periods affected the samples. The small percentage of observed PbO and Cu concentrate particle loss was considered to be within the acceptable experimental error.

Exposed Surface Area of the Attached Particles. The adsorption experiment with phenylphosphonic acid (PPA) on copper oxide coated supports and copper oxide in suspension resulted in two Langmuir adsorption isotherms. Figure 3S (Supporting Information) shows that the adsorption of PPA to particles fixed on supports differed only slightly from sorption to particles in suspension. The conclusion is that only a small fraction of the surface area of the particles was covered by resin. This finding could be confirmed by SEM photographs of support attached particles, showing that an area smaller than about 10% of the particle surface is

TABLE 3. Loss of Particles from Supports after Incubation Times up to 18 Months (Field and Laboratory Data)

material	laboratory/field	soil	% particles loss	incubation time (months)
PbO	F	calcareous sand	<0.2	18
PbO	F	acidic loam	0.5	18
PbO	L	calcareous sand	0.4	4
PbO	F	silty clay	<0.2	18
PbO	F	acidic loam	0.3	18
PbO	L	acidic loam	0.6	4
Cu concentrate	F	silty clay	0.2	18
Cu concentrate	L	acidic loam	<0.2	4

covered by resin. We have assumed that a spherical particle such as PbO is covered to a maximum of 10% of its height by resin. This equals to not more than 10% of covered surface.

Quantification. To quantify the amount of mineral dissolution, particles remaining on the support after exposure were analyzed by XRF. The nondestructive XRF is able to quantify each coated support prior to the incubation and therefore to determine individual start and end concentrations of particles for the experiments. For each substance, we made an individual calibration of the XRF. Figure 4S (Supporting Information) shows the calibration of PbO by XRF versus total dissolution AAS analysis. On the *x*-axis, the measured detector counts acquired by XRF are plotted, and on the *y*-axis the actual elemental concentrations per support, acquired by total dissolution, are shown. With this calibration, it is possible to determine the Pb concentration on the individual support by nondestructive XRF analysis. A second order regression explained 95% of the variance ($R^2 = 0.95$).

Repeated XRF measurements ($N = 10$) with a rotation of the analyzed support by 45° turns after each run showed that the orientation of the support in the sample holder had no influence on the result. Repeated XRF control measurements ($N = 3$) of one support over several months also showed that the instrumental drift was no problem. The coefficient of variation was only 0.08%.

Application. The pot experiments in the laboratory as well as the field tests showed that the stainless steel lancet used for implanting the supports in the field worked without problems. It caused only a minor disturbance of the soil. However, each experimental method for studying particle reactions in soil has to disturb the system to be able to expose the particles. In contrast to the other methods, introduced in the beginning of this paper, our implanting technique caused only a small disturbance because it makes only a thin incision into the soil matrix. To maximize the contact of the particles with the soil, the coated support surface was gently pressed against the soil. After the supports had been implanted, no significant openings were left behind in the soil. The attached nylon thread always allowed relocating the implanting locations at the field sites. In our study, we implanted the supports vertically in the topsoil down to a depth of 20 cm. It is also possible to implant the supports horizontally from the wall of a soil pit.

Cleaning the recovered supports with a soft brush in distilled water allowed removal of virtually all of the attached soil particles. Only under the electron microscope (SEM), very few small soil particles (10–15 μm size) could be observed that had been left on the supports. Energy-dispersive X-ray spectra (EDX) of these particles showed clear elemental signs of soil minerals such as Al, Ti, and Fe. Some of these particles can be seen in the bottom right under the particle of Figure 4.

One of the possible reactions of a mineral particle introduced into soil is the formation of a new phase. Figure 5 shows the surface of a PbO grain that had been buried in the calcareous sand (Table 2) for 4 months. Comparison with the original state (inset, Figure 5) shows that fine crystals had grown on the entire surface of the particle. The picture

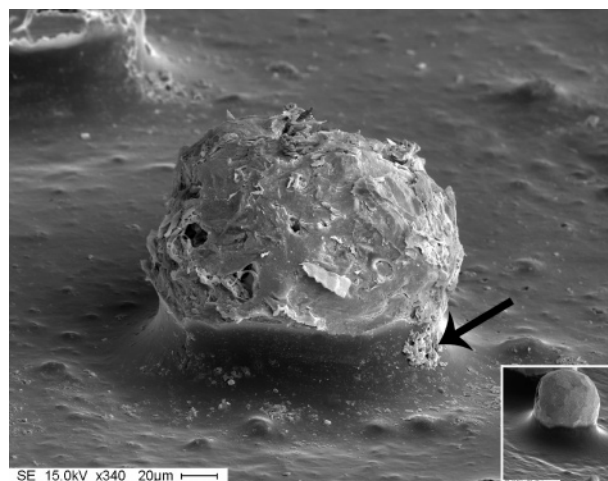


FIGURE 4. PbO particle after recovery from an acidic loam (pH 3.8) after 12 months. Clear signs of dissolution can be seen on the particle surface. The arrow indicates some residual soil particles left over from the cleaning process. The bottom right inset shows an unreacted PbO particle for reference.

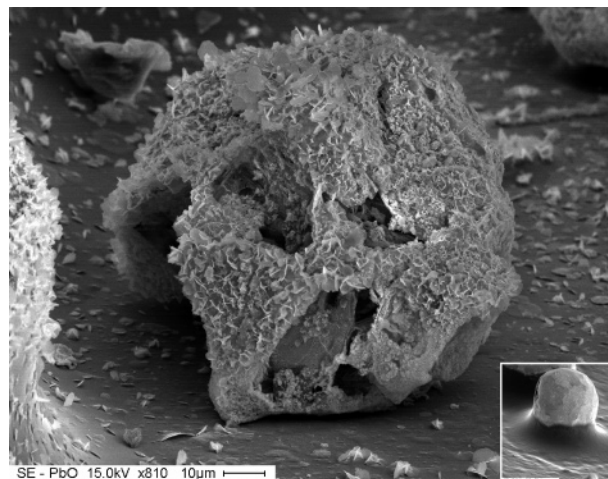


FIGURE 5. PbO particle after recovery from calcareous sand (pH 8.1). A newly formed mineral phase can be clearly seen on the particle surface. This new phase has been identified by micro-Raman spectroscopy as hydrocerussite. The bottom right inset shows an unreacted PbO particle for reference.

shows that even very fine structures and delicate mineral assemblages can be recovered and cleaned of adhering soil particles even after extended exposure in soil under field conditions. The EDX analysis showed that the newly formed metal phase contained lead, carbon, and oxygen. It was identified as hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, by micro-Raman spectroscopy. Formation of lead carbonates in calcareous soils has been previously reported (28, 29).

In addition to mineral transformation, dissolution of the initial phase can also be observed by our new method in

field as well as in laboratory experiments. Figure 4 shows an example of PbO buried in an acidic loamy soil for 12 months. The comparison of this particle with the unreacted particle (inset Figure 4) reveals that significant dissolution occurred during the incubation. PbO is very soluble at a soil pH of 3.8. Still, part of the mineral surface was hardly affected by dissolution. In addition to such qualitative information, the method can also be used to determine weathering rates. To give an example, the metal content of a support equivalent to that shown in Figure 4 decreased from $47 \pm 18 \text{ mg support}^{-1}$ to $36 \pm 13 \text{ mg support}^{-1}$ during 12 months of exposure in the acidic forest soil. This is equivalent to a 24% loss of Pb and corresponds to a dissolution rate of $3.2 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ (normalized to the surface area of the PbO particles).

One of the important advantages of this method is that it provides the ability to measure in a direct way the dissolution rate of fine mineral particulate phases in the field under natural conditions. No preconcentration or refining process is needed prior to the analysis. This ability provides, as far as we know, for the first time direct information on dissolution rates in situ on a particle scale with fine minerals in environmental field experiments. This method will therefore be very useful in the future to refine the insights on the behavior of fine particles or dusts in environmental systems.

Further Applications. This new method is a useful tool for the investigation of mineral transformation and dissolution in different environmental media. We believe that the method can also be used in easier environments such as sediments and natural waters as it showed its applicability to heterogeneous soils. Its main advantage is the easy placement and recovery of the samples and the possibility to obtain both qualitative and quantitative information on mineralogical changes and dissolution rates. Apart from heavy metal phases as used in this study, it may also be used to investigate transformation of other small particles (e.g., silicates) in the environment.

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Supporting Information Available

Four figures showing a scheme of the dust spray gun used to apply the particles (1S), a scheme of the sample insertion process (2S), the adsorption isotherms of phenylphosphonic acid on CuO in bulk suspension and immobilized on the support (3S), and a calibration of PbO for the XRF instrument (4S). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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