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(Editors)

Environmental Chemistry

Green Chemistry and Pollutants
in Ecosystems

With 289 Figures

 Springer

Editors

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Preface

In 1889, the Nobel Prize winner Svante Arrhenius pointed out the existence of a “greenhouse effect” in which small changes in the concentration of carbon dioxide in the atmosphere could considerably alter the average temperature of a planet. About one century later, humans realise that most climate changes are correlated with the increase of the concentration of carbon dioxide in the atmosphere. A such prediction from Svante Arrhenius clearly highlights that more knowledge of environmental mechanisms is needed to cope with actual problems of pollution. Environmental Chemistry is a fast emerging discipline aiming at the understanding the fate of pollutants in ecosystems and at designing novel processes that are safe for ecosystems. Past pollution should be cleaned. Future pollution should be predicted and avoided.

The 69 chapters of this book have been arranged into seven topics that form the core of Environmental Chemistry: Analytical Chemistry, Toxic Metals, Organic Pollutants, Polycyclic Aromatic Hydrocarbons, Pesticides, Green Chemistry, and Ecotoxicology. Most chapters have designed to include (1) a review on the actual knowledge and (2) cutting-edge research results. Thus this book will be useful to students and decision-makers who wish to learn rapidly the essential background of a specific topic, and to scientists who wish to locate the actual frontiers of science in a specific domain.

We wish here to thank all authors for providing high quality manuscripts. We are indebted to Armin Stasch, Luisa Tonarelli and Marion Schneider from Springer for technical assistance. We thank Dr. Christian Witschel, Executive Editor of Geosciences at Springer for having accepted our project to design this book. Last but not least, we thank very much Brigitte Elbisser who has been from 2000 to 2003 the key staff of the European Association of Chemistry and the Environment (ACE), producing Newsletters, taking care of budget and memberships, organising annual meetings, and helping at the book preparation.

Drs. Eric Lichtfouse, Jan Schwarzbauer and Didier Robert

Contents

	Part I	
	Analytical Chemistry	1
1	In-situ Method for Analyzing the Long-Term Behavior of Particulate Metal Phases in Soils	3
2	Analysis of Toxic Metals by Micro Total Analytical Systems (μ TAS) with Chemiluminescence	13
3	Diffuse Infrared Fourier Transform Spectroscopy in Environmental Chemistry	19
4	Detection of Biomarkers of Pathogenic Bacteria by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry	31
5	Multi-Isotopic Approach (^{15}N , ^{13}C , ^{34}S , ^{18}O and D) for Tracing Agriculture Contamination in Groundwater	43
6	^2H and ^{18}O Isotopic Study of Ground Waters under a Semi-Arid Climate	57
7	$^{13}\text{C}/^{12}\text{C}$ Ratio in Peat Cores: Record of Past Climates	65
8	Isotopic Composition of Cd in Terrestrial Materials: New Insights from a High-Precision, Double Spike Analytical Method	75
9	Organic Petrology: A New Tool to Study Contaminants in Soils and Sediments ..	89
10	The Comminution of Large Quantities of Wet Sediment for Analysis and Testing with Application to Dioxin-Contaminated Sediments from Lake Ontario	99
11	Study on the Large Volume Stacking Using the EOF Pump (LVSEP) for Analysis of EDTA by Capillary Electrophoresis	107
	Part II	
	Toxic Metals	119
12	A Framework for Interpretation and Prediction of the Effects of Natural Organic Matter Heterogeneity on Trace Metal Speciation in Aquatic Systems ..	121
13	Binding Toxic Metals to New Calmodulin Peptides	133
14	Leaching of Selected Elements from Coal Ash Dumping	145
15	Storm-Driven Variability of Particulate Metal Concentrations in Streams of a Subtropical Watershed	153
16	A Model for Predicting Heavy Metal Concentrations in Soils	177
17	Phytoremediation of Thallium Contaminated Soils by Brassicaceae	187

18	Mercury Recovery from Soils by Phytoremediation	197
19	Effect of Cadmium and Humic Acids on Metal Accumulation in Plants	205
20	Selection of Microorganisms for Bioremediation of Agricultural Soils Contaminated by Cadmium	215
21	Electrodialytic Remediation of Heavy Metal Polluted Soil	223
22	Electrodialytic Removal of Cu, Cr and As from Treated Wood	235
23	Treatment of Wastewater Contaminated by Mercury by Adsorption on the Crandallite Mineral	243
24	Low Cost Materials for Metal Uptake from Aqueous Solutions	251
25	Removal of Copper(II) and Cadmium(II) from Water Using Roasted Coffee Beans	259
Part III		
Organic Pollutants		267
26	Bioremediation for the Decolorization of Textile Dyes – A Review	269
27	Degradation of the Indigo Carmine Dye by an Anaerobic Mixed Population ...	289
28	Biodegradation of Benzothiazoles by <i>Rhodococcus</i> Bacteria Monitored by ¹ H Nuclear Magnetic Resonance (NMR)	295
29	Biotransformation of Nonylphenol Surfactants in Soils Amended with Contaminated Sewage Sludges	305
30	Quantification of in-situ Trichloroethene Dilution versus Biodegradation Using a Novel Chloride Concentration Technique	317
31	Anthropogenic Organic Contaminants Incorporated into the Non-Extractable Particulate Matter of Riverine Sediments from the Teltow Canal (Berlin) ..	329
32	Behaviour of Dioxin in Pig Adipocytes	353
33	Control of Halogenated By-Products During Surface Water Potabilisation ..	361
34	Organic Pollutants in Airborne Particulates of Algiers City Area	371
35	A Reactive Transport Model for Air Pollutants	383
Part IV		
Polycyclic Aromatic Compounds		391
36	Analysis of High-Molecular-Weight Polycyclic Aromatic Hydrocarbons by Laser Desorption-Ionisation/Time-of-Flight Mass Spectrometry and Liquid Chromatography/Atmospheric Pressure Chemical Ionisation Mass Spectrometry	393
37	Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in Two French Alpine Valleys	409
38	Evaluation of the Risk of PAHs and Dioxins Transfer to Humans via the Dairy Ruminant	419
39	Polycyclic Aromatic Hydrocarbons (PAHs) Removal during Anaerobic and Aerobic Sludge Treatments	431
40	Photodegradation of Pyrene on Solid Phase	441
41	Degradation of Polycyclic Aromatic Hydrocarbons in Sewage Sludges by Fenton's Reagent	449

Part V	
Pesticides	461
42 Pesticide Mobility Studied by Nuclear Magnetic Resonance	463
43 Photo- and Biodegradation of Atrazine in the Presence of Soil Constituents	473
44 Behaviour of Imidacloprid in Fields. Toxicity for Honey Bees	483
45 Impact of a Sulfonylureic Herbicide on Growth of Photosynthetic and Non-Photosynthetic Protozoa	495
46 Abiotic Degradation of the Herbicide Rimsulfuron on Minerals and Soil	505
47 Binding of Endocrine Disrupters and Herbicide Metabolites to Soil Humic Substances	517
48 Potential Exposure to Pesticides during Amateur Applications of Home and Garden Products	529
Part VI	
Green Chemistry	539
49 Carbon Dioxide, a Solvent and Synthone for Green Chemistry	541
50 Mechanochemistry: An Old Technology with New Applications to Environmental Issues. Decontamination of Polychlorobiphenyl-Contaminated Soil by High-Energy Milling in the Solid State with Ternary Hydrides	553
51 Development of a Bioreactor for Cometary Biodegradation of Gas-Phase Trichloroethylene	561
52 Enhanced Solubilization of Organic Pollutants through Complexation by Cyclodextrins	569
53 Chemical Samples Recycling: The MDPI Samples Preservation and Exchange Project	585
54 Photodecomposition of Organic Compounds in Aqueous Solution in the Presence of Titania Catalysts	591
55 Depollution of Waters Contaminated by Phenols and Chlorophenols Using Catalytic Hydrogenation	601
56 Treatment of Wastewater Containing Dimethyl Sulfoxide (DMSO)	615
57 Productive Use of Agricultural Residues: Cements Obtained from Rice Hull Ash	621
Part VII	
Ecotoxicology	629
58 Environmental Metal Cation Stress and Oxidative Burst in Plants. A Review	631
59 The LUX-FLUORO Test as a Rapid Bioassay for Environmental Pollutants	645
60 Effects of Two Cyanotoxins, Microcystin-LR and Cylindrospermopsin, on <i>Euglena gracilis</i>	569

61	A New Bioassay for Toxic Chemicals Using Green Paramecia, <i>Paramecium bursaria</i>	673
62	Detection of Toxic Pollution in Waste Water by Short-Term Respirometry	681
63	Environmental Biosensors Using Bioluminescent Bacteria	691
64	Evaluation of Water-Borne Toxicity Using Bioluminescent Bacteria	699
65	Bacteria-Degraders Based Microbial Sensors for the Detection of Surfactants and Organic Pollutants	707
66	Study of Cr(VI) and Cd(II) Ions Toxicity Using the Microtox Bacterial Bioassay	725
67	Cultured Human Cells as Biological Detectors for Assessing Environmental Toxicity	735
68	Genotoxic Impact of Erika Petroleum Fuel on Liver of the Fish <i>Solea solea</i> ..	743
69	Heavy-Metal Resistant Actinomycetes	757
	Index	769

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Part I

Analytical Chemistry

In-situ Method for Analyzing the Long-Term Behavior of Particulate Metal Phases in Soils

A. Birkefeld · R. Schulin · B. Nowack

Abstract

Soils can act as a sink for anthropogenic and naturally released heavy metals. Among these are heavy metal oxides and sulfides, which are emitted e.g. by mining industry and metal smelting. The dissolution and transformation behavior of these heavy metal phases specifies their fate in the soil and determines whether the metals become bioavailable or could contaminate the groundwater. To gain more information about these dissolution reactions in soils, in-situ methods are needed. We present here a method to fix particulate metal phases on an inert support. This method allows us to expose and recover metal phases in the environment under controlled conditions.

Acrylic glass was chosen as inert polymer substrate for the heavy metal phases as it is stable to weathering. Epoxy resin was used as adhesive film between the acrylic glass support and the heavy metal coating. The fine-grained heavy metal phases are applied onto the epoxy resin using a dust spray gun. The heavy metal coated polymer platelets can be inserted in a controlled way into selected soil profiles and be recovered after definite time intervals. Qualifying and quantifying analysis can be carried out on every single polymer support.

Key words: in-situ method; metal phase transformation; soil pollution; heavy metals

1.1 Introduction

Soils represent an important sink for anthropogenic and natural heavy metals (Alloway and Ayres 1997; Schachtschabel et al. 1998). The fate of heavy metals in the environment is of elemental concern due to potential contamination risks of water, soils and sediments and due to toxicity of heavy metals to plants, animals and humans via the food chain. Soils near urban or industrial settlements have often been polluted by particulate heavy metal phases, mainly through atmospheric transport (Ge et al. 2000). Major anthropogenic heavy metal phases, emitted e.g. by mining and smelting operations, are sulfides (Ketterer et al. 2001) and oxides (Dudka and Adriano 1997). The dissolution and phase transformations of these particulate phases over time influences the bioavailability of the metals in the soil and the transport into the groundwater (Dudka et al. 1995). Knowledge about the physico-chemical phase transformations of heavy metal phases in the long-term aspect is therefore crucial (Ge et al. 2000; Fengxiang and Banin 1997; Li and Thornton 2001). Specific heavy metal phases like oxides can be present in soils even after long time periods (Li and Thornton 2001).

Methods have been established to classify heavy metal phases based on their dissolution behavior from solid phases in soils (Tessier et al. 1979; Brümmer et al. 1986; Ure and Davidson 1995). These sequential extraction methods classify the heavy metals into different groups, e.g. water soluble, exchangeable, organically bound, bound to iron and manganese oxides and bound in silicate structures. These procedures were applied in several studies investigating soils contaminated by mining and smelting activities (Li and Thornton 2001) and on unpolluted soils where heavy metals were added (Ma and Uren 1998). Conversely the exact detection of these phases is not straight forward (Manceau et al. 1996) and generated different approaches for sequential extractions (Ure and Davidson 1995). However, identifying the heavy metal species especially the one from anthropogenic sources is of major concern to assess their toxic behavior in soils (Ford et al. 1999; Henderson et al. 1998; Brümmer 1986).

In the last years extended X-ray absorption fine structure (EXAFS) analysis has also been increasingly used to identify heavy metal phases in soils (Welter et al. 1999; Roberts et al. 2002; Fendorf et al. 1994) but this method is still limited to high metal concentrations. Distinct heavy metal phases have been detected in soils, e.g. lead and zinc in the vicinity of industrial and mining facilities (Welter et al. 1999; Manceau et al. 1996).

To investigate the dissolution and transformation behavior of metal phases directly in the soil an in-situ method is needed. The in-situ dissolution of (soil)-minerals inserted into soil or groundwater horizons has been investigated (Righi et al. 1990; Ranger et al. 1991; Hatton et al. 1987; Bennett et al. 2001). The minerals e.g. vermiculite, were placed in porous bags in the soils and recovered after different time intervals. But these experiments were only designed to investigate soil forming processes. Tsaplina (1996) has reported the behavior of heavy metal oxides mixed into the topsoil of selected locations (PbO, ZnO 500 mg kg⁻¹ and CdO 50 mg kg⁻¹). The samples for this study were collected after four and eight years. Fractions of the applied phases could be recovered by separation from the soil by density fractionation and were then identified by X-ray diffraction (Tsaplina 1996). The final sample analysis showed that about 40 wt% to 50 wt% of the initial heavy metal oxides were still present in the soil.

The sparse amount of literature about the in-situ behavior of heavy metal phases clearly shows that there are methodical and analytical difficulties in this area. In this article we would like to introduce a new in-situ method to investigate the behavior of heavy metal phases in soils (Birkefeld et al. 2004). The concept is to fix the heavy metal phases on a support which can be placed in the soil and which can easily be recovered. This approach allows direct analysis of the heavy metal particles after recovery and determination of their physico-chemical changes. A reinsertion into the soil for further investigation is possible. The method has been developed using heavy metal oxides and sulfides as model substances.

1.2 Experimental

To insert heavy metal phases of interest into the soil with the ability to recover them after certain time segments and to possibly re-apply them, we need the aid of a carrier material. The material should have good mechanical properties for sawing and mill cutting. We choose polymethacrylate (Plexiglas®) because this transparent polymer is resistant to weathering and ageing (Schwarz 2000).

A thin (0.025 g cm^{-2}) layer of epoxy resin (Bisphenol-Epichlorhydrin resin, Suter AG Switzerland) (Suter 1999) was used to mount the metal phases onto the polymer support. Epoxy resin was used due to its resistance against decomposition (Suter 2001). Prior to the application of the resin and the heavy metals, the supports were cut into sections of $2.2 \times 2.2 \text{ cm}$. This size was chosen due to the limited space in the sample holder of the X-ray fluorescence (XRF) analytical instrument. 20 polymer supports were clamped into an acrylic glass frame to hold them together ($11 \times 11 \text{ cm}$). With a commercially available paint roll with a width of 5 cm and a diameter of 3 cm the epoxy resin was applied onto the surface of the polymer supports ($0.12 \text{ g resin/support}$). The frame holder with the polymer supports was placed in a dust sealed chamber with fume extraction hoses. Before the application of the metal phases the epoxy resin covered supports were allowed to dry for 5 min in order to enhance the viscosity of the resin and to avoid complete capillary covering of the applied heavy metal particles. With a commercially available compressed air dust spray gun (SAV 030 025, Schneider Druckluft, Germany) the heavy metal phases were applied from a distance of approx. 1 m (air pressure: 1.5 kg cm^{-2}) onto the epoxy resin covered surface of the supports. The application time (spraying) was 10 seconds. After an overnight drying period at $50 \text{ }^\circ\text{C}$ in a laboratory drying cabinet the heavy metal coated polymer supports were cleaned with a soft brush in deionized water (Nanopure, $>18 \text{ M}\Omega$; 5 ppb TOC) to remove loose excess heavy metal particles from the support surface. After an additional 24 h-drying period at $40 \text{ }^\circ\text{C}$ the polymer supports were ready for use.

The model substance for our method development was a lead oxide from a commercial metal oxide manufacturer (PbO LOX 150 Pennarroya Oxide, Germany). This oxide was produced by direct oxidation of metallic lead and has a minimum content of PbO of 99.8%. Its density is 9.5 g cm^{-3} and the average particle size is about 0.1 mm diameter.

To determine the uncovered, reactive surface area of the particles, adsorption experiments were carried out with phenylphosphonic acid (PPA) (analytical grade; Fluka, Switzerland) in a 0.1 mmolar acetate buffer (pH 4.6). PPA was chosen because of its well-known adsorption characteristics onto a variety of different surfaces e.g. aluminum oxide (Laiti and Öhman 1996). The concentration of the PPA was 10–400 μM . Blank measurements with Plexiglas® and with epoxy resin covered supports showed that they did not adsorb PPA. The initial concentration and the final concentration of PPA after reaction times of 5, 10, 15, 20 and 30 min were measured by ion chromatography analysis (DX 100 ion chromatograph, Dionex USA). The maximum surface capacity of the heavy metal phases was also determined in suspension under the same conditions (10–400 μM PPA in 0.1 molar acetate buffer, pH 4.6). The amount of PPA adsorbed in suspension in mol m^{-2} was then used to calculate the exposed surface area of the resin-immobilized metals. A dissolution experiment with ethylene diamine tetraacetic acid (EDTA) was carried out to get an overview about the dissolution behavior of the mineral substances. The analytical conditions were EDTA 1 mM at pH 4.7 with a reaction time of 1 h.

To establish the amount of heavy metals on each polymer support X-ray fluorescence analysis (XRF) was made on every support before further use (X-Lab 2000, Spectro Germany). Because the XRF analysis requires fine grained samples, the method was externally calibration checked with data from atomic absorption spectrometry (AAS) measurements (SpectrAA 220, Varian Australia) after complete dissolution with EDTA of the heavy metals on the support. For the EDTA dissolution the same samples

were used which were analyzed previously with XRF. The coated polymer supports were placed in Teflon® vessels and 10 ml 0.1 M EDTA (analytical grade, Merck Germany) was added. The vessels were placed in a microwave digestion system (ETHOS, Milestone Italy) and underwent a temperature program with constant pressure control (1. step 400 W for 7 min; 2. step 300 W for 3 min; 3. step 200 W for 40 min). The temperature was held at 160 °C over the whole dissolution process. The polymer supports and the resin were not altered by the EDTA and only the oxide minerals were dissolved. Scanning electron microscopic (SEM) investigations were carried out with a Cam Scan CS44, CamScan – United Kingdom.

1.3 Results and Discussion

1.3.1 Particle Appearance on Support Surface

To show the applicability of the approach several preliminary examinations were carried out. Optical and scanning electron microscopic examinations of the heavy metal covered supports showed the allocation density of the phases (PbO) on the epoxy resin. The metal oxides form almost a single layer on the resin (Fig. 1.1) which gives the conclusion that the cleaning step after hardening of the resin is complete. All of the particles are in contact with the epoxy resin and are therefore attached to the surface of the support. There is no sign of loose particles which could fall off during handling the supports and while resting in the soil profile. This is important to avoid material loss before the proper experiment or during placing or retrieving the supports. The microscopic examination showed that the heavy metal particles were not immersed in the epoxy resin film (Fig. 1.2). Only a certain percentage of their surface is in contact with the epoxy resin. This gives a high amount of uncovered mineral surface which can interact with the soil environment. The epoxy resin used had a high viscosity which avoids a complete coverage of the particles due to the capillary

Fig. 1.1.
SEM surface picture of a polymer support coated with lead oxide. SEM: scanning electron microscope

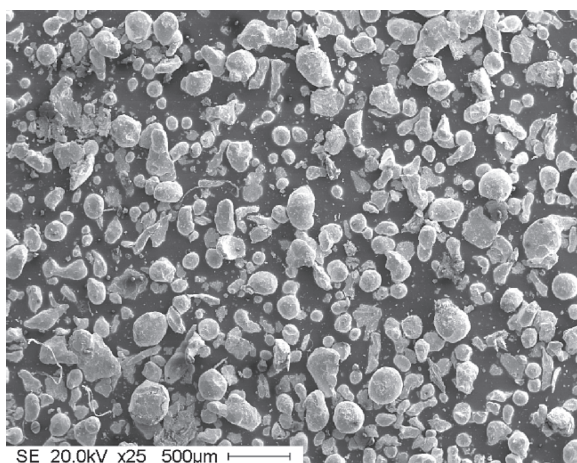


Fig. 1.2.
Lead oxide particles on a polymer support, picture taken at an angle of 70°

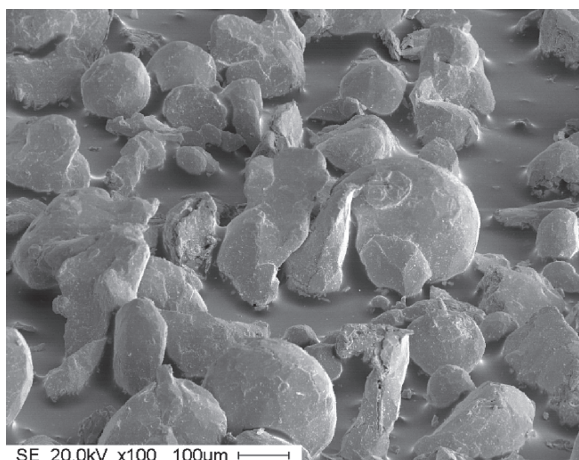


Fig. 1.3.
Substance application chamber: In front the dust spray gun (1) and in the chamber the Plexiglas support (2). The tube is the dust extraction unit (3) (for working safety reasons)



effect of the resin. This effect can be additionally controlled if after preparing the epoxy resin (mixing with the hardener substance), it is allowed to pre-react (hardening) for a few minutes which increases the viscosity. It could be shown that the used technique to attach particulate matter onto a support is suitable.

1.3.2 Coating Process

The coating process itself is not difficult to handle. A constant distance between the dust spray gun and the epoxy covered supports should be used. Also a constant air flow/pressure and a constant spray time should be kept. These are the most favorable conditions to produce polymer supports that are uniformly covered with heavy metal phases. It is self-evident that the application step can only be carried out in rooms with appropriate dust and air extraction units. A fine-dust face mask and an overall should be used to comply with the working safety regulations (Fig. 1.3).

To estimate the amount of applied minerals, every polymer support is weighed before and after the mineral application with a laboratory balance. The mass of the epoxy resin onto the supports was calculated by simple subtraction of the support mass before and after pure resin application on a support test set ($N = 30$).

1.3.3

Support Testing prior Insertion

The mechanical stability and the amount of resin-free particle surface was estimated with special experiments. Simple dissolution with ethylenediaminetetraacetic acid (EDTA) showed that the heavy metal phases can be dissolved without falling off from the surface. This dissolution experiment was carried out to simulate a dissolution process which could take place in a soil. Therefore it was important to see how the heavy metal covered support reacts mechanically if it is going to be recovered from

Fig. 1.4.
Polymer support with lead oxide particles after a dissolution experiment with 1 mM EDTA over 1 h at pH 4.7

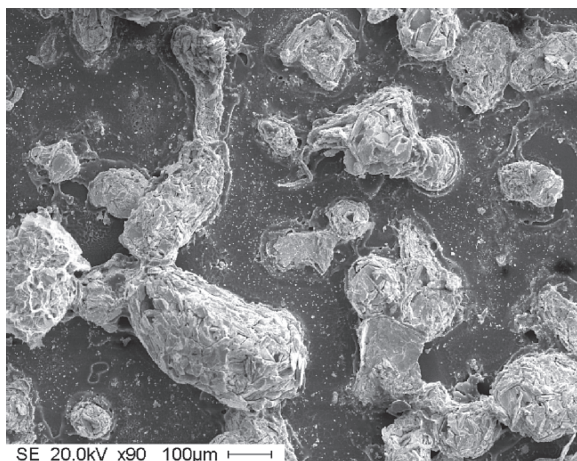
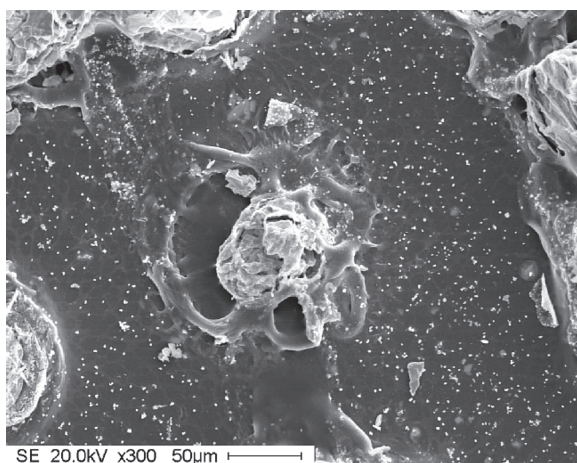


Fig. 1.5.
Polymer support with lead oxide particles after a dissolution experiment with 1 mM EDTA over 1 h at pH 4.7



the soil. It can be seen from Fig. 1.4 that the grains show signs of dissolution but are still attached to the support. Figure 1.5 shows a grain that has been dissolved almost completely. The former contact area of the particle with the support is still visible. The small remaining particle is still attached to the support. This experiment showed the good adhesion stability of the attached particles and their resistance to the cleaning steps. The estimation of the uncovered mineral surface which can directly interact with the soil environment can be determined with adsorption experiments. Preliminary experiments with phenylphosphonic acid (PPA) in an acetate buffered environment (pH 4.7) showed promising results, indicating that PPA is adsorbing onto the mineral surfaces but not onto the carrier material. Comparing the adsorption capacity of the bulk mineral material to the results with the mineral covered support will yield the amount of free reactive surface of the mineral supports. Together with the surface area (analyzed with the Brunauer-Emmet-Teller (BET) nitrogen sorption method) of the bulk mineral substance, we can then calculate the reactive surface area of the supports. This method to estimate the resin-free particle surface is useful to get an overview about the amount of “reactable” particle area.

1.3.4 Analytical Methods

The nondestructive X-ray fluorescence (XRF) analysis is the method of choice for quantifying the metal concentration of the covered polymer supports. With this analysis technique we have a useful tool to monitor e.g. the dissolution behavior of the heavy metals in the soil over different time scales. The supports can be reinserted into the soil after XRF analysis to undergo further reactions. A comparison of the XRF analysis and atomic absorption spectroscopic (AAS) analysis of the same supports has to be performed for each material that is used. The intention of this comparison is to find out whether the XRF results that are obtained using a calibration for powdered metal phases can be used to determine the metal concentration on the supports.

The electron optical analysis with the Scanning electron microscope (SEM) keeps track of the surface changes of the minerals on the supports. Traces of dissolution processes or precipitations on the mineral surfaces can be detected with this method (Bennett et al. 2001). Figures 1.1, 1.2, 1.4, and 1.5 show the application of this method to our samples. As already discussed above this method allows the direct visualization of the dissolution process. Additional coupling with the electron dispersive X-ray probe (EDX) can show the spatial elemental distribution on the supports or even of a mineral grain and its surrounding vicinity. With the use of an “environmental scanning electron microscope, ESEM” there is no need to coat the supports with a conducting surface e.g. gold or carbon. It will provide the same data as a conventional SEM (with attached EDX probe) but will have the same nondestructive benefits like the XRF method with a possible further use of the samples.

A more mineral specific analytical method is the infrared Raman spectroscopy in conjunction with a infrared microscope. This technique can detect certain mineral phases (Sobanska et al. 1999) on the support. Raman spectroscopy could give an indication of occurred phase transformations of the minerals. It might not have the power of the EXAFS technique but it is compact and can be performed in a normal

laboratory environment. Because it is also a non destructive method the supports can be examined before and after insertion into soils. The use of nondestructive analytical methods should be favorized to keep the samples unchanged and open for other examinations.

1.4 Conclusions

The establishment of a method for the in-situ analysis of the reactions of heavy metal phases in soils was successfully carried out. With lead oxide as a model substance it could be shown that the particles are strongly fixed on the polymer supports and survive even extended dissolution without falling off. The method might have the ability to be used with different substances e.g. heavy metal oxides and sulfides, iron oxides or clays. The method can also be used to expose particles to other environments, e.g. natural waters, sediments or technical systems such as water treatment plants. The designated analytical methods are all nondestructive and avoid alterations of the samples that can therefore be further used.

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