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An XAFS investigation of the artefacts caused by sequential extraction analyses of Pb-contaminated soils

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Abstract The chemical processes that occur during sequential extraction of a highly Pb-contaminated soil sample were investigated using XAFS spectroscopy for the identification of the Pb species in the solid residues after each step. The sequential extraction was performed following the procedure described by Salomons and Förstner [1]. It was found that during the sequential extraction serious alteration of the chemical binding forms of the Pb occurs. The most important processes underlying the chemical changes are the re-adsorption of solubilized Pb ions by soil matrix components and the precipitation of insoluble Pb species with anions from the extractant.

Introduction

The chemical, physical and toxicological behavior of a heavy metal in a contaminated soil is dominated by its chemical binding form and the environmental conditions. The analytical determination of heavy metal species in contaminated soil samples is, therefore, an important task for environmental analytical chemistry. Applications include assessment of contaminated sites and development and improvement of cleaning procedures [2, 3]. The most widely used methods are different sequential extraction procedures. These methods are chosen because of their easy and inexpensive feasibility and the lack of suitable direct instrumental analytical techniques for speciation of solid samples.

Despite their widespread use, there has always been the suspicion that sequential extractions might give misleading results due to alteration of the samples during the individual steps of the extraction. Several studies were conducted to test whether certain sequential extraction procedures lead to a redistribution of the analyte or not. One consequence of these investigations was the development of a steadily growing number of new sequential extraction schemes which should be suited better for special types of samples.

Among the methods used in these studies to investigate sample alteration were tests with artificial samples. These samples were prepared by spiking “natural” samples with certain species of the element of interest or by preparing model soils from the most important pure soil compounds (sand, clays, iron and manganese minerals, humic acids). Although the results from these artificial samples may be misleading, since a freshly prepared, relatively simple synthetic soil can never represent an aged, complex natural soil, these investigations yielded valuable insight as to whether significant redistribution occurs during sequential extractions and which of the soil compounds might play the most important role in this process.

In a study that compared the results of the classic Tessier extraction [4] and the three-step BCR method [5] using artificial samples and spiked soil samples, severe redistribution was observed in the presence of humic acid or Fe/Mn oxides. Irrespective of the origin of the lead, the BCR method released the highest amount of lead in the oxidizing step, whereas the Tessier method released the highest amount in the reducing step [6].

In a recent scanning electron microscopy (SEM) investigation [7], problems were also identified with a sequential extraction scheme for the metals Cu, Cr, Fe, and Al in marine suspended matter. The most important result was that often phases, which should be dissolved entirely during an extraction step, are not completely removed even after prolongation of the extraction time. In a later publication focusing on the acetate step of a sequential extraction, the same authors found that the extractant to solid ratio is a very delicate parameter, since too low ratios lead

Dedicated to Professor Dr. Bernd Neidhart on the occasion of his 60th birthday

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Table 1 General outline of the sequential extraction procedure

Step	Extractant	Group
1	NH ₄ -acetate (c[NH ₄ acetate]=1 mol/L), 10 mL, 2 h	Exchangeable cations
2	Na-acetate (c[Na acetate]=1 mol/L)+CH ₃ COOH, pH=5, 10 mL, 5 h	Carbonate bound
3	NH ₂ OH•HCl (C[NH ₂ OH•HCl]=0.1 mol/L)+HCl, pH=2, 50 mL, 12 h	Easily reducible substrates
4	(NH ₄) ₂ C ₂ O ₄ (c[(NH ₄) ₂ C ₂ O ₄]=0.1 mol/L)+(c[H ₂ C ₂ O ₄]=0.1 mol/L +HNO ₃ , pH=3, 50 mL, 24 h	Moderately reducible oxides
5	H ₂ O ₂ (30%), pH=5, 15 mL, 80 °C, 2 h + solution from step 1, 12 h	Organic matter and sulfides
6	HNO ₃ (68%), 120 °C, 2 h	Residual minerals

to incomplete dissolution of the analyte, whereas too high ratios lead to the dissolution of phases which should remain undissolved [8].

In another study, the results of a 5-step extraction procedure and of the 3-step BCR method were compared using a certified reference material. It was found that, at least for Pb, the results of both extractions were not comparable [9]. Conclusions drawn from one of the two extraction schemes are therefore determined more by the chosen extraction procedure than by the sample composition.

The only way to establish whether a certain binding form of the analyte is the result of “natural” aging or weathering of the sample or a result of the analytical method is to employ a direct instrumental speciation analysis method for solid environmental samples that does not require excessive and probably species information-destroying sample preparation procedures. One method that has been found to be appropriate for this task is X-ray absorption fine structure (XAFS) spectroscopy [10, 11]. Using XAFS as a fingerprint method, the relative amounts of Pb compounds can be estimated by linear combinations of reference compound spectra measured under identical experimental conditions. A similar approach was chosen very recently to test sequential extraction schemes for iron in a mining impacted soil [12]. One major advantage of this method is that the samples need almost no specific preparation prior to the measurement of the spectra. The two most important drawbacks are the limited availability of synchrotron radiation sources and the relatively high detection limits of the method. If the measurements are performed in transmission mode the detection limit is around 20 g/kg. The use of fluorescence detectors decreases the detection limit depending on the matrix properties by a factor between 10 and 1000. The method is therefore ideally suited for highly contaminated samples and for the “calibration” of more readily available methods like sequential extractions.

In the present work, a six-step sequential extraction of a lead-contaminated soil was investigated using XAFS spectroscopy to identify the Pb species in the residues after each step of the extraction. This procedure was initially developed for slightly contaminated sediments but is also suitable for highly contaminated soil samples [1].

Materials and methods

Samples and references

Three soil samples investigated came from near a battery factory in Hannover, Germany. Any parts of surface vegetation were removed as described in the general outline of the sequential extraction of Salomons and Förstner [1]. Total Pb contents were between 25 (soil #3) and 140 g/kg (soil #1). A preliminary electron microscope investigation showed that in two of the samples most of the Pb is present in the form of small discrete particles and that no obvious weathering could be detected. The third sample did contain weathered Pb-containing particles. After air-drying 30–40 g of the soil samples were ground as fine as possible using a ball mill. Subsamples of 2 g each were used for the sequential extractions. The first step was performed on 6 samples. After this step one of the six was air dried and the remaining five underwent the second step and so on.

Inorganic Pb reference compounds (PbO_{yellow}, PbCO₃, PbSO₄, Pb(OH)₂•2PbCO₃, PbO₂ and Pb₃O₄) were obtained from E. Merck, Darmstadt, Germany or were prepared from PbNO₃ solutions by using excess amounts of NaCl, Na₂S and oxalic acid solutions (PbCl₂, PbS and Pb oxalate). The remaining reference substances (Pb-clay, Pb-humic acid) were prepared by mixing 20 mL of a solution containing 1.9 mg/L–1900 mg/L Pb acetate with 1 g of the respective soil component [montmorillonite (Erbslöh, Geisenheim, Germany), humic acid (Fluka)]. The suspensions were shaken at room temperature and pH 5 for 24 h to avoid precipitation. Then the pH value was adjusted to 5, 6 or 7, respectively, and the suspensions were shaken for further 48 hours. After this period the pH has not changed by more than 0.25. After centrifugation the solid residues were washed with water and air dried. The resulting concentrations of sorbed or complexed lead were between 1 mg/g and >100 mg/g. All chemicals used were of p.a. grade and used without further purification.

Both samples and reference materials were mixed with polyethylene powder (Uvasol, E. Merck, Germany) and pressed in a hydraulic press to form pellets with a diameter of 13 mm. The sample thickness was chosen so that an X-ray absorbance (μd) of ~2.7 was achieved. This required a sample thickness of 200–300 μm for the samples from the first steps and 200–500 μm for the samples from the later steps from which most of the strongly X-ray absorbing elements, especially Fe and Pb, had already been extracted.

Sequential extraction

The sequential extraction was carried out following the detailed instructions given in literature [1]. Table 1 summarizes the procedure used in this investigation. Metal contents in the extracts were determined by flame AAS.

XAFS measurements

All Pb L₃ edge XAFS spectra were measured at the beamline X1 at the HASYLAB at DESY, Hamburg, Germany. The measurements were performed in transmission mode. N₂ was used in all three

ionization chambers. A lead foil placed between the second and third ionization chamber was used as energy reference. Energy scans were performed using an Si 311 double crystal monochromator. All XAFS spectra were recorded between 12800 and 13900 eV. This energy range was divided into five parts in which the spectra were recorded with different energy step widths ranging from 1.0 eV near the edge to 5.0 eV in front of the edge and at the end of the measured range. A crude energy calibration was done at the beamline by setting the first maximum of the first derivative in the spectra of lead foil to 13035.07 eV. The content of higher harmonic oscillations in the incident monochromatic X-ray beam was reduced by detuning the monochromator crystals so that only 60% of the maximum intensity passed. All spectra were measured at room temperature.

SEM/EDX-measurements

SEM/EDX measurements were performed using a Jeol 840A scanning electron microscope equipped with an energy dispersive detector (Link LZ5) for elemental analysis by use of X-ray fluorescence spectroscopy. The sample holders consisted of aluminium and were coated with an adhesive carbon film to fix the soil samples (both from W. Plano GmbH, Wetzlar, Germany).

Spectra evaluation procedure

The evaluation procedure for XAFS spectra is based on a fingerprint method in which the best fitting linear combination of reference compound spectra is used for the determination of the relative amounts of the respective components in the sample. First tests showed that either the near edge region or the EXAFS region could be used for the fingerprint analysis. In the case of lead an extended near edge region, 13000–13200 eV, was chosen because of the weak EXAFS oscillations on the L_3 edge of diluted, lead-contaminated samples and the more stable results for synthesized mixtures in the extended XANES region.

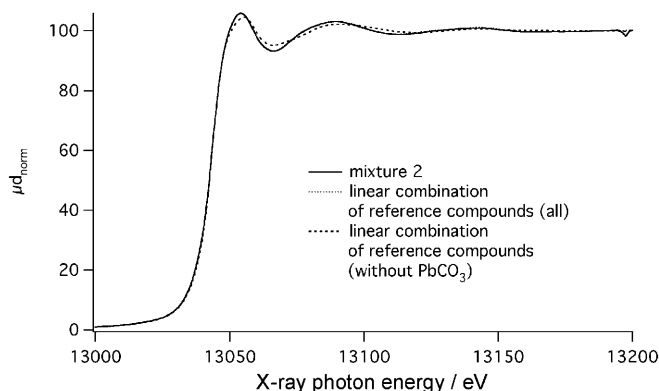


Fig. 1 XAFS spectrum from a synthetic mixture (composition see Table 2) and overlaid the best fitting linear combination calculated from the entire set of reference compound spectra and of the best fit without the spectrum of $PbCO_3$, the large differences demonstrate the consequences of missing reference spectra

Table 2 Relative amounts of Pb in synthetic mixtures as weighed, as calculated from linear combinations of reference compound spectra and as calculated with one missing reference spectrum ($PbCO_3$), see the three spectra in Fig. 1

Compounds	Weighed/%	Calculated/%	Without $PbCO_3$ /%
$PbCO_3$	32.1	37	–
$Pb(OH)_2 \bullet 2 PbCO_3$	30.0	27	21
$PbSO_4$	20.8	18	23
PbS	17.1	18	6
Pb sorbed by clay minerals	–	–	50

The major steps of the evaluation procedure are:

- Background subtraction: The background before and after the absorption edge has to be removed. In this step common functions like polynomials and cubic splines were fitted to the raw data to remove the background.
- Correction of small shifts of the energy-axis calibration: Spectra of a simultaneously measured lead foil were used for the crude and fine calibration of the energy axis. The careful execution of this step is of utmost importance if the actual edge region is used for the fingerprint analysis. Because of the large change of μ at the absorption edge even an energy shift of less than 0.5 eV has a strong influence on the evaluated results. Thus, it is not sufficient to make a one point calibration using, for instance, the first maximum of the first derivative of the spectrum. Therefore, the complete XANES spectrum of the lead foil is used for the energy calibration.
- Normalization of the spectra: A standard XANES normalization procedure is adapted to the spectra by setting the edge jump to a μ_{norm} of 100.
- Calculation of the best fitting linear combination of reference compound spectra: The evaluation of relative amounts of Pb compounds in the sample was done by fitting linear combinations of reference compound spectra between 13000 eV and 13200 eV to the spectra measured from the samples. The best fit was identified using the least mean square method.

To try to reduce the number of possible reference compounds SEM/EDX spectra and historical information were also considered. The utilization of the Levenberg-Marquardt algorithm makes it possible to evaluate linear combinations of all reference compound spectra, but local minima cannot be avoided. Therefore, the results of the first method were verified by an algorithm that uses a mixture between “Brute Force” calculation and minimization. While the data evaluation and the fitting with the Levenberg-Marquardt algorithm was implemented in IgorPro (WaveMetrics, Inc., Lake Oswego, USA), the second fitting algorithm was written in C++. The first fitting program calculates the estimated error (standard deviation) for each of the coefficients in the fits. The standard deviation of the coefficients was 0.5–4% for inorganic compounds and 3–8 % for the other compounds. Several artificial mixtures were synthesized to test the significance of the calculated results. It was found that the relative amounts were correct within $\pm 6\%$ of the total Pb content.

Although both errors have similar values, their meaning is completely different. While the estimated standard deviation incorporates only the signal to noise ratio, the errors evaluated with the artificial mixtures contain not only errors during the measurement and data evaluation but also errors due to noise in the spectra and inhomogeneities in the samples.

The highest risk of false results is caused by missing reference substance spectra. Especially with an increasing number of reference spectra used for the fit, the risk increases that a good fit may be determined with several wrong compounds. Nevertheless, tests with synthetic mixtures showed that it is in most cases possible to identify at least the main components correctly. Fig. 1 shows the Pb XANES spectra of a mixture, the best linear combination of all reference compound spectra and the best linear combination of this data set of reference compound spectra without the spectra of $PbCO_3$. While it is nearly impossible to distinguish between the spectra of the mixture and the linear combination of all reference compound spectra, the significant difference between the mixture

and linear combination of the reduced data set gives a hint that at least one reference compound is missing. The relative amounts (% of total lead content) of the reference compounds of the above mentioned best fitting linear combination and the real amounts by weighing are presented in Table 2.

The problem with missing reference compound spectra is inherent to the method and can by no means be totally avoided.

The only measure to minimize the chances to miss reference components is a careful selection of the set of reference components. Here the results of accompanying analytical procedures (SEM/EDX analysis) and an analysis of the history (origin and presumable chemical fate) of the contamination were important factors for the decision about the used reference components.

Fig. 2 Soil #1: SEM image (BSE detector) of soil #1, particles contain Pb and light elements (O), according to EDX analysis results

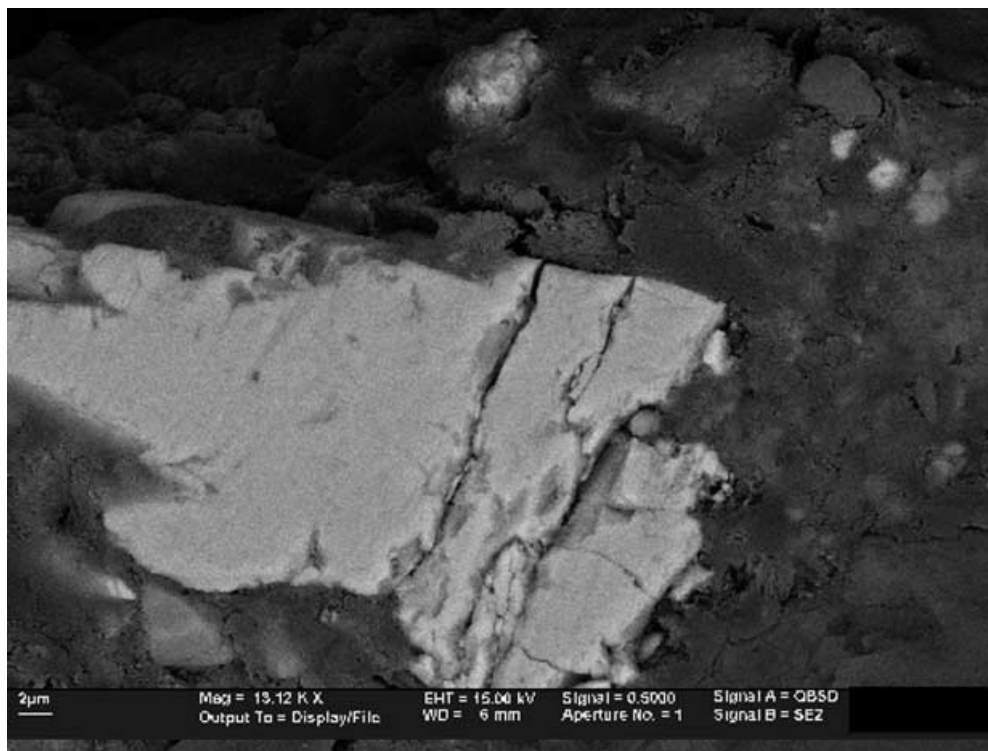
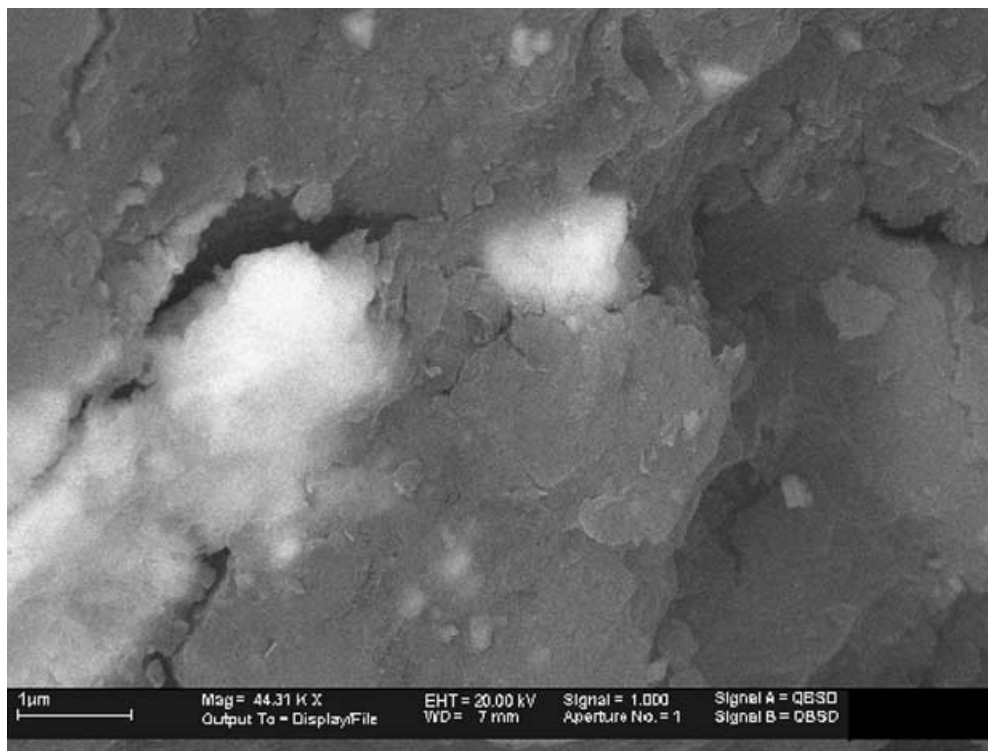


Fig. 3 SEM image (BSE detector) of soil #3, cloudy structures show Pb and matrix element (Si, Al, Fe) fluorescence signals in the EDX spectrum



Results and discussion

Figs. 2 and 3 show scanning electron microscope (SEM) images of two of the three soil samples (#1+#3). Both images were taken with a back scattered electron (BSE) detec-

Table 3 Results of the XAFS determination of Pb species in the original soils samples, results are given in percent of the total Pb content (m/m), nd=not detectable, results written in italics are within the region where the identification is not sure

Compounds	Soil #1	Soil #2	Soil #3
Pb(OH) ₂ •2 PbCO ₃	19%	nd	0%
PbCO ₃	35%	25%	7%
PbCl ₂	10%	nd	0%
PbSO ₄	nd	49%	14%
Pb ₃ O ₄	4%	2%	nd
Pb compl. by humic acid	19%	18%	46%
Pb sorbed by clay minerals	13%	6%	33%

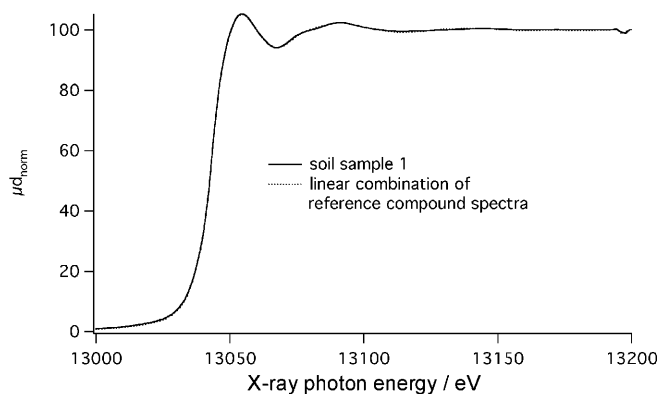
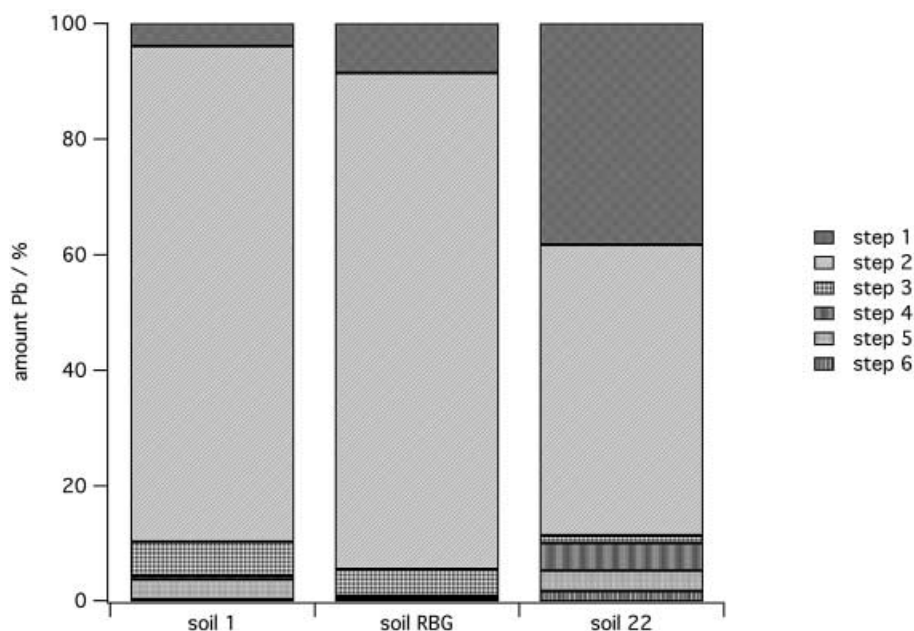


Fig. 4 XAFS spectrum of soil sample #1 and overlaid the spectrum of the best fitting linear combination

Fig. 5 Results of the sequential extractions, relative Pb amounts given in percent of the respective total lead content, all 3 samples seem to contain ~90% of the total lead in the easily mobilizable fractions

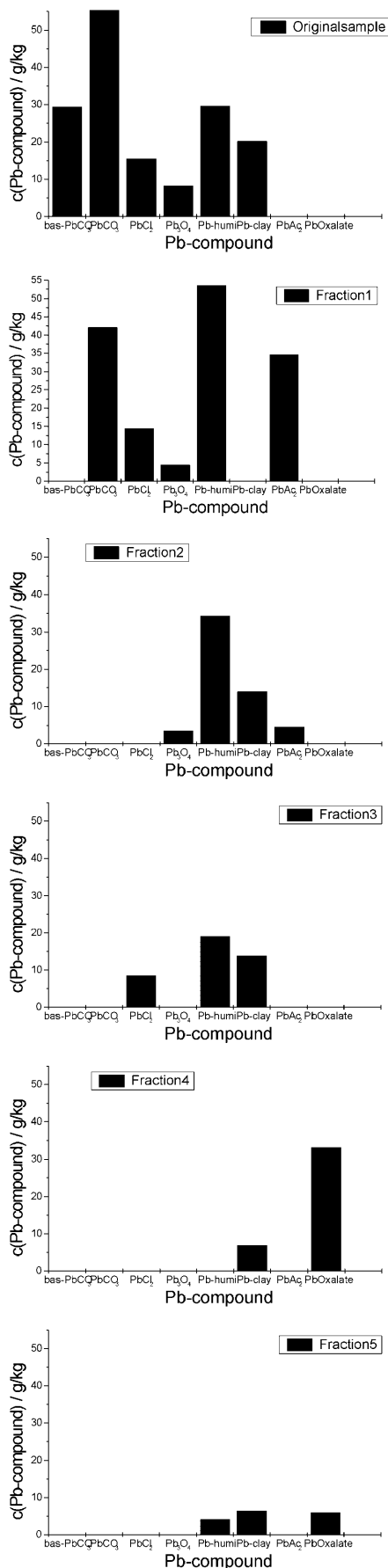


tor. Fig. 2, which was taken from sample 1, shows a typical lead-containing particle for this sample and for sample #2. Almost all the Pb seems to be dispersed over the sample in the form of discrete particles of some insoluble Pb salt.

Fig. 3 shows an SEM image of sample #3. The Pb particles in this sample appear weathered and the lead is found in cloudy structures bound to soil matrix components. This result is confirmed by the analytical findings, which were calculated from the XAFS spectra of the two samples. Whereas sample 1 contains 66% of the total lead as PbCO₃ or basic PbCO₃, sample 3 contains about 80% of the total lead in the form of lead bound to soil matrix components (see Table 3). Fig. 4 shows that the difference between the spectrum of the soil sample and the calculated spectrum is remarkably small. The comparison with Fig. 1 shows that it is only slightly bigger than the difference between the spectrum of the synthetic mixture and the respective calculated spectrum.

In contrast to these results that clearly indicate different chemical binding forms, the results of the sequential extraction procedure show a fairly similar distribution pattern of the lead for all three soil samples (Fig. 5). All samples contained roughly 90% of the Pb in the first two, easily mobilizable fractions. This was a first indication that the result of the sequential extraction procedure used on these three contaminated soil samples is determined more by the procedure itself than by the physical and chemical properties of the samples.

Figs 6a–f and 7a–f display the amounts of the different Pb compounds as determined by XAFS spectroscopy after each step of the extraction procedure. The sequential extraction residues of soil #3 could not be investigated with XAFS measurements, because of the too high detection limit of the measurements in transmission mode. The evaluated data led to the identification of four major effects which affect the reliability of sequential extraction results.



1st Redistribution as a consequence of binding to matrix components. It can be seen from Figs. 7a–c that the amount of lead bound to matrix components, especially on humic acids and clay minerals, varies during the sequential extraction procedure. While the amount of lead bound to humic acids, which actually should be released during the fifth step, shows – after a small increase – a continuous decrease until it is less than the lower detection limit after the fourth step. It would appear that a considerable portion of the lead initially bound to other phases is sorbed on clay minerals during the second step.

2nd Precipitation of sparingly soluble species. The most obvious redistribution of the Pb occurs during the fourth step of the extraction procedure. This step in which easily reducible components should be released is the extraction with a solution of (NH₄)₂C₂O₄/H₂C₂O₄ at pH 3. The XAFS spectra displayed in Fig. 8, which illustrate the nearly complete conformity of the spectrum from the sample and from pure Pb oxalate and the determined amounts of Pb species displayed in Figs. 6e and 7e, show clearly that almost the complete Pb contained in the sample is transferred into sparingly soluble Pb oxalate. This explains why the amount of lead released in this step is negligibly small (<2 % of the total Pb for samples #1+2, see Fig. 5). From soil 3 about 6% of the total lead is released during this step. This corresponds to the fact that the total lead content in this sample is a factor 3–4 smaller than in the samples 1+2. Obviously the released content is solely dependent on the solubility of Pb oxalate and not on sample properties.

Precipitation of a sparingly soluble compound, although not as pronounced as in step 4, also takes place during the 3rd step in which a solution containing chloride ions is used. Figs. 6c and d for sample 1 and Figs. 7c and d for sample 2 display the relative amounts of the Pb compounds before and after the third step. As a result of the occurrence of chloride ions in the extractant, a part of the Pb is precipitated as PbCl₂.

3rd Initially unexpected dissolution of species. As noted above, the analytical findings of the sequential extraction shown in Fig. 5 disagree with the results of the determination of the species composition by XAFS spectroscopy displayed in Table 3. Soil sample #2 was found to contain the largest part of its Pb content as PbSO₄, whereas in sample #1 the major part of the lead is identified to be lead carbonate by the results of the XAFS spectra evaluation. The result of the sequential extraction suggests fairly similar Pb species, compare Fig. 5. The fact that PbSO₄ was dissolved during the first two steps was unexpected but model calculations using PHREEQC [14] and laboratory experiments [H. Stichnothe, pers. communication] showed that the high solubility of the PbSO₄ from sample #2 during the first two steps of the sequential extraction

Fig. 6a–f Results of the XAFS determination of chemical species in the solid residues after the respective step of the sequential extraction of soil #1

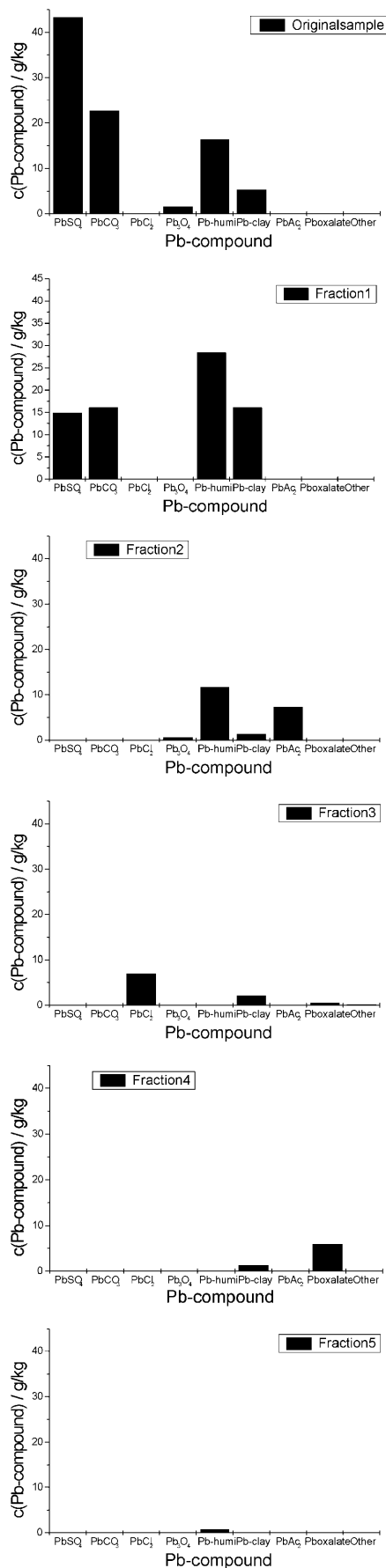


Fig. 7a–f Results of the XAFS determination of chemical species in the solid residues after the respective step of the sequential extraction of soil #2

procedure is caused by the formation of easily soluble complexes with the acetate anions of the extractant.

Since naturally occurring anions do not produce this effect, this result cannot be transferred to environmental processes and one loses the ability to derive predictions about the behavior of the lead under environmental conditions from the results of this sequential extraction procedure.

4th Precipitation of species with good solubility. A problem that probably only occurs in very highly contaminated samples, like those described here, is the precipitation of compounds with a reasonable or even good solubility. Figs. 6b, c and Fig. 7c show that during the first steps, which are conducted using acetate-containing solutions, Pb acetate is precipitated. Pb acetate has a solubility of 44.3 g/L in water (20 °C). [13].

This is probably the least problematic alteration of the sample composition, since it is possible to solve the Pb acetate by additional washing steps or prevent precipitation at all by use of higher liquid/solid ratios.

Summarizing the forgoing, it can be said that although there might be less problematic samples, in particular samples with lower Pb contents, the investigated procedure is obviously not suited for metals which form sparingly soluble oxalates. Due to the almost complete transformation of the remaining lead into Pb oxalate, it is clear that all consecutive steps are solely determined by the sequential extraction procedure and not by any sample property. It should be emphasized that conclusions drawn from the results of the sequential extraction must take the formation of sparingly soluble substances into account if they are to have any analytical basis.

Whether this sequential extraction procedure is suited for the analysis of other metals and whether another sequential extraction procedure is suited for the analysis of highly lead-contaminated soils are questions that remain to be answered in future systematic investigations.

Despite the problems outlined in this paper, the first two steps were found to do what they are supposed to do.

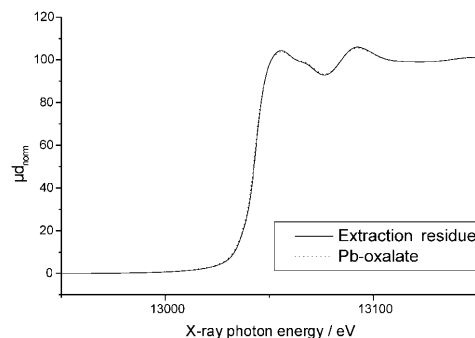


Fig. 8 XAFS spectra from the residue after the fourth step and overlaid of pure Pb oxalate

After the second extraction step no carbonates are left in the sample. For the easily mobilizable part of the lead, especially the carbonates released during the first two steps, the extraction procedure yields correct results. This result indicates that it should be possible to find single extractions, for example with a constant pH and carefully selected extractants, that will yield valuable results for the assessment of contaminated sites.

Conclusions

XAFS spectroscopy offers a unique capability to evaluate the processes occurring during sequential extractions and thus enables a critical assessment to be made of the various procedures for their applicability to different types of samples.

The presented results show that the interpretation of sequential extractions bears a high risk of severe misinterpretation due to redistribution of the analyte during the sequential extraction steps. This risk is obviously increased if procedures, which were initially developed for lower contaminated samples or other sample types, are used on highly contaminated soil samples.

During the investigated sequential extraction, the precipitation of lead with oxalate ions constituted the most severe alteration of the sample. This underlines the importance of a critical use of the different procedures with respect to the possible formation of sparingly soluble compounds of the analyte. Nevertheless, the problem of adsorption of analyte on matrix compounds is probably in general the more severe problem, since it cannot be

avoided even with sample type adapted extraction procedures.

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