The release of zinc and lead from mine tailings

Evaluation of leaching tests, soil water sampling, and sequential chemical extractions with special focus on sphalerite bearing flotation residues with anoxic conditions

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(Nele Schuwirth)

Abstract

Mining and processing of metal ores are important causes of soil and groundwater contamination in many regions worldwide. Metal contaminations are a serious risk for the environment and human health. The assessment of metal contaminations in the soil is therefore an important task.

A common approach to assess the environmental risk emanating from inorganic contaminations to soil and groundwater is the use of batch or column leaching tests. In this regard, the suitability of leaching tests is a controversial issue. In the first part of this work the applicability and comparability of common leaching tests in the scope of groundwater risk assessment of inorganic contamination is reviewed and critically discussed. Soil water sampling methods (the suction cup method and centrifugation) are addressed as an alternative to leaching tests. It has to be regarded that it is not possible with any leaching test to entirely reflect natural conditions. Several parameters distinctly deviate from natural conditions which complicates a transfer from leaching test results to the field. A conversion of leaching test results, as is proposed by the (already withdrawn) DIN19735, is impossible. Correlations between results obtained by different methods, regarding different kinds of materials and different sites, are not significant. This is due to different chemical/physical leaching processes. Reasons for limitations of the comparability of leaching test results are exposed and recommendations are given for the expedient application of leaching tests for groundwater risk assessment.

Leaching tests are usually carried out in open contact with the atmosphere disregarding possible changes of redox conditions. This can affect the original metal speciation and distribution, particularly when anoxic samples are investigated. The influence of sample storage on leaching test results of sulfide bearing anoxic material from a former flotation dump is investigated in a long-term study to assess oxidation kinetics. The release of Zn increases with increasing storage time and is doubled within 20 days. Since the oxidation of the sulfide-bearing samples leads to a significant overestimation of metal release, a feasible modification for the conduction of common leaching tests for anoxic material is proposed, where oxidation is prevented efficiently.

A comparison of leaching test results to soil water analyzes have shown that the modified saturation soil extraction (SSE) is found to be the only of the tested leaching procedures, which can be recommended for the assessment of current soil water concentrations at anoxic sites if direct investigation of the soil water is impossible due to technical reasons.

The vertical distribution and speciation of Zn and Pb in the flotation residues as well as metal concentrations in soil water and plants were investigated to evaluate the environmental risk arising from this site due to the release of metals.

The variations in pH and inorganic C content show an acidification of the topsoil with pH values down to 5.5 in the soil and a soil water pH of 6 in 1 m depth. This is due to the oxidation of sulfides and depletion in carbonates. In the anoxic subsoil pH conditions are still neutral and soil water collected with suction cups is in equilibrium with carbonate minerals. Results from extended x-ray absorption fine-structure (EXAFS) spectroscopy confirm that Zn is mainly bound in sphalerite in the subsoil and weathering reactions lead to a redistribution of Zn in the topsoil. A loss of 35% Zn and S from the topsoil compared to the parent material with 10 g kg^{-1} Zn has been observed. 13% of total Zn in the topsoil can be regarded as mobile or easily mobilizable according to sequential chemical extractions (SCE). Zn concentrations of 10 mg L^{-1} were found in the soil water, where pH is acidic. Electron supply and the buffer capacity of the soil were identified as main factors controlling Zn mobility and release to the groundwater. Variable Pb concentrations up to 30 µg L^{-1} were observed in the soil water. In contrast to Zn, Pb is enriched in the mobile fraction of the oxidized topsoil by a factor of 2 compared to the subsoil with 2 g kg^{-1} Pb. 80% of the cation exchange capacity in the topsoil is occupied by Pb. Therefore, plant uptake and bioavailability are of major concern. If the site is not prevented from proceeding acidification in the future, a significant release of Zn, S, and Pb to the groundwater has to be expected.

Results from this study show that the assessment of metal release especially from sulfide bearing anoxic material requires an extensive comprehension of leaching mechanisms on the one hand and on weathering processes, which influence the speciation and the mobility of metals, on the other hand. Processes, which may change redox and pH conditions in the future, have to be addressed to enable sound decisions for soil and groundwater protection and remediation.

Zusammenfassung

Der Abbau und die Verarbeitung von Metallerzen sind eine häufige Ursache für Boden- und Grundwasserkontaminationen in vielen Regionen der Welt. Schwermetallkontaminationen sind eine ernstzunehmende Gefahr für Mensch und Umwelt. Daher ist die Erkundung und Beurteilung von Schwermetallkontaminationen in Böden eine wichtige Herausforderung.

Ein häufiges Verfahren für die Abschätzung des Gefährdungspotenzials von anorganischen Kontaminationen für Boden und Grundwasser ist der Einsatz von Elutionsverfahren (Schüttel- und Säulenversuche). Die Eignung von Elutionsverfahren für die Beurteilung von Sickerwasserkonzentrationen ist umstritten. Im ersten Teil dieser Arbeit wird die Anwendbarkeit und Vergleichbarkeit von Elutionsverfahren im Rahmen der Sickerwasserprognose von anorganischen Kontaminationen kritisch diskutiert und bewertet. Als praktikable Alternative zu den Elutionsverfahren werden Verfahren für die Beprobung von Sickerwasser (Saugkerzen und Zentrifugation) dargestellt.

Mit keinem Elutionsverfahren ist es möglich, Feldbedingungen exakt widerzuspiegeln. Einige Parameter weichen deutlich von den Bedingungen im Feld ab, was eine Übertragung von Ergebnissen aus Elutionsverfahren auf Freilandverhältnisse erschwert. Eine Umrechnung von Ergebnissen zwischen unterschiedlichen Elutionsverfahren ist nicht möglich. Korrelationen zwischen Ergebnissen aus unterschiedlichen Verfahren mit unterschiedlichen Materialien von unterschiedlichen Standorten sind nicht signifikant. Dies ist auf unterschiedliche chemische und physikalische Freisetzungsprozesse zurück zu führen. Empfehlungen für den sinnvollen Einsatz von Elutionsverfahren im Rahmen der Sickerwasserprognose werden in der Arbeit gegeben.

Elutionsverfahren werden normalerweise in offenem Kontakt zur Atmosphäre durchgeführt, ohne die Redox-Bedingungen zu berücksichtigen. Vor allem bei ursprünglich anoxischen Proben kann dies zu einer Veränderung der Schwermetall Speziierung und Verteilung führen. An sulfidhaltigem Material aus einer ehemaligen Flotationshalde wurde der Einfluss der Probenlagerung auf die Ergebnisse von Elutionsverfahren in einer Langzeitstudie untersucht, um Aufschluss über die Oxidationskinetik zu erhalten. Die Freisetzung von Zink stieg mit der Länge der Probenlagerungsdauer an und verdoppelte sich innerhalb von 20 Tagen. Da die Oxidation der sulfidhaltigen Proben zu einer erheblichen Überschätzung der Schwermetallfreisetzung führt, wird eine einfach durchzuführende Modifikation der Elutionsverfahren vorgeschlagen, bei der eine Oxidation der Proben verhindert werden kann. Ein Vergleich von Ergebnissen aus Elutionsverfahren mit Sickerwasseranalysen hat ergeben, dass der modifizierte

Bodensättigungsextrakt als einziges der getesteten Elutionsverfahren für die Abschätzung der aktuellen Sickerwasserkonzentrationen an anoxischen Standorten empfohlen werden kann für die Fälle, in denen das Sickerwasser aus technischen Gründen nicht direkt beprobt werden kann.

Um das Gefährdungspotenzial der ehemaligen Flotationshalde durch die Freisetzung von Schwermetallen abschätzen zu können, wurde die vertikale Verteilung und Speziierung von Zn und Pb in den Flotationsrückständen sowie die Schwermetallkonzentration in Sickerwasser und Pflanzen untersucht. Die pH-Werte und Kohlenstoffgehalte zeigen eine Versauerung des Oberbodens mit Boden-pH-Werten bis 5.5 und Sickerwasser-pH-Werten von 6 in 1 m Tiefe. Dies ist auf die Oxidation von Sulfiden und einer Abreicherung von Karbonaten zurückzuführen. Im anoxischen Unterboden sind die pH-Bedingungen neutral und das Sickerwasser aus den Saugkerzen befindet sich im Gleichgewicht mit Karbonaten.

Ergebnisse aus Untersuchungen mittels "Extended X-Ray Absorption Fine Structure" (EXAFS) Spektroskopie an der Zn K-Kante bestätigen, dass Zn im Unterboden hauptsächlich als Sphalerit vorliegt und Verwitterungsreaktionen im Oberboden zu einer Umverteilung in andere Zn Spezies führen. 35% des Zn und S wurden aus dem Oberboden bereits ausgetragen, bezogen auf das Ursprungsmaterial mit 10 g kg^{-1} Zn. 13% des Zn im Oberboden können als mobil bzw. leicht mobilisierbar angesehen werden, wie Sequentielle Chemische Extraktionen (SCE) gezeigt haben. Im schwach sauren Sickerwasser in 1 m Tiefe wurden Zn Konzentrationen von ca. 10 mg L^{-1} festgestellt. Die Zufuhr von Elektronen und die Pufferkapazität des Bodens wurden als wichtigste Steuerparameter für die Zn Mobilität und Freisetzung ins Grundwasser identifiziert. Variierende Pb Konzentrationen von bis zu 30 µg L^{-1} wurden im Sickerwasser beobachtet. Im Gegensatz zu Zn wird Pb im oxidierten Oberboden mit einem Faktor von 2 angereichert, verglichen mit dem Unterboden mit Pb Gehalten von ca. 2 g kg^{-1}. 80% der Kationenaustauschkapazität des Oberbodens ist mit Pb belegt. Daher sind die Fragen der Pflanzenaufnahme und Bioverfügbarkeit von vorrangiger Bedeutung. Falls der Standort in Zukunft nicht vor voranschreitender Versauerung geschützt wird, ist mit einem signifikanten Austrag von Zn, S und Pb ins Grundwasser zu rechnen.

Die Ergebnisse dieser Studie zeigen, dass die Beurteilung der Freisetzung von Schwermetallen, vor allem bei sulfidhaltigem anoxischen Material, ein umfassendes Verständnis sowohl der Freisetzungsprozesse als auch der Verwitterungsprozesse, die die Mobilität der Schwermetalle beeinflussen, erfordert. Prozesse, die die Redox- und pH-Bedingungen in der Zukunft verändern können, müssen berücksichtigt werden, um angemessene Entscheidungen für den Boden- und Grundwasserschutz und für die Sanierung treffen zu können.

Danksagung

Contents

1 Introduction

Heavy metals are ubiquitous in the environment. High metal availability, arising from mining and industrial activities, disposal of sewage sludge or soil acidification, is an increasing problem in agriculture and forestry (Barcelo and Poschenrieder, 1990). Heavy metal release from soil or polluted material may affect soil and groundwater quality as well as plant and animal health.

Mining and processing of metal ores can be important causes of environmental degradation. Although mines are classified on the basis of their predominant products, they produce large quantities of other elements as coproducts. As a result, metal ore processing usually leads to multi-elemental contamination of the environment. Zn and Pb processing is an important historical source of environmental contamination with Zn, Pb, Cd, and other elements (Dudka and Adriano, 1997).

Some heavy metals (e.g., Cu and Zn) are essential for plant and animal health. However, at environmental concentrations above those necessary to sustain life, toxicity may occur. Other heavy metals (e.g., Cd and Pb) are not known to be essential to plants and animals. Toxicity may occur when these metals become concentrated in the environment above background levels (Selim and Amacher, 1997). Metal toxicity causes multiple direct and indirect effects in plants which concern practically all physiological functions (Barcelo and Poschenrieder, 1990). Poor plant growth and soil cover caused by metal toxicity can lead to metal mobilization in runoff water and subsequent deposition into nearby bodies of water (Lasat, 2000). The trace element uptake from contaminated soils can lead to plant contamination. Consequently, plant toxicity and the potential for transfer of contaminating elements along the food chain exist (Dudka and Adriano, 1997).

Zn and Pb are often found together in ore deposits, but the metals have different environmental behavior and biological effects. Zn is phytotoxic, and large concentrations in the soil have adverse effects on crops, livestock, and man (Oliver, 1997). Pb is less phytotoxic than Zn. However, it has been known to be toxic to animals since the 2nd century BC in ancient Greece. Pb is a widespread contaminant of the soil: it generally arises from pollution from mineral and industrial wastes and from atmospheric deposition. Soil has a large capacity to immobilize Pb because clay and organic matter adsorb it (Oliver, 1997). Pb poisoning is one of the most prevalent public health problems in many parts of the world (Nriagu, 1988), especially the intake of concentrations regarded as nontoxic over long periods (Davies and Wixson, 1987). Exposure to Pb can occur through multiple pathways, including inhalation of air and ingestion of Pb in food, water, soil, or dust. Excessive Pb exposure can cause seizures, mental retardation, and behavioral disorders. The danger of Pb is aggravated by low environmental mobility, even under high precipitations (Lasat, 2000).

Heavy metals in the soil environment can be involved in a series of complex chemical and biological interactions. Several of the reactions include oxidation-reduction, precipitation-dissolution, volatilization, and surface-solution phase complexation (Selim and Amacher, 1997). In soil, metals are associated with several fractions (Lasat, 2000): (1) in soil solution as free metal ions and soluble metal complexes; (2) adsorbed to inorganic soil constituents at ion exchange sites; (3) bound to soil organic matter; (4) precipitated such as oxides, hydroxides, and carbonates; and (5) embedded in structure of the silicate or other minerals. For phytoextraction to occur, contaminants must be bioavailable (ready to be absorbed by roots). Bioavailability depends on metal solubility in soil solution. Only metals associated with fractions 1 and 2 (above) are readily available for plant uptake.

A common approach to assess the environmental risk emanating from inorganic contaminations to soil and groundwater is the use of batch or column leaching tests. Leaching tests are used for groundwater risk assessment of contaminated sites if it is not possible to investigate groundwater directly due to a lack of monitoring wells, if it is not possible to sample sufficient amounts of soil water for instance with suction cups, or soil water sampling causes systematic errors due to sorption or filter effects, or if contaminated material (e.g., excavation material, demolition waste, rail track ballast, recycling material) has to be assessed prior to a future deposition as building or filling material (Grathwohl and Susset, 2001). In the latter case there is no seepage water yet.

Additionally, they are used for worst case scenarios to simulate changing soil properties. The suitability of leaching tests for the assessment of soil water concentrations and predictions of heavy metal mobility in the field is still a controversial issue (Förstner and Thöming, 1997; Pueyo et al., 2003) and subject of the first two chapters of this work.

In order to make technically sound and economically wise decisions about remediation, acknowledge of the contamination speciation is critical as speciation affects fate and transport and bioavailability phenomena (Sparks, 2005). Although no generally accepted definition of the term exists, speciation can broadly be defined as the identification and quantification of the different, defined species, forms or phases in which an element occurs (Alloway, 1999; Tack and Verloo, 1995).

A frequently used approach to investigate the binding form of metals in soils, sediments, and waste materials are sequential chemical extractions (SCE). Several SCE procedures have been developed in the last 30 years (Salomons and Förstner, 1980; Shuman, 1985; Tessier et al., 1979; Ure et al., 1993; Zeien and Brümmer,

1989) which are reviewed e.g., by Filgueiras et al. (Filgueiras et al., 2002). SCE have been subject of critical discussion (Bermond, 1992; Bermond, 2001; Martin et al., 1987; Nirel and Morel, 1990; Tessier and Campbell, 1991). There is general agreement that the partitioning of trace elements obtained by SCE is operationally defined. Effectiveness of the SCE is depending on the selectivity of the extractants. A lack of selectivity makes the specific metal leaching from the target mineralogical phase troublesome (Bermond, 2001; Filgueiras et al., 2002). Artifacts that may occur are redistribution of metal species (readsorption and reprecipitation) (Belzlie et al., 1989; Bermond, 2001; Ho and Evans, 1997; Ho and Evans, 2000) and alteration due to sample pretreatment (Davidson, 1999; Kersten and Förstner, 1987; Rapin et al., 1986; Wang et al., 2002). The latter is of particular impact when dealing with anoxic samples (Stephens et al., 2001; Wallmann et al., 1993).

A promising approach to improve the assessment of metal partitioning is the combination of SCE with spectroscopic methods like x-ray absorption fine structure spectroscopy (XAFS) (Bostick et al., 2001; Guest et al., 2002; Juillot et al., 2003; Kim et al., 2003; Mangold et al., 2000; Ostergren et al., 1999; Parkman et al., 1996; Peltier et al., 2005; Scheinost et al., 2002; Thöming et al., 2000). Over the past few years, the development and utilization of synchrotron-based techniques such as micro-x-ray absorption fine structure (micro-XAFS), micro-x-ray fluorescence (micro-XRF) spectroscopy and micro-tomography have revolutionized our ability to directly speciate metal(loid)s in contaminated soils and plants. Such investigations provide valuable insights as to contaminant forms and associations in soils and plants and enhancing remediation efforts such as in phytoremediation (Sparks, 2005). In combination with SCE these methods were used to investigate the significance and effectiveness of SCE for the speciation of Zn (Bostick et al., 2001; Peltier et al., 2005; Scheinost et al., 2002) and Pb (Mangold et al., 2000; Ostergren et al., 1999; Thöming et al., 2000).

Results from Scheinost et al. 2002 suggest that sequential extractions give excellent estimates of the quantity of easily mobilized species, which may be overlooked by XAFS. However, sequential extractions fail to identify and quantify Zn in mineral phases because of non-specific dissolution. In combination with XAFS, sequential extractions significantly improved the qualitative and quantitative Zn speciation (Scheinost et al., 2002).

In section 2, the theoretical background of leaching tests and the main leaching controlling parameters (pH, redox, ionic strength, reaction kinetics, surface, and speciation) are discussed. Experiences with common leaching tests (the German DEV S4 test (S4), saturation soil extraction (SSE), ammonia nitrate extraction (ANE), and pH_{stat} tests) are compiled and an emphasis is set on the comparability of leaching tests. In addition, the comparability between batch tests and column tests is discussed and comparison studies are reviewed. As a feasible alternative, soil water sampling strategies (the suction cup method and centrifugation) are outlined.

In section 3, the applicability of three currently used leaching tests (S4, SSE, and ANE) for the assessment of metal release from anoxic sites were assessed, and results are compared to soil water samples obtained by centrifugation and suction cups. Furthermore, the influences of sample storage and oxidation on leaching test results are investigated. For the prevention of sample oxidation, causing lowered pH and increasing heavy metal release, a feasible modification was developed, which offers the possibility to assess the leaching behavior under anoxic conditions.

Aim of section 4 is the investigation of chemical processes involved in the redistribution and mobilization of metals from an anoxic mine waste tailings impoundment during weathering and oxidation. The spatial element distribution is assessed in a soil profile developed from this tailing to determine metal mobilization and element losses. The speciation of metals is investigated to explore processes leading to a mobilization of metals and pollution of soil and groundwater. Therefore, SCE were applied to quantify the fraction of mobile and easy mobilizable metals. Dr. A. Voegelin from the working group of Prof. Dr. R. Kretzschmar from the Institute of Terrestrial Ecology (ITÖ), Department of Environmental Sciences, ETH Zurich, performed Zn k-edge x-ray absorption fine structure spectroscopy (EXAFS) measurements of selected samples from the soil profile to identify the residual solid phases. Results and discussion of these measurements were kindly provided by Dr. A. Voegelin and Prof. R. Kretzschmar to contribute to this work. Furthermore, XRF and carbon analyzes of this section were performed at the ITÖ.

In section 5, the release of Zn and Pb from sulfide bearing flotation residues of a small scale mine in Western Germany is investigated with focus on metal transfer to soil solution. Beside total contents of the solid material, the soil solution is investigated with suction cups. The influence of oxidation on total contents was assessed and pH effects on leaching behavior were investigated with pH_{stat} tests. In addition, plant samples were analyzed to quantify metal uptake by plants. Isotopic analyzes were performed to assess the seepage velocity. These investigations and modeling of the soil solution provide an insight in current and future processes, which can cause environmental pollution.

Parts of this work were submitted for publication in the following paper: Schuwirth, N. & Hofmann, T.: Comparability of and alternatives to leaching tests for the assessment of the emission of inorganic soil contamination. Journal of Soil and Sediments (accepted and online published).

2 Comparability of leaching tests and soil water sampling as an alternative for the assessment of inorganic soil contaminations

Leaching tests are laboratory tests where the investigated material is brought into contact with an eluent to investigate the leachability of certain constituents of the investigated material. On the basis of the used technology, leaching tests can be divided into batch and column tests. They are used for groundwater risk assessment of contaminated sites if:

- It is not possible to investigate groundwater directly due to a lack of monitoring wells.
- It is not possible to sample sufficient amounts of soil water for instance with suction cups, or soil water sampling causes systematic errors due to sorption or filter effects.
- Contaminated material (e.g. excavation material, demolition waste, rail track ballast, recycling material) has to be assessed prior to a future deposition as building or filling material (in this case there is no seepage water yet) (Grathwohl and Susset, 2001).

Additionally, they are used for worst case scenarios to simulate changing soil properties. The suitability of leaching tests for the assessment of soil water concentrations is still a controversial issue (Förstner and Thöming, 1997). The aim of this chapter is to review and critically discuss the applicability and comparability of leaching tests in the scope of groundwater risk assessment of inorganic contamination and to discuss soil water sampling methods as alternative.

2.1 Theoretical background of leaching tests

With leaching tests, chemical reactions are investigated that can modify the concentration of metals in soil solution, such as adsorption-desorption, dissolution-precipitation, reduction-oxidation, and complexation-decomplexation (Sahuquillo, 2002). Depending on the leaching process, various parameters can control the leaching behavior of metals.

The release of a certain contaminant can be limited either by the availability (reactive amount) of the contaminant in the investigated material. Or it can be limited by reaching distribution equilibrium between the solid and the liquid phase controlled by the solubility of the contaminant or by sorption processes (Figure 1).

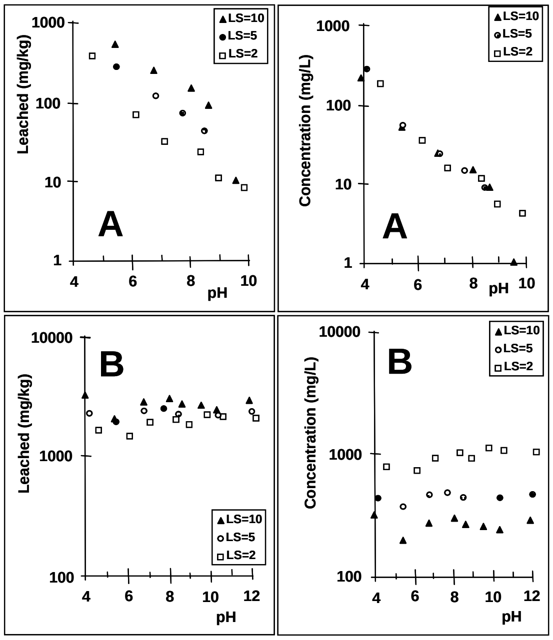

Figure 1: Illustration of solubility control (A) versus availability control (B) of batch leaching. Data expressed in mg L^{-1} reflect solubility control when data for different L/S ratios coincide (A). Data expressed in mg kg^{-1} reflect availability control, when data for different L/S ratios coincide (B), Si (A) and Cl (B) leaching in batch tests with different L/S ratios (modified after van der Sloot et al. 1998).

Leaching test results can be expressed either as leachate concentration (mg L^{-1}) or as a constituent release (mg kg^{-1} dry mass) (Andres et al., 2002; van der Sloot et al., 1998). If the leaching process is solely availability controlled, the concentration (in mg L^{-1}) strongly depends on the liquid-to-solid (L/S) ratio. The higher the L/S ratio, the lower is the concentration due to dilution. The constituent release (in mg kg^{-1} dry mass) is in this case not affected by the L/S ratio. If the leaching process is limited only by the solubility or another distribution equilibrium, the L/S ratio has no influence on the concentration (in mg L^{-1}), but on the release (in mg kg^{-1} dry mass) (Figure 1). In nature, there is often a mixture between both processes.

However, the L/S ratio in a leaching test can also affect the pH or other leaching controlling parameters. Additionally, other test conditions like the type of agitation, contact time, temperature, and eluent can differ. This complicates the comparison of different test methods (as discussed in section 2.3).

It is often noted that one leaching test alone will never be suitable for a reliable risk assessment (Blankenhorn, 1994; Lewin, 1996; Quevauviller et al., 1996;

Sommerfeld and Schwedt, 1996; van der Sloot et al., 1996). This is due to the fact that different factors influence the leaching behavior. Only a combination of different methods can provide an understanding of processes, which is imperative for long-term risk assessment.

2.1.1 Leaching controlling parameters

Potential important leaching controlling parameters for inorganic contaminants are pH, redox, dissolved organic carbon (DOC), speciation (binding form), and reaction kinetics. The leachability of particular contaminants is controlled by a limited number of parameters that may be more pronounced in one material relative to another (van der Sloot et al., 1996). The influence of different parameters controlling leaching in a wide range of different materials and an overview about different leaching test procedures is described and discussed in detail in van der Sloot et al. (1998). The release of contaminants in the field may additionally be influenced by the interaction with plants. Plants may accumulate metals and influence chemical and microbial conditions in the rhizosphere. These aspects as well as climatic effects are usually not considered during the performance of laboratory leaching tests. This increases the uncertainty of the transferability of leaching test results to the field.

pH

In many cases, the pH value is the most important parameter controlling leaching of metals and metalloids (Dijkstra et al., 2004; Förstner, 1998; Förstner and Thöming, 1997; Hamer et al., 2003; Hursthouse, 2001; Sommerfeld and Schwedt, 1996; Thöming and Calmano, 1998; van der Sloot et al., 1998; Yin et al., 2002). Many dissolution-precipitation reactions are strongly pH dependent. Additionally, sorption processes are pH dependent as well, since surface charges may change as a function of pH (van der Sloot, 1996). At low pH, cationic heavy metal sorption to variably charged surfaces is generally weaker than at neutral pH, due to competition for surface sites by protons and repulsive charge effects. At neutral to a slightly alkaline pH, cation sorption generally increases due to deprotonation of the surface sites and the more favorable surface charge of (hydr)oxide minerals and organic matter, resulting in a lower solution concentration. At alkaline pH values, sorption to solid surfaces is reduced due to inorganic and organic complexation of cations in solution. Towards higher pH values, complexation with dissolved organic matter becomes more important because of increased DOC concentrations in solution (Dijkstra et al., 2004). Anionic contaminants show a reverse sorption behavior (Figure 2).

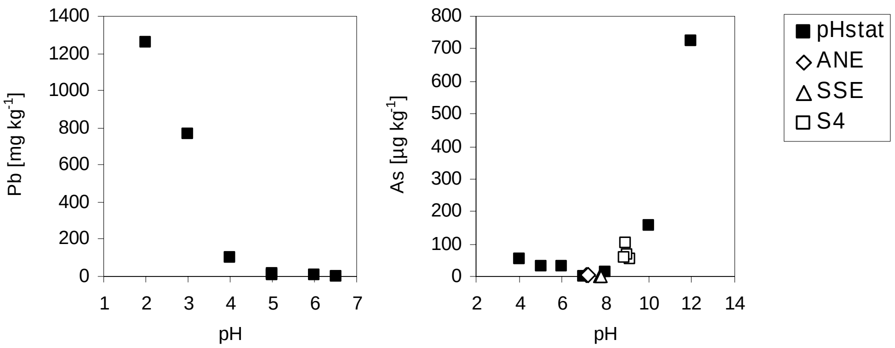

Figure 2: pH dependency of batch leaching test results, Pb (left) and As (right) release from excavation material; pH_{stat} test (pHstat), ammonia nitrate extraction (ANE), saturation soil extraction (SSE), S4 test (S4), compare to Table 1

For a long-term assessment of the mobility of inorganic contaminants, information about acid immission and internal acid formation is of particular importance, in relation to the buffer capacity of the soil or contaminated site and their environment (Förstner, 1998).

The pH of the soil depends on the base neutralization capacity and acidity of the liquid phase and, furthermore, on the acid neutralization capacity of the soil (especially carbonate content). For this reason, soil pH varies non-linearly with a changing L/S ratio (Thöming and Calmano, 1998). The pH has a different influence on different metals. Results from Voegelin et al. (2003) indicate that acidic inputs into contaminated soils may lead to increased Cd and Zn leaching long before the acid neutralization capacity of the soil is depleted. On the other hand, Pb and Cu leaching will be strongly retarded until the soil leachate itself becomes acidic.

Redox conditions

Numerous authors confirm that redox conditions can play a major role for the release of inorganic contaminants. However, this aspect is not taken into account during the performance of leaching tests conducted in open contact with the atmosphere (BLfW, 2001; Hage and Mulder, 2004; Karius and Hamer, 2001; Rapin et al., 1986; Rudek and Eberle, 2001; van der Sloot et al., 1994).

Release of inorganic contaminants under oxidizing conditions (in contact with the atmosphere) can differ in orders of magnitude compared to release under reducing conditions. To assess the environmental impact of reducing materials, an important question arises in estimating whether the material will remain reduced or become oxidized. Leaching tests performed without precautions may lead to higher leaching rates than are likely to occur in the field (Hofmann and Schuwirth, 2004). On the other hand, components leaching under reducing conditions may not show up in the standard test and lead to problems in the ultimate application (van der Sloot, 1991). This circumstance is also used in sequential chemical extractions to evaluate the leachability under different redox conditions (e.g. Wallmann et al. (1993)). Since changes in leachability in orders of magnitude may occur, it is important at least to be aware of when such conditions may play a role (van der Sloot et al., 1998). Reducing conditions may occur in different scenarios: in deep soil layers, in sediments (only the top layer is generally oxidized), in sulfide containing wastes and industrial slag, in sewage sludge and in wastes deposited under biologically active conditions (van der Sloot, 1996).

Redox conditions are of particular importance if metals occur as sparingly soluble reduced or oxidized species. In this case, a change in redox potential can lead to transformation into better soluble species and an increasing release. Changes in redox potential are generally closely linked to a change in pH. Under specific conditions, oxidation of sulfide may lead to production of acidic solutions (e.g. acid mine drainage) (van der Sloot, 1996).

It is found to be essential to preserve the speciation of extractable constituents during sampling, storage and pretreatment. This aspect is of special importance if the sample is an anoxic soil or sediment. The influence of sample storage and pretreatment of anoxic samples was investigated, e.g. by Rapin et al. (1986). No storage method tested completely preserved the initial metal partitioning of the sediments. Among the preservation methods tested, those involving the drying of the sediment (freeze-drying, oven-drying) had especially marked effects and should be avoided. Acceptable preservation techniques would include freezing or short-term wet storage (1-2 °C). Cu, Fe, and Zn were found to be particularly sensitive to sample pretreatment.

Ionic strength

In many cases, the ionic strength is not an issue of major concern (van der Sloot, 1996). It may be relevant in cases where materials contain highly soluble salts. In those cases, leaching behavior is affected very strongly by the salts causing analytical problems, sample preservation problems and different behavior of leaching processes. Typical for all leaching tests is a high dilution of the soil solution due to the addition of water (Bittersohl et al., 2000). Ionic strength is lowered resulting in exchange processes, which can lead to a change in the cationic composition. For special contaminants, microbial alteration can occur, favored by high water contents and internal heat development during the continuance of the test.

Ionic strength has an influence on the surface potential as well (Dankwarth and Gerth, 2002). An increase in ionic strength decreases the surface potential, anion sorption is favored and concentrations in leaching tests decrease. This has to be taken into account for the assessment of As for instance. It leads to the problem that ANE may underestimate As concentrations in soil water, whereas As concentrations in S4 tests may be overestimated in some cases.

Reaction kinetics

Some of the chemical dissolution reactions occurring in solids are relatively fast. In this case, equilibrium based reactions and equilibrium reaction constants can be used to describe the leaching system (van der Sloot et al., 1998). However, for slow reactions, the contact time becomes a major parameter. Additionally, changes in pH or redox can occur during an experiment. Such changes can affect the release of constituents dramatically (van der Sloot et al., 1998). In single batch extractions, kinetic aspects are lost and may lead to erroneous conclusions if very short-term leaching effects are dominating the outcome (e.g. wash-off effects). In already aged and stable materials, kinetic aspects of leaching appear to have less influence (van der Sloot, 1996). In any case, the addition of the eluent leads to an initial disequilibrium. In case of processes with slow solution kinetics, equilibrium is not reached until a certain time (Hofmann, 2002).

Batch leaching tests like BSE, S4 or ANE are designed to approach equilibrium. Whether or not equilibrium is reached in column tests depends on the flow rate and the length of the column as well.

Surface

Many leaching processes depend on the reactive surface and grain size of the material. For this reason, it has to be recognized that grain size reduction can influence leaching test results. If possible, the material should therefore be investigated in its original size and composition (Schroers, 2002). However, for worst case assessment, it can be useful to take crushed or grinded samples (Hirschmann and Förstner, 2000; Hofmann, 2002; Karnuth, 2003) because of faster equilibration.

Speciation

The ecological effects of heavy metals in soils are closely related to the content and speciation of the elements in the solid and liquid phases of soils (Brümmer et al., 1986). Specific and non-specific adsorption are judged as most important processes of heavy metal binding. Heavy metal adsorption on soil particles is not only restricted to the formation of surface complexes, but can also take place in the interior of minerals (intraparticle sorption). For the assessment of metal mobility and availability in soils, the determination of concentration as well as speciation either in the soil solution or in comparable aqueous equilibrium solutions of soil samples is necessary. Additionally, the transfer of metals from solid pools to the liquid phase and vice versa has to be assessed (Brümmer et al., 1986).

2.2 Experience with common leaching tests

Four leaching test methods are mentioned in the German Soil Protection Ordinance for groundwater risk assessment and shall be shortly discussed here. Two of them (the German DEV S4 test (S4, (DIN 38414-4, 1984)) and the saturation soil extraction (SSE)) are using deionized water as leaching agent. The ammonium nitrate extraction ((DIN 19730, 1997), ANE) is performed with 1 molar ammonium nitrate solution. The pH_{stat} test uses diluted acid or base continuously adjusted to a predefined pH value. The four methods differ furthermore in L/S ratio, contact time, the amount of sample used, the kind of agitation, and the pretreatment of the sample (Table 1).

Table 1: Conditions of common batch leaching tests (S4: German DEV-S4 test; SSE: saturation soil extraction; ANE: ammonium nitrate extraction)

	S4	**SSE**	**ANE**	**pH_{stat} test**
eluent	deion. water	deion. water	1 M NH_4NO_3	diluted acid/base
L/S	10:1	around 1:2	5:2	10:1
contact time	24 h	2 * 24 h	2 h	24 h
sample mass	100 g	250 g	20 g	100 g
agitation	end over end	none	shaking	stirring
pretreatment	none	air drying	air drying	none

Their application as well as advantages and disadvantages are discussed in detail in HLUG (2001), LUA (2002). The SSE is often favored because of its more realistic L/S ratio and its renunciation of agitation. An often mentioned disadvantage of the SSE is that the addition of water is adjusted to the yield point. This criterion is not valid for coarse grained or clay rich material. Furthermore, it is depending on the judgment of the person who carries out the test. This would have a negative influence on the reproducibility. However, compared to other leaching tests, reproducibility seems not to be worse as current investigations show (Durner et al., 2004; Kapp, 2003).

The S4 is a well established routine method, which is widely used in Germany and other countries as well. However, it has to be mentioned that this leaching test has been subject to strong criticism in the last twenty years (Förstner and Thöming, 1997). The major problem is the high L/S ratio of 10:1, which leads to a significant dilution compared to real soil solutions. The mechanical stress due to shaking is another point of criticism. The method is found to be particularly insufficient for the prediction of the mobility of heavy and half metals that usually occur as sparingly soluble oxides, hydroxides, and carbonates (Förstner, 1998). Sommerfeld and Schwedt (1996) observed a significant dependency on the kind of agitation at investigations of sediments and sewage sludge. In another study, the S4 test was found to be unsuitable for the assessment of the environmental impact of waste – especially waste combustion residues – because it tends to underestimate contaminant concentrations (Faulstich and Tidden, 1990). After LUA (2002) observed concentrations according to the S4 method cannot be directly compared to soil water concentrations at the sampling point as it has been recommended in earlier publications (e.g. in Blankenhorn (1994)).

The ANE is commonly used for the assessment of the bioavailable and exchangeable heavy metal fraction (Gupta et al., 1996). Due to competing sorption of the ammonium, it usually mobilizes higher amounts of cationic contaminants compared to deionized water and real soil solutions. Assessment of anionic constituents (e.g. As) by this method is particularly critical. For these reasons, it cannot be recommended for groundwater risk assessment.

The pH_{stat} test is a useful tool for the evaluation of the leaching behavior under predefined pH conditions since pH is the dominant leaching controlling parameter in many cases. It can be used for the determination of the buffer capacity of the soil and the mobilizable amount under varying pH conditions as well.

With the pH_{stat} test it is possible to evaluate the kind and probability of the worst case of the seepage water development (Cremer and Obermann, 1992), as well as the long-term leaching behavior of solid material (Sommerfeld and Schwedt, 1996), and different release scenarios (Kosson et al., 2002). Especially in combination with thermodynamic modeling, it also permits conclusions about release processes (Dijkstra et al., 2004; Meima and Comans, 1997; van der Sloot et al., 1994). Furthermore, with the help of pH_{stat} tests, it is often possible to explain the differing results of other batch leaching tests.

An alternative to the pH_{stat} test is the CEN:prTS14429. In this test procedure, parallel sub-samples are leached at a fixed L/S ratio with leachants containing pre-selected amounts of acid or base in order to reach stationary pH values at the end of the extraction period. This is a relatively cheap batch method to assess pH dependence. It avoids the need for expensive equipment and produces very comparable results. However, pH_{stat} tests as well as column tests are not in the process of becoming international standard.

2.3 Comparability of different leaching tests

2.3.1 Correlation of batch leaching test results

A question of major interest is the comparability and correlation between the results of different batch leaching tests. In the past, an attempt was made to find a statistical correlation between the ANE, S4, and SSE in the (DIN V 19735, 1999), which has already been withdrawn by now. Preliminary regression parameters for the conversion of S4 and ANE results to SSE results were calculated on the basis of 185 samples from southern Germany. Lichtfuss (2000) comes to the following evaluation of this attempt: A fundamental lack of the DIN V 19735 involves the disregard of the partially immense deviation of several pairs of variates along the regression line during the calculation of SSE values (Figure 3). Beside methodical reasons, different speciation of elements in different soil samples may be the cause for these huge deviations. This means that the relationship between concentrations in the leachate and the SSE is not very close by nature, even when methodical biased errors could be avoided. According to the outcome of interlaboratory studies and the consideration of statistical analyses of the basis data, the DIN V 19735 is no acceptable way for estimation of SSE concentrations. There is no equality between these three methods.

Förstner and Thöming (1997) conclude that the correlation of ANE and SSE is of poor significance for some elements, so that the ANE should not be used for groundwater risk assessment.

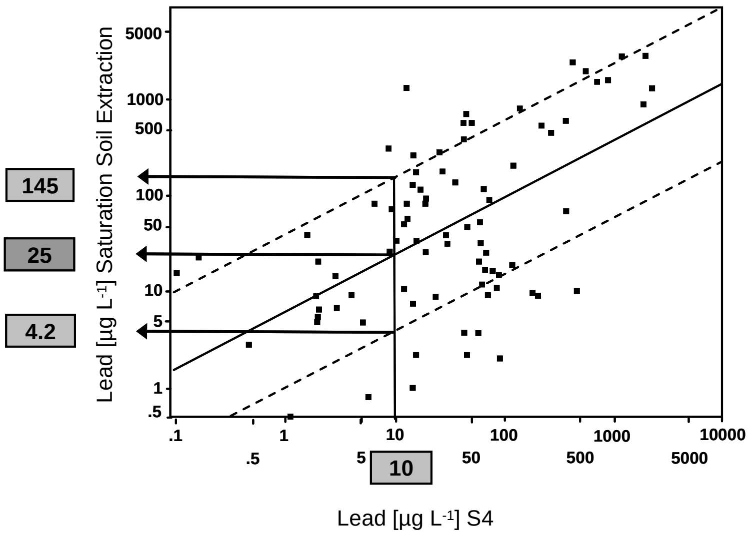

Figure 3: Exemplary illustration of the relationship between Pb concentrations in saturation soil extraction (Y) and S4 eluate (X) on a logarithmic scale. Original data from DIN V 19735, solid line: regression equation Y = 6.298 * X 0.5938, dashed lines: 68%-confidence interval, graphical derivation of an Y value and its confidence interval from an X value, modified after Lichtfuss (2000)

Both leaching tests (ANE and S4) and their transformation to soil water concentrations are generally not suited for long-term prognoses because they do not take changes of the soil matrix with time into account (e.g. buffer capacity).

In Figure 3, only the 68%-confidence interval is shown. The 95%-confidence interval, which is usually used, would show even higher deviations.

2.3.2 Basic considerations about the comparability of batch tests with column tests

In general, batch tests are designed to approach equilibrium between the solid and the liquid phase (even though this assumption is not valid in every case), whereas column tests can be performed under both equilibrium and non-equilibrium conditions, depending on the flow rate and the length of the column. Flow rates chosen are usually much faster than natural seepage water velocities due to technical requirements. The length of the column is limited and usually shorter than the thickness of the unsaturated zone. For these reasons, non-equilibrium can occur when leaching processes are kinetically limited. In this case, typical breakthrough curves show initially higher concentrations decreasing with time.

To prove equilibrium, flow interruptions are necessary (Brusseau et al., 1997; Totsche, 2001), or the same column test has to be performed with different flow rates. If the test runs under non-equilibrium conditions, the determination of rate parameters is possible with the help of different flow rates. Due to flow interruptions, the contact time of the liquid phase is increased. The concentrations increase after the flow interruption if the release process is rate limited and there was non-equilibrium before (Figure 4). Depending on the duration of the flow interruption, initial concentrations can possibly be reached.

If a column test is conducted under equilibrium conditions, concentrations only decrease due to depletion of the constituent of the solid phase. If column tests shall be compared with batch tests like the S4 or SSE, for example, it is important to know if the column test is performed under equilibrium conditions or not. Otherwise, a decreasing concentration due to limited kinetics could be mistaken for a depletion of the constituent.

If reaction kinetics are limiting the release rate and equilibrium is not reached, results are dependent on the contact time during the test. In this case, a comparison between the different batch and column tests is not possible in general, if reaction rate parameters are unknown.

For column tests, reaction velocity and flow velocity of the eluent are inversely proportional. Equilibrium is more likely to occur the faster the reaction kinetics and the slower the flow velocity. This can be mathematically described by the Damköhler number. The Damköhler number is a dimensionless characteristic (D_a) given by:

$$D_a = L\ R\ k\ v^{-1}$$

with L: column length [L], R: retardation factor [-], k: reaction rate constant [T^{-1}], and v: average velocity [$L\ T^{-1}$]. This value gives insight in the degree of (non)equilibrium in a certain system during a certain (dimensionless) time after a change in the influent concentration (Michalak and Kitanidis, 2000; van de Weerd et al., 1998; Wehrer and Totsche, 2003; Wehrer and Totsche, 2005). Damköhler numbers exceeding 10 indicate near equilibrium conditions. A decrease in the Damköhler number indicates an increasing control by the reaction rate constant (Wehrer and Totsche, 2005).

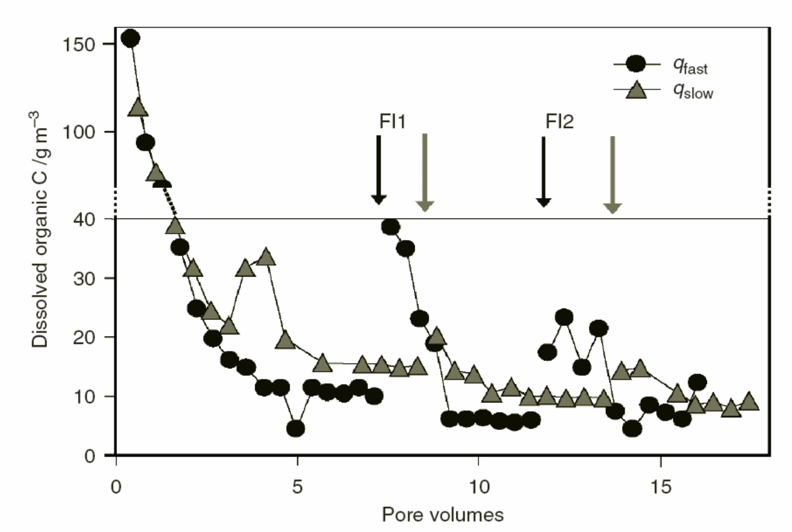

Figure 4: Column tests with flow interruptions (arrows), (Wehrer and Totsche, 2005), dissolved organic C release of soil material contaminated with non-aqueous phase liquids

The initial concentration of a column test strongly depends on the experimental design. If the column is saturated with water before the start for pre-equilibration, then higher initial concentrations will occur and the initial concentrations will possibly reflect field concentrations. However, if the column test is started immediately without pre-equilibration, initial concentrations will be lower and depend on the flow velocity and column length. In this case, the maximum concentration depends additionally on the sampling interval due to averaging effects.

Concentrations of batch experiments like S4 or SSE for kinetically controlled leaching processes under non-equilibrium depend on the reaction velocity and the contact time during the test. In this case, a correlation to column test cannot be found. In Karnuth (2003) it is shown that 24 h are not sufficient for some elements to reach equilibrium (e.g. Cr and Mo) in the leaching of recycled building rubble. However, a continuation of the experiment can have negative effects as well since the conditions cannot be maintained. Due to carbonation (penetrating CO_2 through plastic bottles) and oxidation, conditions in a prolonged test can change, leading to non-equilibrium conditions.

If equilibrium conditions are maintained during the experiments, the result of comparison between column and batch leaching tests depends on the release process. Therefore, two extreme and idealized situations can be considered (Figure 5):

Case A: Leaching process is availability controlled. The leaching constituent is only available to a limited extent, solubility is high and the concentration is not limited at the L/S ratio used in the tests.

Case B: Leaching process is solubility controlled, maximum concentrations are reached at the occurring L/S ratio, availability is high and no depletion of the solid phase can be noticed during the tests.

In nature, often a mixture of both processes occurs, where either the one or the other process dominates.

Focusing on the measured concentrations in mg L^{-1} in case A (1), it may occur by chance that concentrations of SSE are in the range of the initial concentrations of the column test and S4 concentrations are comparable to column test concentrations after a higher cumulative L/S ratio. However, there is no physically based correlation between both. Whereas concentrations in the batch tests are controlled by the total available amount of the constituent and the L/S ratio, the concentration in the column test arises from a depletion of the solid phase (and transport processes like hydrodynamic dispersion), because the dissolved constituent is carried out of the column. As a result, we cannot expect a physically based correlation between measured concentrations of batch and column test, when the constituent release is availability controlled. However, in case A (2), the released amount in mg kg^{-1} dry mass corresponds between the different test methods.

In case B (1), the same concentrations in mg L^{-1} are achieved in the different leaching tests because maximum solubility is determining the measured concentration.

The constituent release (case B (2)) is dependent on the L/S ratio and increases linearly with an increasing cumulative L/S ratio.

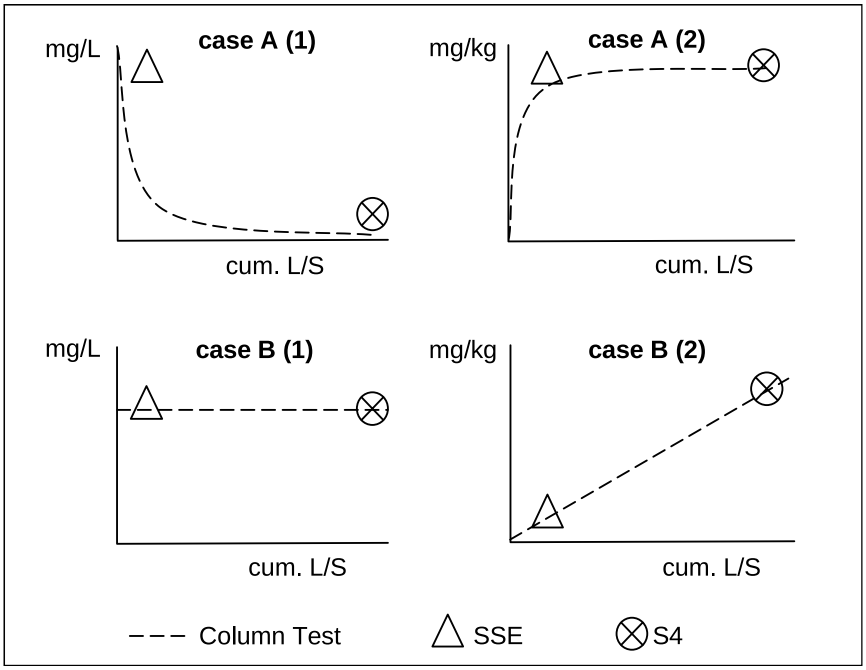

Figure 5: Theoretical schematic breakthrough curves of column tests and results of S4 and SSE tests, presented as measured concentration (mg L^{-1}) = (1) and released constituent (mg kg^{-1} dry mass) = (2) in different release processes: case A = availability control, case B = solubility control, cum. L/S = cumulative liquid-to-solid ratio of the column test and corresponding L/S ratio in the batch test, respectively

2.3.3 Literature review of comparison studies

In general, it is notable that different studies about the comparability of leaching tests covering a wide range of different kinds of material come to quite different conclusions. It has to be regarded that many of these studies are not published yet and that they are only available as so called "gray literature" so far. Additionally, results from the project network “Sickerwasserprognose” funded by the German BMBF (Federal Ministry of Education and Research) (see (Oberacker and Eberle, 2002; Rudek and Eberle, 2001)), are awaited by the end of 2005.

Utermann et al. (1998) present investigations about heavy metal release of 63 topsoil and subsoil samples from Niedersachsen, Germany. They show an element specific correlation between extracted amounts of ANE and SSE as well as S4 and SSE with regression coefficients of $r^2 = 0.622$ to 0.875 and $r^2 = 0.435$ to 0.817, respectively (Figure 6).

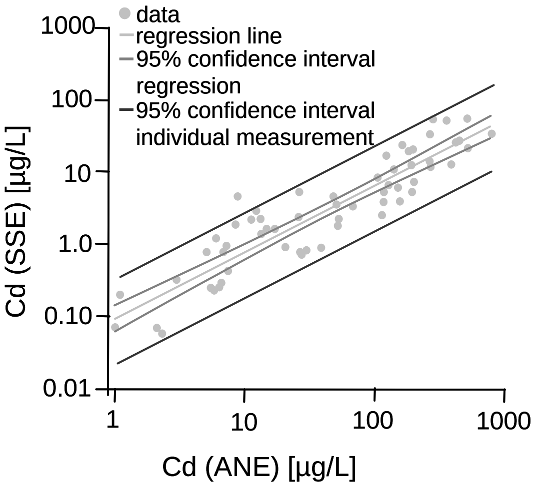

Figure 6: Regression curve for the relationship between Cd concentrations in the ANE and its concentration in the SSE, modified after Utermann et al. (1998)

They recommend the direct determination of SSE concentrations as a measure of soil water concentrations rather than recalculate them from the results of other leaching tests. In the case of an indirect determination with the help of regression analyses, the ANE is favored compared to the S4. A comparison with regulatory limits has to consider the element specific confidence intervals.

In Bielert et al. (1998), and Bielert et al. (1999), a study about the comparison of leaching tests and lysimeter studies of not anthropogenically contaminated farmland is presented. A correlation between leaching test results (SSE, S4, ANE, aqua regia extraction) is only found for few elements and some method combinations. In most cases, results for the investigated soils show no sufficient correlation.

In Dankwarth and Gerth (2002), the As concentration in seepage water of contaminated soils at an old tannery site is assessed using batch and column experiments. They conclude that seepage water concentrations can be assessed by non-saturated column tests. However, S4 and SSE come to comparable leachate concentrations. ANE is found to be not suitable for assessing extractable arsenate.

Kapp (2003) presents results of a comparison of leaching tests of soil samples from a Pb contaminated shooting range. The destruction of the soil structure due to high water addition and end-over-end shaking during S4 leaching is very intensive. However, it does not compensate the dilution effect. So concentrations in the SSE are usually higher than S4 concentrations.

Karnuth (2003) investigated the leaching behavior of inorganic contaminants from recycled demolition waste material in comparison to field lysimeter studies. According to the results, neither ANE and pHstat test at pH 4 nor batch tests following the S4 and the Modified S4 enable a proper assessment of leaching from recycled materials under natural conditions. A combination of long-term tests (with material in the original grain size) where samples are not shaken, and batch tests performed with varying L/S ratio (with ground material) is proposed. This enables a better control of factors like friction, which occur when the S4 and Modified S4 are carried out. Results derived from this test combination provide useful information on solubility and availability of substances. Nevertheless, a comparison with field tests shows comparable maximum concentrations only for a few elements.

BLfW (2001) compares in the second interim report from March 2004 preliminary results of column tests, SSE (also modified with a constant L/S ratio of 1:1), S4, ANE, and lysimeter experiments. They investigated three reference materials from the BMBF project network “Sickerwasserprognose”. The preliminary results show that leaching tests are not comparable with each other. In most cases, SSE shows highest and S4 lowest concentrations. SSE results are approximately comparable with column test results after the exchange of the first pore volume. Results from S4 and modified SSE seem to be comparable with column test results after the exchange of several pore volumes (> 3 pore volumes). (This conceptual approach stands in contrast to the basic considerations about the comparability of batch tests with column tests in section 2.3.2.) According to this study, the SSE concentrations overestimate the mean lysimeter concentration in most cases, whereas S4 concentrations are able to predict them relatively well. However, SSE seems to be suitable for the estimation of maximum concentrations of the lysimeter seepage water from the investigated reference materials.

Durner et al. (2004) compared different leaching tests (S4, SSE, pH_{stat} at pH 4, ANE and unsaturated column tests) at several materials. According to their results, SSE is the only method which could be regarded as close to nature with respect to equilibrium conditions. This is due to the narrow L/S ratio and minor addition of mechanical energy. Anyhow, it causes problems with non-standardized instructions and small leachate amounts. According to this study, it is in general possible to relate concentrations from different leaching tests to results of a certain time frame of the column tests. (This conceptual approach stands in contrast to the basic considerations about the comparability of batch tests with column tests in section 2.3.2.). Whereas a prognosis due to the completely different leaching test conditions, with respect to eluent, contact time, and agitation, is not possible.

2.4 Direct soil water sampling as alternative to leaching tests

As an alternative to leaching tests, soil water can be investigated directly. For the sampling of soil water, different methods are available. The application of suction cups and centrifugation of soil samples shall be discussed in this section. Other methods are described for instance in Sposito (1998) and Bufflap and Allen (1995b).

2.4.1 Suction cups

The applicability of suction cups for soil water sampling is described in detail in the DVWK Merkblatt 217 and in Bittersohl et al. (2000), and Borho (2000). An overview about installation, sampling strategy, sampling systems, different materials as well as advantages and disadvantages of different types of suction cups on the basis of practical experience is given in Nitsche (2003). In Grossmann et al. (1987) and Grossmann and Udluft (1991), a review about different materials, installation recommendations, and sorption behavior as well as the influence of the applied vacuum and effects of preferential flow, filtration, precipitation, degassing and microbial processes inside the sampling system is presented. Different suction cup materials were also tested by Rais et al. (2006) to investigate the sorption of trace metals in the presence and absence of dissolved organic carbon. The measurement of redox potential inside the suction cups is described in Uhlig et al. (2002). As measurements with suction cups are presented in Wenzel et al. (2002).

In general, suction cups are used especially for long-term monitoring purposes and to investigate the seasonal variability of soil water concentrations. The method enables the direct and repeatable sampling of soil water. Measured concentrations can be used directly for the comparison with limit values (LUA, 2002). Measured concentrations are independent from the applied vacuum if the soil water is in equilibrium with the solid phase, depending on the seepage water velocity and sampling depth.

Problems can occur with sampled soil water amounts in coarse grained material with low water contents. For sites with heterogeneous contaminant distribution or where preferential flow tends to play a major role for contaminant release and transport, the application of suction cups cannot be recommended due to the small average volume of one suction cup and the need for huge numbers of suction cups in such cases.

Related methods are suction plates (Bittersohl et al., 2000; Kosugi and Katsuyama, 2004) and pan samplers (Barbee and Brown, 1986).

2.4.2 Centrifugation

The centrifugation method is well-established in the field of pore water sampling in sediments. For the sampling of soil solution it is used less frequently so far. Fundamentals about the centrifugation method are described, for instance, in Bufflap and Allen (1995b), Edmunds and Bath (1976), Elkhatib et al. (1987), HLUG (2001), Hofmann (2002), LfUG and LfW (2001), and Winger et al. (1998). A comparison to other methods is given in Bufflap and Allen (1995a) and Bufflap and Allen (1995b) (squeezing, dialysis, and suction filtration); in Elkhatib et al. (1987), Kinniburgh and Miles (1983) (immiscible liquid displacement methods); and in Winger et al. (1998) (dialysis and vacuum methods). The influence of different speeds is investigated in Edmunds and Bath (1976), Elkhatib et al. (1987), Grieve (1996), Kinniburgh and Miles (1983), and Winger et al. (1998).

In contrast to the suction cup method, centrifugation is a fast and simple method, which is also applicable for the assessment of large and heterogeneous contaminations. The application of this method requires sufficient high water contents of the investigated material. For this reason, coarse grain sizes often cause problems. It is often seen as a disadvantage that large sample quantities are needed for this method. The method may also be suitable for anoxic samples if centrifugation is conducted as soon as possible after sampling and the material is transported in air tight vessels with a minimized air volume. It can be expected that concentrations are relatively independent on the applied centrifugal acceleration if the soil water is in equilibrium with the solid phase. If a moderate rotation speed is chosen, the amount of ions released from the double layer is negligible (Bittersohl et al., 2000).

2.5 Conclusions and recommendations

Conclusions on the comparability of leaching tests

Previous practical experience and fundamental research studies show that a conversion of leaching test results, as is proposed by the (already withdrawn) DIN V 19735 (1999), is impossible.

Correlations between results obtained by different methods, regarding different kinds of material and different sites, are not significant. This is due to different leaching processes. There is no physically based correlation between concentrations (in mg L^{-1}) of column and batch tests when the leaching process is availability controlled, even under ideal conditions.

Recommendations for groundwater risk assessment

It has to be regarded that it is not possible with any leaching test to entirely reflect natural conditions (and this was not the original intention during the development of batch leaching tests anyway). Several parameters distinctly deviate from natural conditions (see section 2.1.1) which complicates a transfer from leaching test results to the field.

For short-term risk assessment, soil water should be sampled and investigated directly by suction cups (for monitoring purposes) or centrifugation (for inventory purposes). If this is not possible, the SSE or analogous batch tests for coarse material with a narrow L/S ratio should be applied. A suggestion could be a modified saturation soil extraction where a soil column is saturated and the eluate is removed by suction at the bottom of the column as is proposed by Gerth and Förstner (2003). With this method, an unsaturated column test could follow in the same vessel.

In order to assess the long-term leaching behavior, total contents of the contaminant in the investigated material have to be taken into account additionally. Furthermore, it is essential to understand the dominant physical and chemical leaching processes and to figure out the main leaching controlling parameters. Therefore, the following methods are recommended: pH_{stat} tests (or as an alternative the CEN:prTS14429, see section 2.2) at different pH provide an insight to leaching processes and possible future leaching scenarios. Batch tests similar to the S4 procedure with different L/S ratios are useful to find out whether the release process is solubility or availability controlled. Additionally, it is possible to determine the maximum solubility and maximum availability with this method.

Furthermore, unsaturated column tests provide an insight into leaching processes and releasable amounts even though they require great experimental effort.

Other leaching tests like S4 or ANE are not suitable for the estimation of field soil water concentrations.

If the speciation is a critical leaching parameter, sequential chemical extractions could be applied. These are elaborate methods, which have to be interpreted with care, since extraction steps are operationally defined and the selectivity of the leaching agents is questionable. However, they could give valuable hints on the quantity of easily mobilizable contaminants and the release under variable conditions. Investigations with x-ray absorption spectroscopy can solve the problem of speciation, especially for mineral phases, but these elaborate methods are widely applied for research studies and less frequent used for risk assessment of contaminated sites.

For the assessment of the transport of the contaminant to the groundwater, it has to be taken into account that inorganic substances are not degradable. After saturation of the binding capacity of the soil, an undiminished contaminant breakthrough to the groundwater has to be expected. The source concentration stands for the starting concentration as well as the possible maximum at the end of the soil passage (point of compliance, transition between the water saturated and unsaturated zone) (Gerth, 2001). Sampling point should be the contamination source where the highest concentrations occur (BLfW, 2001). For some elements like As, Cr, Sn, the toxicity strongly depends on the binding form, which can change during the displacement from the source to the groundwater surface. This has to be taken into account for environmental risk assessment.

3 Methods for the assessment of metal concentrations in soil water at anoxic sites

3.1 Introduction

Leaching tests are used for groundwater risk assessment of contaminated sites alternatively to soil water and groundwater investigations. They are inevitable for the assessment of contaminated material prior to a further deposition. However, the suitability of leaching tests for the assessment of soil water concentrations is still a controversial issue.

A detailed overview about various leaching test procedures for different applications is given in van der Sloot et al. (1998). Beneath other parameters like pH, dissolved organic carbon (DOC), speciation, reaction kinetics, specific surface area and test conditions like the liquid-to-solid (L/S) ratio, temperature, contact time, kind of agitation etc., redox conditions can play a major role in controlling leaching behavior of inorganic contaminants. This aspect is not taken into account when leaching tests are carried out in open contact with the atmosphere (Hage and Mulder, 2004; Kersten and Förstner, 1987; Rapin et al., 1986; Rudek and Eberle, 2001; van der Sloot, 1991; van der Sloot, 1996; van der Sloot et al., 1994; van der Sloot et al., 1998).

Redox conditions are of particular importance if metals occur as sparingly soluble reduced or oxidized species. In this case, a change in redox potential can lead to transformation into better soluble species and an increasing release. Attention should be paid to the sample pretreatment in particular, since oven drying as well as freeze-drying affects metal speciation (Kersten and Förstner, 1987). Changes in redox potential are generally closely linked to a change in pH. Under specific conditions, oxidation of sulfide may lead to production of acidic solutions (e.g. acid mine drainage) (Åström, 1998a; Åström, 1998b; Jerz and Rimstidt, 2004; Morse and Luther, 1999; Sohlenius and Öborn, 2004; Sracek, 2004; van der Sloot, 1996).

The important equilibrium and rate determining parameters for the sulfide breakdown and the formation of acid mine drainage include temperature, pH, concentration of dissolved oxygen, concentration of oxidants other than oxygen, concentration and types of anions, particle size/surface area, rate of oxygen transfer, rate of electron transfer, presence and concentration of microorganisms, availability of nutrients (da Silva, 2004; Edwards et al., 2000; Garcia et al., 1995; Pugh et al., 1984; Rimstidt et al., 1994; Rodriguez et al., 2003; Weisener et al., 2003; Williamson and Rimstidt, 1994).

In this section, the leaching behavior of sulfide-bearing flotation residues from a former ore mine in northern Rhineland-Palatinate, Germany, was investigated. The applicability of three currently used leaching tests (the German DEV-S4 (S4), Saturation Soil Extraction (SSE), Ammonium Nitrate Extraction (ANE)) was assessed, and results compared to soil water samples obtained by centrifugation and suction cups. Furthermore, the influence of sample storage and oxidation on leaching test results was investigated. For the prevention of sample oxidation, causing lowered pH and increasing heavy metal release, we developed a feasible modification, which offers the possibility to assess the leaching behavior under anoxic conditions.

3.2 Material and methods

3.2.1 Material/Field site

The samples investigated were collected at a site in the state of Rhineland-Palatinate, Germany, where sulfide-bearing flotation residues of a former ore mine were deposited until 1961. Characteristics of the samples are summarized in Table 2. At depths below approximately 30 to 50 cm, the local hydrology and the presence of sulfide minerals result in anoxic conditions and pH values around 7. Oxidation of the deposited material in contact with the atmosphere leads to an oxic topsoil with pH values around 5. The total concentration of selected trace and major elements was determined using a wavelength-dispersive X-ray fluorescence spectrometer (WDXRF) (Phillips, MagiX Pro). Total carbon and sulfur content were determined with a LECO analyzer CS 225.

Table 2: General characteristics of the soil samples

	Range of the whole profile	P3-0.45	P3-0.7
Depth [m]	0-5	0.30-0.45	0.6-0.7
Color		gray	gray
Clay [% (wt)]	35-40	35	35
Silt [% (wt)]	60-65	65	65
Loss of ignition [% (wt)] (DIN 18128, 1990)	4.0-5.5	3.97	4.75
Water content [% (wt)] (DIN 18121-1, 1998)	42-59	51.6	55.4
Total contents [g kg^{-1} (dw)]			
Pb	1.5-12.6	2.74	1.49
Zn	0.2-13.3	10.06	10.09
C (DIN ISO 10694, 1996)	1.2-21.8	3.2	3.6
S (DIN ISO 15178, 2001)	0.2-9.6	6.3	7.2

3.2.2 Leaching tests

Three different leaching tests (S4 (DIN 38414-4, 1984), ANE (DIN 19730, 1997), and SSE according to (BBodSchV, 1999)) were applied to 17 samples of a soil profile from 0 to 5 m depth, from each vertical 30 cm section. All chemicals used were of analytical grade (p.a.). Deionized water was produced with the water purification system arium® 611 DI (Sartorius). All materials in contact with the leachate were pre-cleaned with 0.14 M HNO_3 solution for at least 24 h and subsequently rinsed two times with demineralized and once with deionized water.

German DEV-S4 test according to DIN 38414-4 (S4)

In this standardized procedure, 100 g of each sample were leached for 24 h with deionized water at a L/S ratio of 10. Sample agitation was performed by using and end-over-end shaker. The S4 tests were modified using air dried samples for a better comparison with the ANE and SSE.

Ammonium Nitrate Extraction (ANE)

In this standardized procedure, 20 g of each air dried sample were leached for 2 h with 50 ml of a 1 M ammonium nitrate solution at a L/S ratio of 5:2. Sample agitation was performed using a shaking table.

Saturation Soil Extraction (SSE) (BBodSchV, 1999)

In the saturation soil extraction 250 g of the air dried sample were moistened with deionized water, stirred, and stored for 24 h at 5 °C in an air tight vessel. Afterwards the sample is transferred to a centrifuge vessel and deionized water is added until the yield point. After stirring, the sample is again stored for 24 h at 5 °C and then centrifuged for 30 min at 5 °C with a speed of 2000 *g*. The leachate is decanted and filtered through a 0.45 µm membrane filter (Schleicher & Schuell, 47 mm).

In addition, for the investigation of oxidation kinetics, S4 tests were performed in 45 parallels at increasing storage time. 45 1L-PE-bottles were filled with 150 g of a homogenized field moist bulk sample from 30 to 45 cm depth contributing to 100 g dry mass immediately after sampling. Samples were stored at 5°C in closed bottles to prevent evaporation. From time to time the bottles were opened for a few minutes to exchange the air inside the bottle. Leaching tests were started in triplicates after a storage time between 0 and 450 days by the addition of about 1000 g deionized water, leading to a L/S ratio of 10.5 ± 0.2.

Modified leaching tests

In the scope of this study, a modification of the leaching tests was developed to prevent oxidation of the samples. Therefore, the samples were filled in previously prepared bottles directly in the field after homogenization. The bottles were already weighed and filled with the leachant in the laboratory. In order to minimize the volume of air inside the bottle, the amount of sample and leachant was adjusted to the bottle-volume, regarding the L/S ratio. Therefore, preliminary tests are necessary. Drying and storage of the samples was obviated. The tests were started directly in the field. After the transfer to the laboratory, the bottles were weighed again for a precise determination of the sample mass. The water content was determined with an aliquot of the sample (DIN 18121-1, 1998). For the SSE the first step of drying, moistening, and storing for 24 h was omitted and the extractions were started in the field by the addition of deionized water up to the yield point. The leaching tests were performed in triplicates on sub-samples of 60 to 70 cm depth. In addition, the influence of flushing of the leachant with argon and performance of the S4 test inside a glove box under oxygen free atmosphere was investigated.

All leachates were filtered through 0.45 µm membrane filters (Schleicher & Schuell, 47 mm). The filters were precleaned with deionized water, the first approximately 3 ml of the filtrate was discarded and pH and electrical conductivity (EC) were measured. The final leachates for major cation and metal analyses were preserved with nitric acid (p.a.) to pH 2. Major cations were analyzed by flame photometry (Eppendorf, ELEX 6361), and major anions by ion chromatography (IC) (Methrom, 761 Compakt IC, column: Metrosep A SUPP5). Heavy metals (Zn, Pb, Fe, Mn) and Mg were analyzed by flame atomic absorption spectrometry (F-AAS, Solar, Unicam 989) with a detection limit of 0.1 mg L^{-1} and inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Elan 6100) with a detection limit of 0.001 mg L^{-1}, respectively. Alkalinity has been determined immediately after filtration manually by Gran titration with 0.1 m HCl (Appelo and Postma, 1999).

The L/S ratio is generally defined as the amount of leachant in contact with the sample material related to the amount of dry matter (weight/weight), taking the moisture of the sample into account by adding it to the liquid and subtracting it from the solid amount.

The soil pH was determined in $CaCl_2$ solution according to DIN ISO 10390, (1997).

3.2.3 Soil water sampling

To assess the comparability of leaching tests to seepage water concentrations, soil water was sampled with suction cups and by centrifugation of soil samples. The suction cups used in this study were made of polyethylene (Ecotech) with a diameter of approximately 32 mm and shaft lengths between 1 and 3 m. Vacuum was applied by a footpump and the soil water was sampled inside the shaft of the suction cup. The suction cups were installed in three different depths of 1 m, 2 m, and 3 m at a distance of about 1 m from the sampling point of the soil samples used for leaching tests and centrifugation.

For centrifugation, soil samples were transported in air tight PE-vessels. Afterwards the samples where centrifuged immediately in the laboratory at 5°C for 30 min with a speed of 1100 *g* in a two part Teflon centrifuge tube with a volume of 400 ml, the upper part of which drained into the lower part through a 4 mm diameter hole (Figure 7). A small amount of fiberglass and filter paper of the appropriate diameter (Blauband, Schleicher & Schuell, Nr. 300210) was placed over the bottom of the Teflon tube to prevent the transfer of fine particles to the extracted soil solution.

The soil solution samples obtained by suction cups and centrifugation were filtered and analyzed in the same way as the leachates.

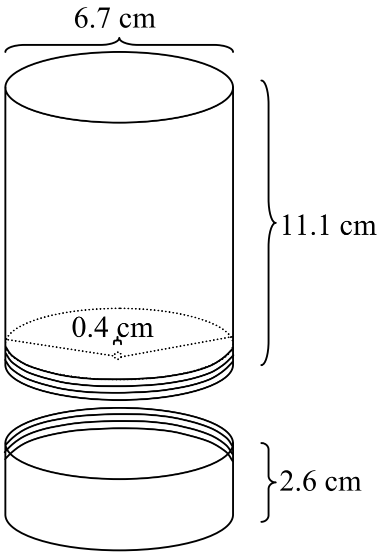

Figure 7: Teflon centrifuge tube

3.3 Results and discussion

Results from the leaching tests of the investigated soil profiles are presented in Figure 8. The topsoil shows soil pH values determined in $CaCl_2$ solution down to 5.4. With increasing depth, soil pH increases up to 7 from 2 m on. The pH in the soil solution obtained by centrifugation and suction cups is typically one pH value higher. The pH from SSE and ANE are significantly lower. This is due to oxidation reactions of the sulfide-bearing soil samples during drying and storage.

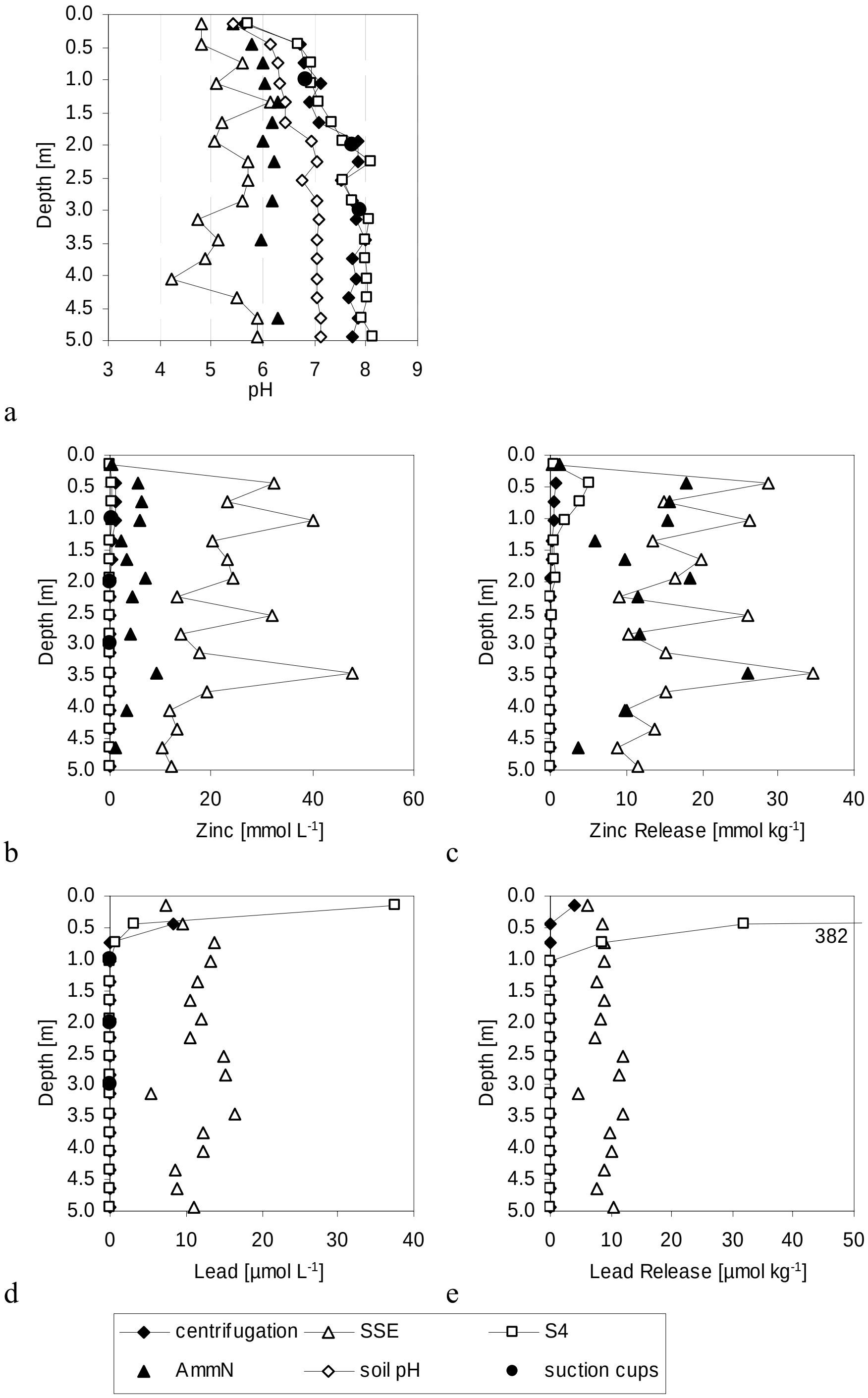

Figure 8: Results of unmodified leaching tests of the soil profile a: pH values of centrifugation, SSE, S4 tests, ANE, suction cups, and soil pH determined in $CaCl_2$ solution; b: Zn concentrations in mmol L^{-1}; c: release of Zn in mmol kg^{-1} dry mass; d: Pb concentrations in µmol L^{-1}; e: release of Pb in mmol kg^{-1} dry mass

The influence on the pH of S4 leachates is not visible due to dilution caused by the high L/S ratio of 10. Zn concentrations in ANE are up to 500 times and in SSE up to 3000 times higher than in the centrifugate.

The released amount of Zn in mg kg^{-1} dry mass is similar in SSE and ANE. This is a hint for a limited availability of Zn according to the oxidized amount. The same effect can be observed for the release of Pb. Pb concentrations in SSE vary between 5 and 17 µmol L^{-1} whereas the concentrations in centrifugates and suction cup samples are below 0.5 µmol L^{-1}. ANE concentrations vary between 150 and 410 µmol L^{-1}, released amounts vary between 400 and 1300 µg kg^{-1} dry mass. They are not shown in Figure 9 for clarity reasons.

These results indicate that leaching tests of anoxic sulfide-bearing material carried out in contact with the atmosphere without an adjusted sample pretreatment lead to a significant overestimation of the release in the field.

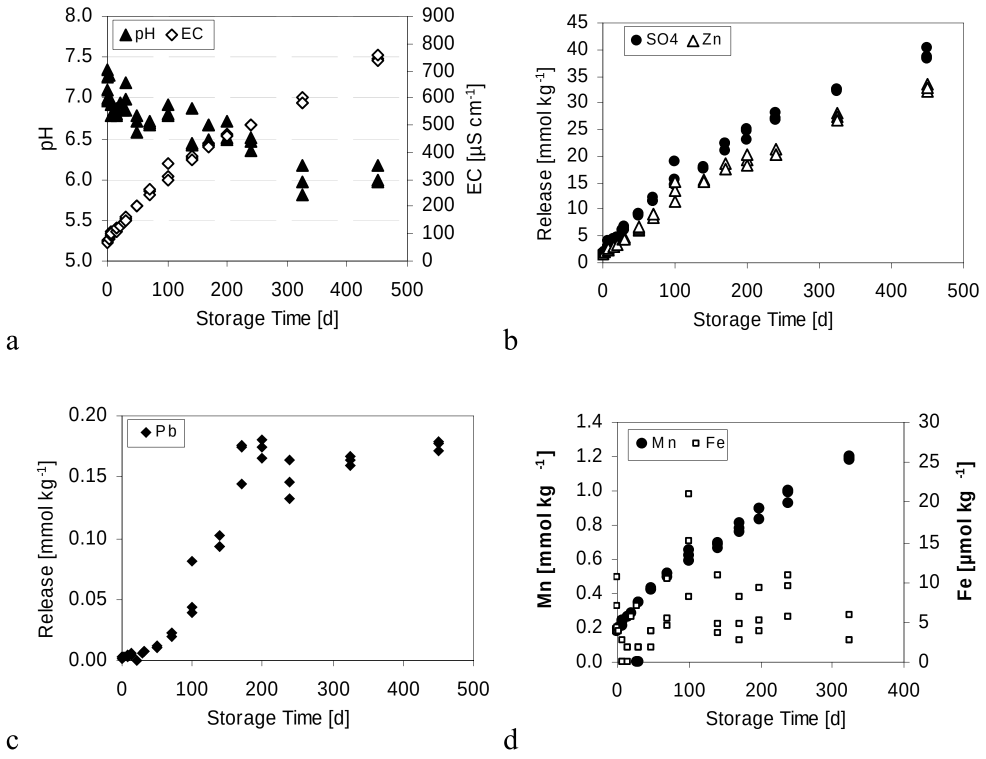

Figure 9: Results from S4 leaching tests of sample P3-0.45 at increasing storage time of the sample; a: pH and electrical conductivity (EC) in µS cm^{-1}; b: release of Zn and sulfate in mmol kg^{-1} dry mass; c: release of Pb in mmol kg^{-1} dry mass, d: release of Mn in mmol kg^{-1} and Fe in µmol kg^{-1} dry mass

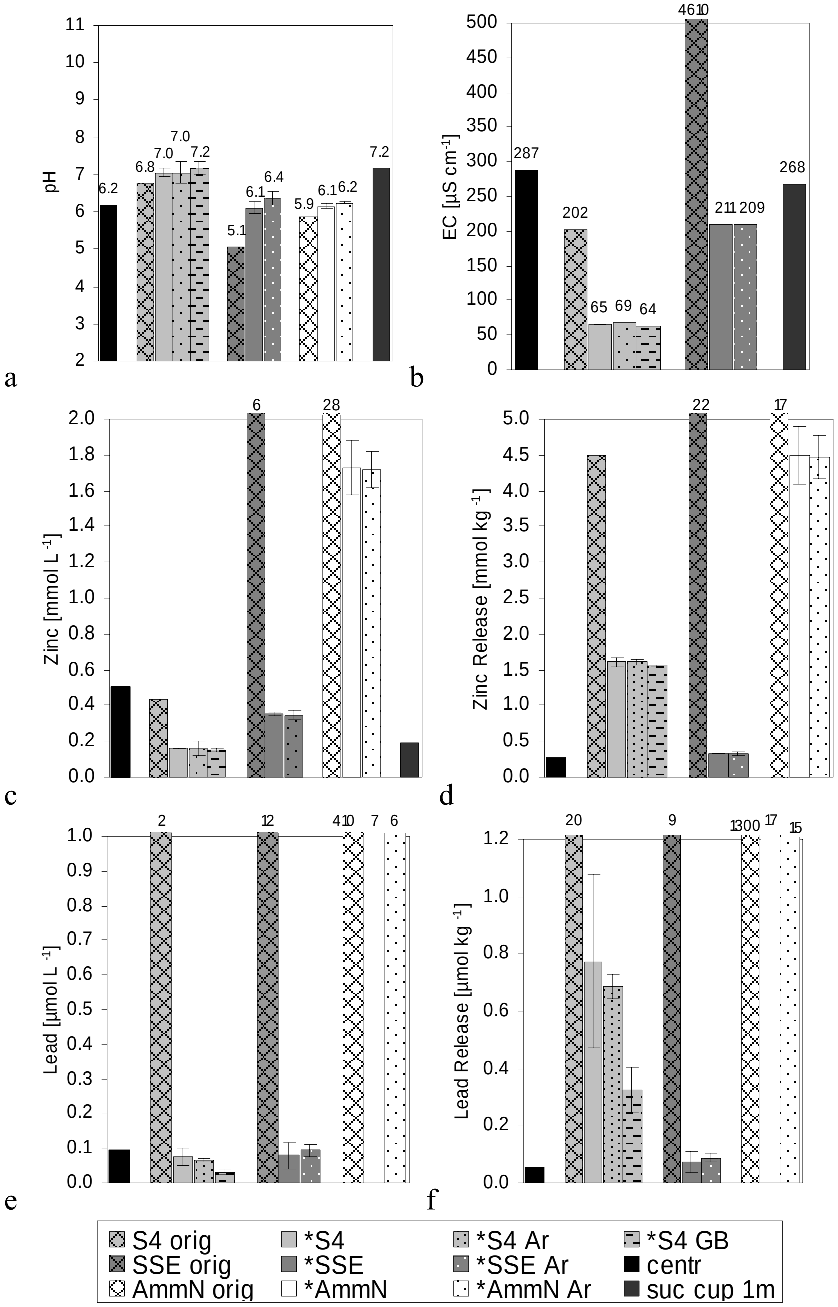

Figure 10: Results of modified leaching tests (*S4, *SSE, *ANE) and soil sampling by centrifugation (centr) from sample P3-0.7 of 0.6 to 0.7 m depth and by suction cup in 1 m depth (suc cup 1 m), a: pH of the leachate, b: electrical conductivity (EC), c: Zn concentrations in mmol L^{-1}, d: released Zn in mmol kg^{-1} dry mass, e: Pb concentrations in µmol L^{-1}, f: released Pb in µmol kg^{-1} dry mass;
leachate previously flushed with argon (Ar), dotted columns; S4 tests conducted inside a glove box (GB), dashed columns; original unmodified leaching tests from related depth, checkered columns; leaching tests carried out in triplicates, error bars show standard deviation

In Figure 9 results from S4 tests of sample P3-0.45 at increasing storage time are presented. The pH slowly drops with increasing storage time from values around pH 7 down to pH 6 after about one year. The electrical conductivity (EC), as a measure of dissolved ion content in the leachate, rises with a slope of 2.5 µS cm^{-1} per day during the first three month. This is corresponding to the increasing release of Zn and sulfate. Zn release (R_{Zn}) increases linearly with increasing storage time (t_S) within the first 200 days and can be expressed in the following form:

$$R_{Zn} = 0.09\ t_S + 1.9 \qquad (1)$$

with a value of determination (r^2) of 0.977. Subsequently the slope decreases.

However, after 450 days a plateau phase has not been reached so far. The release of Pb increases fast after an initial phase of slow oxidation. After 200 days of storage time it seems to be more or less constant with 0.16 ± 0.01 mmol kg^{-1}.

Figure 10 shows a comparison of the different modified leaching experiments. As described before, sample drying and storage have been omitted and the tests have been started directly in the field in previous prepared bottles to prevent oxidation. For comparison, unmodified leaching results from a sample of related depth (referred to Figure 8) are shown (checkered columns). In all cases, pH values of unmodified leaching tests are lower and concentrations as well as released amounts of Zn and Pb are much higher than in the modified leaching tests. Centrifugates, SSE and ANE provide pH values around 6. pH values of S4 tests and suction cups are slightly higher around 7. With ANE, the highest amounts of Zn are released due to competing sorption of the ammonium. Zn concentrations and released amounts of the modified SSE are in a similar range as in the soil solution obtained by centrifugation. Modified S4 tests show lower concentrations but remarkably larger released amounts in mg kg^{-1} dry mass. This is due to the unrealistic high L/S ratio in the S4 test compared to natural water content in the soil. Obviously, the effect of argon flushing (dotted columns) and the performance inside a glove box (dashed columns) is small.

The observed pH values and Zn concentrations indicate that with this modification of the leaching tests it is possible to prevent oxidation of the samples efficiently. Pb is released in far less amounts compared to Zn, which are presented in µmol L^{-1} and µmol kg^{-1} respectively. Again, with ANE the highest amounts are released whereas Pb concentrations as well as released amounts of the modified SSE are in a similar range as in the centrifugates. Modified S4 tests show also similar concentrations but tenfold higher released amounts due to the L/S ratio. The effect of argon flushing is small and results are coincident regarding the standard deviation. The performance of S4 tests inside a glove box seems to have a wider influence on the release of Pb compared to Zn. Only half as much Pb is released here. According to this result, a partial oxidation of Pb bearing phases in the modified S4 test can not be excluded.

3.4 Conclusions

Leaching tests after BBodSchV (1999), DIN 19730 (1997), and DIN 38414-4 (1984) are not suitable to estimate current soil water concentrations of heavy metals like Zn and Pb in sulfide-bearing flotation residues. Oxidation of the samples during sampling, storage, and pretreatment leads to a transfer of sparingly soluble sulfides like sphalerite into more soluble species. pH value is lowered, which increases the metal mobility additionally.

For this reason, a modification of the leaching tests is proposed where oxidation is prevented substantially. According to our results, argon flushing does not improve results significantly. The performance of S4 tests inside a glovebox had no influence on the release of Zn. However, it has a significant influence on the release of Pb, which occurs in much lower concentrations in this material compared to Zn, which has to be taken into account for the interpretation of leaching results. Compared to the tests without modification the overestimation of Pb release still seems to be tolerable, regarding that the results provide a conservative assessment. The performance of SSE inside a glove box still has to be investigated.

Nevertheless, the modified SSE seems to be the only of the tested leaching procedures, which provides more or less realistic results to estimate current heavy metal release in the field. ANE is not suitable because a leachant is used which releases considerably higher amounts of cationic metals due to competing sorption. The S4 test usually underestimates concentrations due to the high L/S ratio, which leads to dilution effects (Förstner, 1998; Förstner and Thöming, 1997). However, released amounts in mmol kg^{-1} dry mass are significantly overestimated by this method. Since there is no sufficient way to directly convert results from S4 tests and ANE to SSE (Förstner and Thöming, 1997; Karnuth, 2003; Lichtfuss, 2000; Mathews, 2001) (compare to section 2) the application of this two methods for the assessment of heavy metal release in the field can not be recommended.

4 Vertical distribution and metal speciation of sphalerite (ZnS) bearing mine waste tailings

4.1 Introduction

Sulfide bearing mine tailings are a serious environmental problem in many regions worldwide (Dudka and Adriano, 1997; Shu et al., 2001; van Geen et al., 1999). Pyrite (FeS_2) containing mine tailings piles undergoing oxidation are a major source of acid mine drainage (AMD) containing metal contaminants (Impellitteri, 2005). Although mines are classified on the basis of their predominant products, they produce large quantities of other elements as coproducts. As a result, metal ore processing usually leads to multi-elemental contamination of the environment (Dudka and Adriano, 1997). Typical contaminants occurring in association with Zn and Pb ore mining activities include Al, As, Cd, Cu, Hg (Bridge, 2004).

Zn and Pb are often found together in ore deposits, but the metals have different applications and biological effects. Zn is a physiologically essential element for all organisms (Dudka and Adriano, 1997). However, Zn at high concentrations is phytotoxic, and Zn contamination of soils can have adverse effects on crops, livestock, and man (Oliver, 1997). Poor plant growth and reduced soil cover caused by metal toxicity can lead to enhanced soil erosion and metal mobilization in runoff water with subsequent deposition into nearby water bodies (Lasat, 2000).

In contrast, Pb has no known positive biological function and creates serious environmental and health hazards (Dudka and Adriano, 1997). Pb is less phytotoxic than Zn, and Pb uptake by plants from contaminated soils bears the potential for Pb transfer along the food chain.

The weathering of sulfidic mine tailings often results in anoxic conditions, since oxygen delivery may be slower than local oxygen consumption through oxidation reactions. High water contents and fine grain sizes may retard the oxygen delivery and promote the development of anoxic conditions (Mascaro et al., 2001). Under anoxic conditions, sulfide minerals are of low solubility and the release of metals is impeded. The mobilization of metals from sulfidic tailings is caused by an interaction of oxidation and acidification processes. Trace metals and metalloids like As may be associated with Fe-monosulfides and pyrite or be present as discrete sulfide minerals. The oxidation of these sulfides leads to the transformation of sulfide into oxidized sulfur species (i.e., SO_4^{2-}) and the release of metals and As into solution. The released trace elements may subsequently react with organic or mineral surfaces or leach into surface and groundwater. In oxidizing environments, iron oxides are likely to precipitate and it is possible that certain metals are co-precipitated in, or adsorbed onto, these oxides, whereas others are leached out of the soil (Sohlenius and Öborn, 2004). The oxidation of sulfide minerals may cause a decrease in pH, which can also affect the mobility of heavy metals and As (Cappuyns and Swennen, 2005; Simpson et al., 1998).

The critical pH value for the desorption of Zn is around 5 (Alloway, 1999). The desorption of Pb requires pH values 1 to 2 magnitudes lower.

While oxidative surface reactions on iron sulfide minerals have been extensively studied (Rimstidt and Vaughan, 2003), far fewer studies have focused on the dissolution of other sulfide minerals such as sphalerite (ZnS) (Salomons, 1995; Weisener et al., 2003). The direct oxidation of sphalerite does not release acid in itself (overall reaction):

$$ZnS + 2\,O_2 \rightarrow Zn^{2+} + SO_4^{2-} \qquad [1]$$

However, subsequent hydrolysis of the Zn^{2+} ions releases protons and may lead to pH values around 5.5 in an unbuffered solution (Banks et al., 1997):

$$Zn^{2+} + H_2O \rightarrow Zn(OH)^+ + H^+ \qquad (pK\ 8.96) \qquad [2]$$

Additionally, protons may be released through sorption of Zn^{2+} ions on mineral surfaces or humic substances. The hydrolysis of 1 mol Zn^{2+} cations and concurrent adsorption on oxides or hydroxides as a bidentate complex can result in the release of about 1.7 mol H^+ into solution (Kinniburgh, 1983). At low pH (<3) the oxidative dissolution of sphalerite may be catalyzed by abiotic Fe^{3+} reduction (Eq. [3] and [4]) and subsequent oxidation of Fe^{2+} by *Thiobacillus ferrooxidans* (Garcia et al., 1995). If Fe^{2+} is not completely reoxidized or leached with the soil water, Fe^{3+} mediated sphalerite oxidation may lead to acidification.

$$ZnS + 2\,Fe^{3+} \rightarrow Zn^{2+} + S^0 + 2\,Fe^{2+} \qquad [3]$$

$$Zn^{2+} + S^0 + 4\,H_20 + 6Fe^{3+} \rightarrow Zn^{2+} + SO_4^{2-} + 6\,Fe^{2+} + 8\,H^+ \qquad [4]$$

In contrast, the oxidation of pyrite by oxygen as well as Fe^{3+} directly releases acid (overall reaction) (Rimstidt and Vaughan, 2003):

$$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2\,H^+ \qquad [5]$$

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 16\,H^+ + 2\,SO_4^{2-} \qquad [6]$$

Soil pH is a result of both acid producing and acid neutralizing processes. The dissolution of carbonate minerals (calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) or carbonates of Sr, or Mn) can neutralize AMD. However, only a fraction of the total amount of carbonates may be available for buffering acid input because the precipitation of iron hydroxide and calcium sulfate can form coatings around the particles and prevent further neutralization (Salomons, 1995). Field and experimental evidence indicates that carbonates dissolve in the order calcite, dolomite, ankerite (Ca(Fe, Mg, Mn)$(CO_3)_2$), siderite ($FeCO_3$) (Al et al., 2000). While initial siderite dissolution may exert a neutralizing effect, continued dissolution may produce additional acidity through the oxidation of the released ferrous iron and subsequent iron oxide precipitation (Paktunc, 1999). While the neutralization of acidity by carbonates is a relatively fast process, further acidity may be neutralized by slower reactions of protons with silicate minerals (Salomons, 1995).

In the Devonian sedimentary rocks of the low mountain ranges of Germany, Zn and Pb ore deposits can be found. These deposits where mined since Roman times until the middle of the last century in a number of local small-scale mines. Mining-activities lead to a large number of unprotected small-scale mine tailings impoundments, which result in a considerable heavy metal contamination of soil and groundwater (Wieber and Knoblich, 1995).

In this work, we studied the fine-grained Zn and Pb containing flotation residues from one of these mines. The objective was to gain a more detailed understanding of the processes that determine the environmental fate of Zn, Pb and other trace elements in weathering fine-grained flotation residues under field conditions. For this purpose, we analyzed sample cores from the flotation residues for the vertical distribution of major and trace elements and the variations in pH, inorganic and organic C content. The chemical behavior of Zn, Pb, Fe, and Mn were further characterized by sequential chemical extractions (SCE) and the speciation of Zn by Zn K-edge EXAFS spectroscopy. The results from this study allow for a more detailed assessment of present and future environmental risks arising from the weathering of this type of flotation residue tailings.

4.2 Material and Methods

4.2.1 Field site description

In this study, we investigated a former tailings pond of a Zn/Pb/Ag ore mine in northern Rhineland-Palatinate, Germany, which was operated until 1961. The original ore deposit mainly consists of sphalerite, silver-bearing galena (PbS), and chalcopyrite ($CuFeS_2$). Pyrite occurs as accessory mineral. Further accessory minerals are siderite, ankerite, dolomite, calcite, and limonite (FeO(OH) nH_2O). Gangue is quartz (Hünermann, 1955). To extract the ore, the material was crushed, ground and subsequently processed in a flotation plant using organic agents such as Flotol, Sapinol, and potassium ethyl xanthate (Slotta, 1983). For the deposition of the flotation residues, a 70 m long and 25 m high dam was built (Figure 11). It was originally designed for a retaining capacity of 500 m length and 25 m depth. The tailings were pumped through a pipeline over the dam crest to be deposited by several discharges, providing an adequate tailings beach. With increasing distance to the dam the flow velocity decreased, leading to a distal deposition of the fine grained material. The small creek was redirected in a brick pipe. The pipe ran underneath the tailings pond and ended below the dam, directing the creek water back in to its former bed (Figure 11). Outlet discharge structures drained the clarified sewage of the tailings pond directly into the creek canal (Herbst, 1962). The flotation dump was used from 1946 until the mining activities were stopped in 1961. The largest part of the former tailings pond was later on covered with coarse detritus. Only the rear area is still directly accessible, which is covered with different grasses and rush. In this part, the thickness of the fine grained flotation residues ranges from 3 to 7 m. The residues show high water contents and water logging can be observed at the surface. Basis of the flotation dump is the former natural grown soil surface.

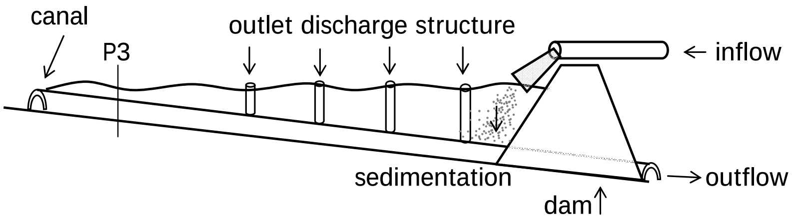

Figure 11: Schematic sketch of the deposition of the flotation tailings (not in scale) with the position of the soil profile P3

4.2.2 Soil sample collection and characterization

A soil core (P3) with 80 mm diameter and 5 m depth was collected in the rear part of the flotation dump (Figure 11). Bulk samples of 30 cm thickness were taken from the soil core at 0 to 5 m depth. Soil samples were labeled after the soil core (P3) and the depth (in m) of the lower limit below ground surface. The core samples were wrapped firmly in plastic and transferred into a glove box under oxygen free conditions (N_2/H_2 95/5 v/v%) within 4 h to preserve redox conditions.

The total metal contents of the soil samples were analyzed by energy-dispersive X-ray fluorescence spectroscopy (Spectro, X-Lab 2000, Kleve, Germany, 32 mm pressed wax-tablets) and the total C concentration was measured using a CHNS elemental analyzer (LECO, CHNS-932, St. Joseph, MI). The carbonate contents were determined by extracting 0.5-1.0 g of soil in 50 mL of boiling 1 M H_2SO_4 and CO_2 trapping using NaOH beads. The entrapped CO2 was quantified gravimetrically using an analytical balance (AT 261 Delta Range, Mettler-Toledo, Greifensee, Switzerland). Organic C was calculated as the difference between total and inorganic C. X-ray diffraction (XRD) spectra were recorded from powdered soil samples (Seifert, XRD 3000 TT, Ahrensburg, Germany, Cu-Kαradiation, 3 to 100 °2θ, 0.02° steps). The soil pH was determined at a solid-solution ratio of 2 g/5 mL in 0.01 M $CaCl_2$ solution using a glass electrode.

For the selection of samples to be investigated for metal speciation, the Ti and Zr contents were used as reference, because Ti and Zr are elements, which are insusceptible to weathering reactions. Ti concentration of the fine-grained gray flotation material averages 0.1 mol kg^{-1} (Figure 12). Zr averages 1.5 mmol kg^{-1} and shows the same distribution pattern as Ti (not shown). Only soil samples from the first centimeters and rust colored, sandy soil samples (e.g. P3-0.34), which appear within the first 50 cm as intermediate layers, show lower Ti and Zr concentrations. This may be due to higher concentrations of quartz sand since also Si concentrations are elevated in these particular samples (Table 3). For further investigations, only samples from the fine-grained gray material with similar Ti and Zr concentrations were chosen for SCE to improve the comparability and to avoid misinterpretations due to different original compositions.

4.2.3 Sequential chemical extractions

In order to characterize the extractability of Zn, Pb, Fe, and Mn, a five-step sequential chemical extraction (SCE) was carried out on three samples from the soil profile. The homogenized sample from 13 to 16 cm (P3-0.16) was chosen to represent the topsoil. The sample from 60 to 70 cm (P3-0.7) was selected as a sample from the transition zone where the soil pH is already lowered, and a sample from 2.3 to 3 m depth (P3-3.0) was chosen to represent the anoxic subsoil. The same samples were also analyzed by XRD for the determination of the bulk mineralogical composition. The speciation of Zn in these 3 samples and 2 additional samples from the topsoil was further investigated by Zn K-edge EXAFS spectroscopy. The SCE were conducted in a glove box under nitrogen atmosphere using oxygen free extractant solutions to preserve redox conditions. Agitation and centrifugation were conducted outside the glove box in air tight centrifugation vessels. The SCE was started with 6 replicates. After each extraction step, one subsample was withdrawn for EXAFS analysis, resulting in triplicates for the last two steps. Field moist soil corresponding to 8 g dry mass was initially weighed into 400 mL air-tight PE centrifuge tubes and subsequently subjected to five extraction steps (extraction parameters and references given in brackets):

Step 1) Extraction with 200 mL 1 M NH_4NO_3 (24 h, 20°C, (Zeien and Brümmer, 1989)).

Step 2) Extraction with 200 mL 1 M NH_4OAc (24h, 20 °C, pH 6, (Zeien and Brümmer, 1989)).

Step 3) Extraction with 200 mL 0.04 M $NH_2OH{*}HCl$ in 25% HOAc (6 h, 96 +/- 3 °C, pH 3, (Tessier et al., 1979)).

Step 4) Extraction with 0.025 M NH_4-EDTA (1.5 h, 20 °C, pH 4.6 (Zeien and Brümmer, 1989)).

After each extraction (steps 1-4), the solutions were centrifuged (15 min, 770 *g*, 20°C) and the supernatant withdrawn, filtered through 0.45 µm membrane filters, and acidified to pH < 2. 100 mL of the extractant from the previous step were used to wash the soil sample for 10 min at 20 °C to reduce artifacts due to redistribution of metals remaining in the entrapped extractant solutions. After the separation of the washing solution (centrifugation, filtration, acidification), the extracts were combined and analyzed for Ca, K, and Na using flame photometry (Eppendorf, ELEX 6361, Hamburg, Germany) and for Zn, Pb, Fe, Mn, and Mg using flame atomic absorption spectrometry (Solar, Unicam 989, Cambridge, UK).

In the final step 5, the residual fraction was determined by total digestion. For this purpose, the extracted samples were dried and 200 mg of each sample were added to 4 mL 48% HF, 2 mL of 65% HNO_3, and 4 mL of approx. 72% $HClO_4$ in a Teflon beaker and heated in 10 h to 150 °C. This temperature was kept constant for 2 h. After cooling, the mixture was fumed of at 180 °C in a closed system for 12 h. This residue was redissolved by heating with 2 mL HCl, 0.6 mL HNO_3, and 10 mL deionized water to 150 °C for 2 h. After cooling to room temperature, the solution was diluted to 100 mL and transferred into PE flasks. No visible residues were left after this procedure. All acids used were surface distilled. Trace and major ions were analyzed by ICP-OES (Fisons Instruments, Maxim I, Manchester, UK). Analyses of blank extractions were below the analytical detection limit for all extraction steps.

4.2.4 Zn K-edge EXAFS spectroscopy

Zn K-edge (9659 eV) EXAFS spectra of selected untreated or sequentially extracted soil samples were measured at the X-ray absorption (XAS) beamline at the Angstroemquelle Karlsruhe (ANKA), Germany. The ring was operated at 2.5 GeV with a beam current of 130 mA. The Si(111) monochromator was detuned by 40% using a software-controlled monochromator stabilization. Soil and reference samples were prepared as pellets and measured in transmission and/or fluorescence mode using a 5-element solid state detector. All measurements were performed at room temperature. The sequentially extracted soil sample from 60-70 cm depth was measured by Dr. Maarten Nachtegaal at the Dutch Belgian Beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The raw data were transformed into *k*-space using the WinXAS software (Ressler, 1998). The pre- and post-edge background correction was performed by fitting a first and second order polynomial function, respectively. The E_0 was determined as the inflection point of the Zn K-edge (2nd derivative equal to zero). The μ_0 was fit using a cubic spline function and minimizing the amplitude of the Fourier transform at radial distances (*r*) less than 0.9 Å. Linear combination fitting (LCF) was based on an extensive collection of reference spectra including Zn complexed by organic substances, Zn adsorbed to metal oxides and clay minerals, and Zn in primary and secondary minerals. Based on preliminary data analyses and soil chemical constraints, the following 4 spectra were considered in the final LCF fits: ZnS (sphalerite), Zn adsorbed to montmorillonite (SWy-2, pH 5.7, 48'000 mg kg^{-1} Zn), Zn in trioctahedral smectite (25% Zn and 75% Mg in octahedral sheet, synthesized according to Decarreau (1981), and Zn-containing goethite (2% Zn – 98% Fe, synthesized according to Schwertmann and Cornell (1991), and Zn sorbed to purified humic acid (pH 6.0, 350 mg kg^{-1} Zn). LCF analysis was started with the reference giving the best one-component fit (defined as the one with the lowest normalized sum of squared residuals (NSSR=$\Sigma_i(\text{data}_i\text{-fit}_i)^2/\Sigma_i\text{data}_i^2$)). Additional references were considered to significantly improve the fit if the NSSR decreased by more than 10%. The software package from the beamline 10.3.2 of the Advanced Light Source (written by Mathew Marcus, ALS, Berkeley, USA) was used to perform the LCF analysis.

4.3 Results and discussion

4.3.1 Vertical distribution of major and trace elements and variation of pH

Figure 12 shows the vertical profiles of soil pH, TIC, TOC, and the total contents of Ca, Mg, Zn, Mn, Cd, S, Pb, Fe, and Ti. Below 2 m, the flotation residues have a neutral pH around 7.0. A pronounced decrease in pH from 7.0 to 6.4 is followed by a further slow decrease to pH 6.0 at 50 cm depth. The topsoil sample is again clearly more acidic with a pH of 5.5. Similar to the pH, the TIC decreases toward the surface from values around 170 mmol kg^{-1} in the subsoil down to 22 mmol kg^{-1} in the topsoil. Ca concentrations increase almost linearly with depth. For Mg no clear trend can be observed along the soil profile. Zn, Mn, Cd, and S show a relatively homogeneous distribution in the subsoil below about 0.6 m depth. These elements decrease toward the surface and show lowest contents in the top 20 cm. In contrast to the other metals, Pb shows no depletion but an enrichment in the top cm of the topsoil, where the TOC concentrations are highest.

With XRD analysis, the minerals quartz, illite, muscovite, and zeolite could be identified in all three soil samples. In addition, sphalerite could be identified in the middle and deep sample (P3-0.7 and P3-3.0) but not in the topsoil sample (P3-0.16).

Table 3: Soil characteristics of samples studied by SCE, XRD and EXAFS

Sample name	P3-0.06	P3-0.16	P3-0.34	P3-0.7	P3-3.0
Depth [cm]	4-6	13-16	26-34	60-70	230-300
Color	gray-brown	gray-brown	rusty-red	gray	gray
Water content [% (wt)]	n.a.	42.3	n.a.	55.4	54.9
Total contents [mmol kg^{-1} (dw)]					
Zn	10	4	10	155	136
Pb	27	13	9	7	8
Fe	261	405	320	353	387
Mn	2.1	0.9	0.9	11.5	13.7
Cd	0.035	0.005	0.017	0.115	0.117
As	0.5	1.1	1.1	0.9	0.9
Cu	3.5	4.0	0.4	8.1	6.3
S	9	25	50	162	168
Ti	61.4	109	45.2	109	96.3
Zr	1.37	1.54	1.26	1.61	1.52
Si	10379	9994	12686	9870	9916
TC	2067	215	96	260	386
TIC	55	75	52	146	215
TOC = TC - TIC	2012	140	44	114	171
SCE/XRD		x		x	x
EXAFS	x	x	x	x	x

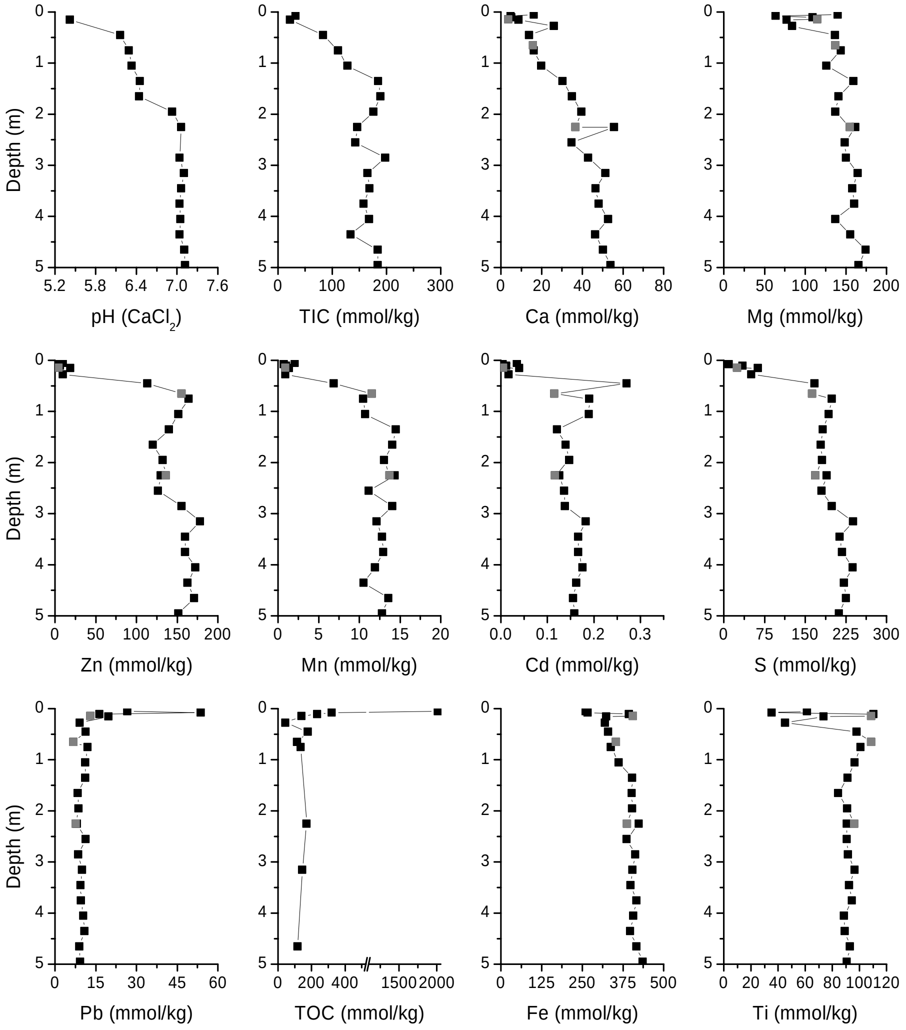

Figure 12: Soil pH (0.01 M CaCl$_2$), total inorganic carbon (TIC), Ca, Mg, Zn, Mn, Cd, S, Pb, total organic carbon (TOC), Fe, and Ti contents in mmol kg^{-1} dry mass of the soil profile. Samples additionally investigated by SCE and Zn K-edge EXAFS are shown in gray symbols.

4.3.2 Sequential chemical extractions

Data from SCE are depicted in Figure 13. There is a general agreement, that results from SCE are operational defined (Filgueiras et al., 2002) and do not necessarily reflect true chemical species. Metals extracted in the first step

(NH_4NO_3) are usually assumed to represent water soluble and exchangeable cations. The second step (NH_4OAc) mainly extracts weakly complexed metals and metals bound by carbonates (easily mobilizable). The third step ($NH_2OH{*}HCl$) is designed to extract metals bound by Fe/Mn (hydr)oxides. However, Peltier et al. (2005) could show that in step 3 also freshly formed amorphous sulfides can be dissolved whereas primary minerals such as sphalerite and galena seem to be unaffected (Peltier et al., 2005; Svete et al., 2001). The fourth step (NH_4-EDTA) is assumed to extract metals bound by organic matter. In the last step, the residual fraction is extracted by total digestion.

The different soil acidity of samples from different depth is reflected in the pH of the first leachate. In the topsoil sample, the pH in the first step is acidic (pH 4.1) whereas the deeper samples show nearly neutral pH (6.6). This agrees well with soil pH measurements (Figure 12) and has a major impact on desorption of the different metals which strongly depends on pH.

In all three samples, Fe was mainly released in step 3 and step 5 , the steps for the removal of Fe/Mn (hydr)oxides and residual mineral phases. In the topsoil sample, no Fe was released in the first two steps, according to low solubility of Fe oxides at oxic conditions (Cornell and Schwertmann, 1996; Scheinost et al., 2002). Differences between the investigated samples from different depths are small (Figure 13). It is likely that released Fe subsequently re-precipitates as (hydr)oxides in contact with oxygen.

In the two subsoil samples, more than 90% of Mn is released during the first three steps with 50 to 60% in step 3, the step for the removal of Fe/Mn (hydr)oxides. This indicates that Mn is mobilizable to a large extent in the parent material. In the topsoil sample, all Mn was found in the residual step. Mn contents in this sample are considerably lower than in the parent material (Figure 12, Table 3), which shows that large amounts have been mobilized and leached out due to oxidation and weathering of the tailing. The amount of Mn found in the residual phase of the two deeper samples corresponds well with the total content of the topsoil sample (Figure 13). This suggests that all Mn extracted in the first three steps is already released from topsoil which is now depleted except for the residual fraction.

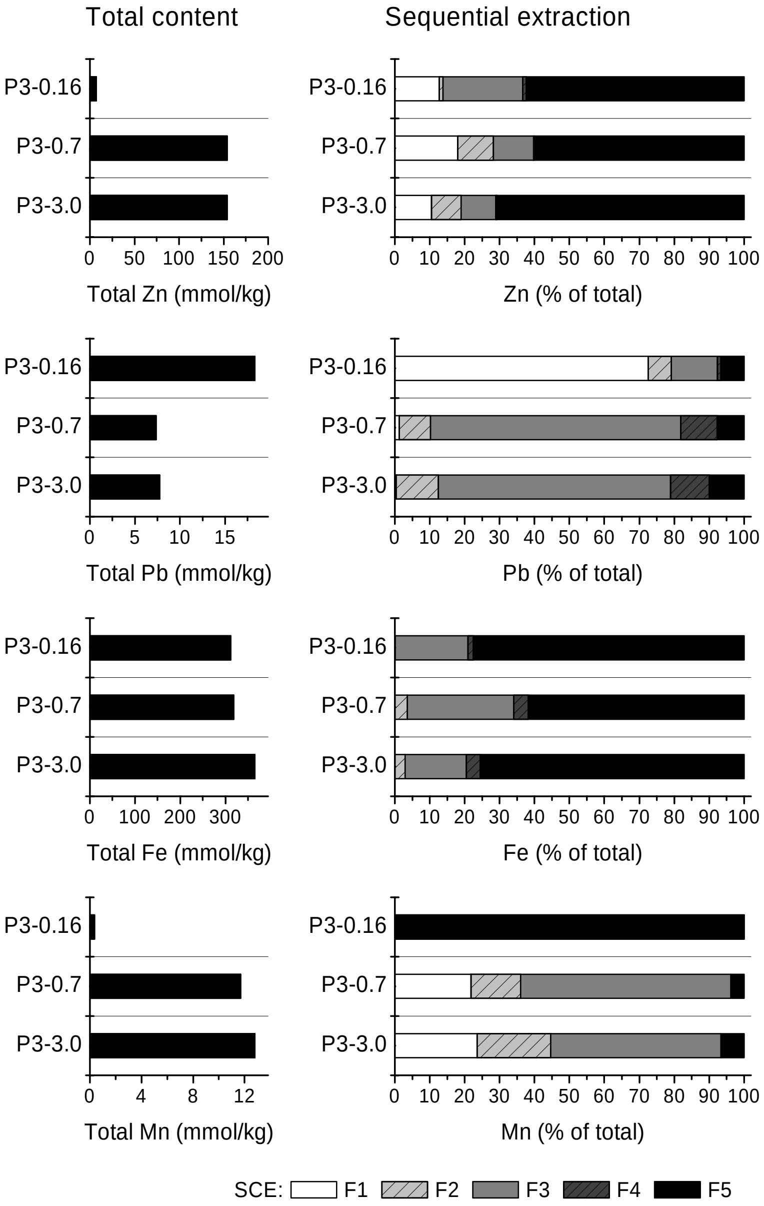

Figure 13: Total extracted amount of Zn, Pb, Fe, and Mn of all five steps in mmol kg^{-1}, percent of Zn, Pb, Fe, and Mn extracted by sequential chemical extractions in samples P3-0.16, P3-0.7, and P3-3.0; F1 (NH_4NO_3), F2 (NH_4OAc), F3 ($NH_2OH*HCl$), F4 (NH_4-EDTA), F5 ($HF/HNO_3/HClO_4$)

Zinc

In the two subsoil samples, Zn is released in all extraction steps except for step 4, the step designed for the release of metals bound to organic matter. The topsoil sample from 0.13-0.16 m depth (P3-0.16) contains far less Zn (4 mmol kg^{-1}) than the deeper samples (150 mmol kg^{-1}). In the topsoil sample, 23% of Zn was extracted in the third step and 62% in the last step of the SCE, suggesting that Zn is predominantly bound in residual minerals and iron(hydr)oxides (since only 0.4 mmol kg^{-1} of Mn were found in this sample, extracted in the residual step). 13% of Zn was extracted in step 1 and can be regarded as mobile or easily mobilizable. No Zn was extracted in the second step, designed for the extraction of weakly complexed metals and metals bound by carbonates. This is in agreement with carbon measurements (Figure 12), which show that the topsoil is already depleted in TIC. More than 60% of Zn was extracted in the last step in all three samples, indicating that most Zn is bound by residual minerals such as sphalerite.

Lead

More than 65% of Pb in the subsoil was extracted in step 3, the step designed for the dissolution of Fe/Mn(hydr)oxides. In the topsoil sample, Pb was predominantly extracted in the first step (73%), indicating that the major part of Pb was present as mobile or easily mobilizable species. In the first step of the SCE, 80% of all cations released are Pb, which means that in the topsoil the largest fraction of the cation exchange capacity is occupied by Pb. 13% of Pb in the topsoil was released in the third step and 7% in both the second and the residual step.

Originally, Pb has been present as galena in the ore deposit (Hünermann, 1955). However, it is not unlikely that galena has already been oxidized during flotation (Harvey and Yen, 1998; Madhuchhanda et al., 2000) to form anglesite (da Silva et al., 2003). This would explain why the residual fraction of Pb is small in all three samples.

4.3.3 Zn K-edge EXAFS spectroscopy

Zn is the most relevant contaminant of the investigated site in terms of quantity. To get complimentary information about the residual Zn species in the different depths on a molecular scale, the three samples from SCE and two additional samples from the topsoil were investigated by Zn K-edge EXAFS spectroscopy.

The Zn K-edge EXAFS spectra of untreated and sequentially extracted soil samples and the corresponding Fourier transforms are shown in the Figure 14A and B, respectively. The figure also shows the spectra of the reference compounds, which were used for linear combination fitting. The results of the

LCF analysis are listed in Table 4 and the fitted EXAFS spectra are shown in Figure 14A (offset thin dashed lines).

The untreated samples from 230-300 cm and 60-70 cm depth clearly exhibit the characteristic features of the sphalerite EXAFS spectrum (Figure 14A). Also, the first shell peak in the Fourier transform approximately matches the position of the first shell peak of sphalerite, which corresponds to the nearest S atoms coordinated to Zn. However, closer inspection of the Fourier transforms shows that for the untreated samples from 60-70 cm and 230-300 cm, the first shell peak is slightly shifted to the left of the Zn-S peak from sphalerite, indicating a minor contribution from Zn species with Zn coordinated to O atoms. In the spectra of the untreated soil samples collected at 13-16 cm and 26-34 cm depth, the spectral features of sphalerite have mostly disappeared and the first-shell peak in the Fourier transform approximately coincides with the position of the Zn-O peaks of the references for adsorbed and crystalline Zn species (Figure 14). However, the peak in the EXAFS spectra at 7.5 Å^{-1} indicates that some sphalerite is still present in these samples (Figure 14A, arrows). In the topmost sample from 4-6 cm depth, finally, no spectral contribution from sphalerite is visible anymore, and Zn appears to be exclusively present in adsorbed or precipitated species containing Zn coordinated to O.

While the identification of sphalerite was unequivocal from the EXAFS spectra collected at 60-70 and 230-300 cm depth, the selection of further references for LCF analysis was complicated by the limited number of sample spectra and by the strong contribution from sphalerite in the majority of the spectra. The selection of references was therefore based on preliminary testing of an extensive set of reference spectra of adsorbed and crystalline Zn species and on chemical considerations discussed below. However, the choice of the additional references was found to have little influence on the LCF results for sphalerite.

The LCF of the sample from 230-300 cm indicates that Zn in the unweathered flotation residue is predominantly contained in sphalerite. The fitted sphalerite fraction (73%) closely corresponds to the residual fraction from the SCE (71%, Figure 13). Furthermore, the best LCF of the extracted sample from 230-300 cm depth was obtained by using the sphalerite reference only. In combination, the LCF and SCE results for that sample suggest that during the SCE, sphalerite was mostly retained in the residual fraction. In the spectra from 60-70 cm and 13-16 cm, the sphalerite fraction decreases to 65% and 15% respectively. In contrast to the extracted sample from 230-300 cm depth, the extracted samples from 60-70 cm and 13-16 cm reveal an increasing contribution from other residual Zn species, in which Zn is coordinated to O. The LCF of the spectra of the untreated and treated samples from 13-16 cm and the sample from 26-34 cm consistently improved if the reference spectrum of Zn-substituted goethite was added. In contrast, reference spectra for Zn adsorbed to ferrihydrite or coprecipitated with ferrihydrite, did not improve the LCF. Incorporation of Zn into newly forming goethite is possible, as the sample from 26-34 cm depth exhibited a distinct rusty-red color indicating Fe-oxide formation and as Fe-oxide rich zones were also found around root channels in 13-16 cm depth. From the interpretation of the SCE protocol, on the other hand, goethite would have been expected to dissolve during the 3rd step of the SCE, while the LCF indicated a contribution of 40% Zn-goethite in the extracted sample from 13-16 cm. The improvements in the LCF obtained by the Zn-goethite reference might therefore also be due to the presence of another recalcitrant species with similar spectral features. The EXAFS spectrum of the sample from 4-6 cm was clearly distinct from the spectra of deeper soil samples (Figure 14A) and the LCF did not indicate any contribution from sphalerite in that spectrum (Table 4). While the EXAFS spectrum does not exhibit the distinct spectral features of the ZnMg-clay reference containing 25% Zn and 75% Mg in its octahedral sheets, its envelope and frequency match that of the ZnMg-clay reference spectrum. This suggests that the spectral contributions of Zn adsorbed to soil clay minerals or soil organic matter reduce any sharp features of Zn contained in ordered structures. Such an interpretation is supported by the LCF, which yields 53% contribution from the Zn sorbed montmorillonite reference and 38% contribution from the ZnMg-clay reference. The ZnMg-clay reference spectrum used in the LCF analysis was chosen from a wide range of references, which exhibit similar spectral features depending on the ratio of light and heavy atoms in their octahedral sheets (Zn_xMg_{1-x}-clays with x ranging from 0.03 to 1; Zn in layered double hydroxides (LDH), Zn sorbed in the hydroxy-aluminum interlayers of clay minerals or in the gibbsitic sheets of lithiophorite). All of these phases have been identified before in pristine or contaminated soils (Juillot et al., 2003; Manceau et al., 2004; Manceau, 2000; Panfili et al., 2005; Scheinost et al., 2002; Voegelin et al., 2005). The formation of Zn-bearing LDH is unlikely due to the relatively low pH of the topsoil samples, and the formation of Zn-bearing lithiophorite can be excluded as major species based on the small Mn content (Table 1). We therefore assume that the spectral contribution fit by the ZnMg-clay reference results from the presence of Zn in the octahedral sheets of clay minerals or/and Zn sorbed into the Al-hydroxy interlayers of clay minerals. These species likely also resist the first 3 steps of the SCE and their presence in the spectrum from the extracted sample from 13-16 cm would be chemically realistic. Considering the organic carbon content of 24.2 g kg^{-1} in the sample from 4-6 cm, some association of Zn with organic matter could be expected. However, considering the similarities in the reference spectra for Zn adsorbed to montmorillonite and humic acid, this fraction was likely included in the fraction fit with the montmorillonite reference.

Table 4: Linear combination fit (LCF) results for untreated and sequentially extracted soil samples from different sampling depths. Reference spectra and the LCF spectra are contained in the Figure 14A.

Depth (cm)	Treated	Sphalerite (%)	Montm.[†] (%)	Clay[‡] (%)	Goethite[§] (%)	SUM (%)	NSSR[¶] (×100)
4-6	—	—	53	38	—	91	4.54
13-16	—	15	46	—	26	87	7.83
13-16	SCE3	39	—	24	40	103	9.96
26-34	—	16	61	—	10	87	5.09
60-70	—	65	17	18	—	100	2.44
60-70	SCE 4	80	17	—	—	97	1.30
230-300	—	73	—	21	—	94	1.82
230-300	SCE 4	94	—	—	—	94	0.87

[†] Zn adsorbed to montmorillonite; [‡] synthetic smectite containing 25% Zn and 75% Mg in octahedral sheet; [§] Goethite with Zn substituting 2% of Fe; [¶] normalized sum of squared residuals = $\Sigma_i(\text{data}_i\text{-fit}_i)^2/\Sigma_i\text{data}_i^2$.

4.3.4 Distribution and fate of Zn and Pb in the flotation residues

Zinc: The analysis of the EXAFS spectra shows that in the unaltered flotation residues Zn is predominantly present as sphalerite, and that the fraction of sphalerite decreases with decreasing profile depth. The stability of sphalerite mainly depends on redox conditions. At anoxic conditions sphalerite is of low solubility (log K_{sp}: -20.6 at 25°C in water, for $ZnS_s \rightarrow Zn^{2+}{}_{aq} + S^{2-}{}_{aq}$ (Weisener et al., 2003)). Electron supply by O_2 may lead to a transformation into soluble sulfate (Garcia et al., 1995) and a significant depletion of the soil in S and Zn due to leaching. Significant amounts of dissolved sulfate in soil and groundwater may be the consequence.

The EXAFS spectra further indicate that sphalerite is retained in the residual fraction of the SCE. However, with decreasing profile depth, this residual fraction also contains increasing amounts of other Zn species. The exact identification of these species is complicated by the limited number of spectra and the strong contribution of the sphalerite signal in most spectra. However, spectra collected from samples of the oxidized topsoil (<34 cm) suggest the presence of Zn-substituted goethite (or a species with similar spectral features) and of Zn bound in the octahedral sheets of Zn-bearing phyllosilicate and/or in the hydroxyl-aluminum interlayers of clay minerals.

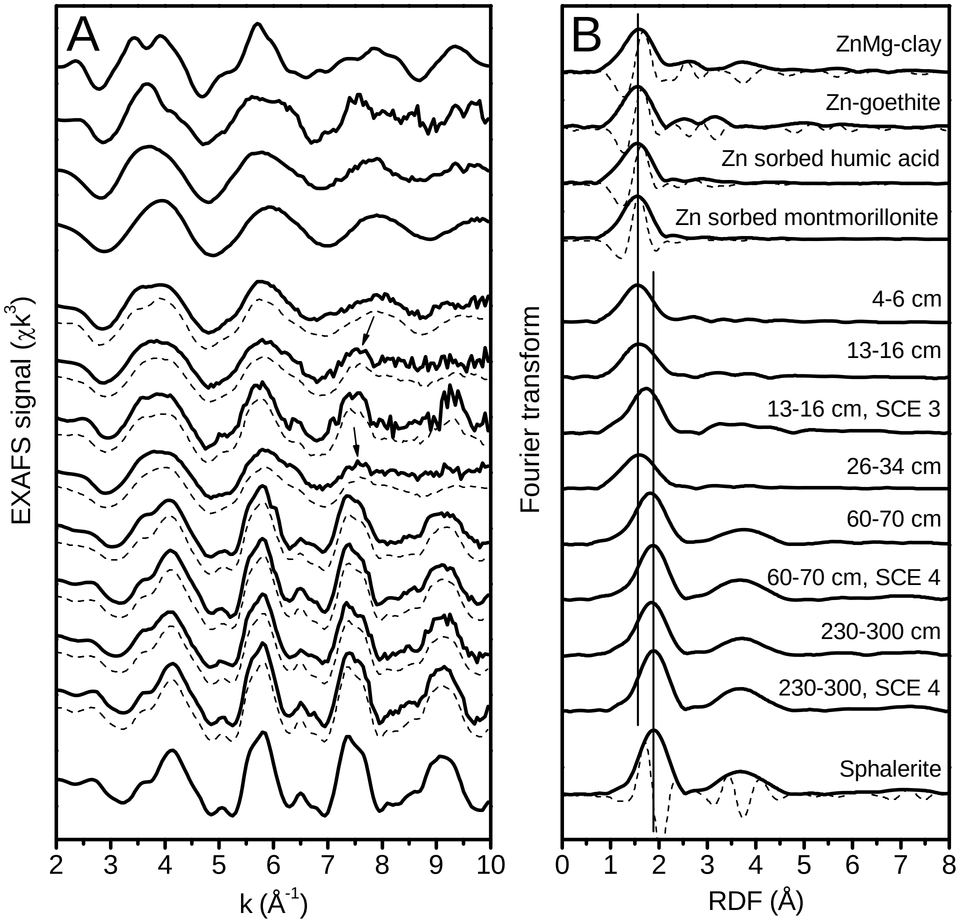

Figure 14: (A) Zn K-edge EXAFS spectra of untreated and sequentially extracted soil samples from increasing profile depths and reference spectra (solid lines). LCF spectra of the soil samples are offset for clarity (thin dashed lines). Details indicated by arrows are mentioned in the text. (B) Fourier transforms of the EXAFS spectra of soil samples and references (solid lines = magnitude; thin dashed lines = imaginary part of Fourrier transformed reference spectra). Vertical lines mark the approximate positions of the peaks for first shell O and S coordinated with Zn in the reference spectra.

SCE results indicate that Zn is partly redistributed into mobilizable species (Figure 13). Acidic pH leads to a transfer to the aqueous phase by desorption and/or dissolution and leaching to the subsoil, where the pH is still neutral and metals are retarded due to adsorption, surface complexation and/or (co)-precipitation.

Originally, pyrite has been present in the ore deposit (Hünermann, 1955). The oxidation of pyrite in a great extent would lead to a considerable acidification. If other sulfides with a lower rest potential are coexistent, pyrite oxidation will be diminished due to galvanic interactions (Domènech et al., 2002; Jeong and Lee, 2003; Kwong et al., 2003). It is possible that the coexistence of sphalerite retards the oxidation of pyrite and prevents much lower pH conditions so far.

Results from this study were found to agree with processes occurring in acid sulfate soils (ASS). In ASS of coastal regions of Finland and Sweden, the oxidation of sulfide-minerals (particularly pyrite) leads to an acidification of the topsoil (Åström, 1998c; Sohlenius and Öborn, 2004). The element distribution shows a similar pattern. Zn and also Cd are probably mobilized from ASS due to the low pH or partly due to the oxidation of discrete sulfide minerals (Sohlenius and Öborn, 2004). It is suggested that the immobilization in the transition zone is caused either by the increase in pH, the decrease in O_2 supply or by the combined action of both of these changes. In the reduced zone, where O_2 is unavailable and pH is high, the concentration is higher than in the ASS, whereas distinct concentration maxima are located in the narrow transition zone of most but not all investigated sites (Åström, 1998c).

Lead shows enrichment in the topsoil in the mobile fraction compared to the parent material (Figure 12). Results from total content analysis suggest that this is due to an interaction with soil organic matter. Diffusion processes and/or plant uptake may play a major role controlling Pb enrichment at the surface. The transfer of Pb to the soil solution strongly depends on pH. pH dependant sorption behavior of the different metals strongly correlates with hydrolysis constants (Herms and Brümmer, 1984; Voegelin et al., 2003). Pb has one of the largest first hydrolysis constants of any divalent cation (pK 7.6 for $Pb^{2+} + H_2O \rightarrow PbOH^{+} + H^{+}$ (Alloway, 1999)). In the presence of abundant surface sites, as expected for this soil, Pb should be quickly removed from solution by adsorption (Wang and Benoit, 1996). However, a further decrease in pH below 4 could lead to significant desorption of Pb and substantial pollution of the groundwater.

4.3.5 Conclusions

EXAFS results confirm that Zn is mainly bound in sphalerite in the subsoil. Weathering reactions lead to a redistribution of Zn in the topsoil. A loss of 35% Zn and S from the topsoil compared to the parent material has been observed. Pb is enriched in the mobile fraction of the topsoil by more than a factor of 2 and 80% of the cation exchange capacity is occupied by Pb. This indicates that questions of bioavailability and plant uptake are of major concern.

The combination of SCE and EXAFS improved the assessment of Zn speciation in the soil profile of the flotation dump. SCE allowed a quantification of mobilizable species and EXAFS analyzes enabled a determination of the residual Zn phases which could not be differentiated by SCE.

Oxidation of sulfide minerals leads to an acidification of the flotation residues to a pH of 5.5, where buffering minerals are already depleted. Proceeding acidification would lead to a significant release of Zn, S, and Pb and cause a substantial pollution of the groundwater.

5 The release of Zn and Pb from flotation residues of a Zn/Pb-sulfide mine

5.1 Introduction

Contaminated mine drainage water has become one of the major hydrogeological and geochemical problems arising from mankind's intrusion into the geosphere (Banks et al., 1997). Release of soluble metal contaminants and acidity from mining sites can pose serious chemical risk to sensitive surface and groundwater supplies in the surrounding environment. Assessment of this risk and design of suitable management strategies require quantitative predictions of the rates and extent of physical, chemical and biological processes that control contaminant release at a site (Strömberg and Banwart, 1999). The extent of metal-sulfide oxidation, the H^+ buffering properties of the sediment/soil material, and the amount of easily mobilized chemical elements are factors that control the extent of geochemical dispersion and environmental impact caused by the oxidation of sulfide-bearing fine-grained sediments (Åström, 1998a). The ecological impact of heavy metals in soils is particularly determined by the soluble and easily mobilizable fraction, which can be regarded as the available and displaceable part (Herms and Brümmer, 1984). The major changes that occur in redox conditions between oxic waters and anoxic sediments can have profound influences on the speciation and bioavailability of many trace metals (Morse and Luther, 1999).

The dissolution of sulfide minerals in aerobic aqueous conditions is a major contributor to acid mine drainage (AMD) and toxic release. The effects on the environment by acidic wastewater are well recognized (Evangelou and Zhang, 1995; Weisener et al., 2003).

Considerable effort has been directed toward understanding the oxidative surface reactions of the Fe sulfide minerals that contribute to AMD. Far fewer studies have focused on the dissolution of Zn sulfide than of Fe sulfide (Weisener et al., 2003). One important aspect is the transport of gaseous O_2 to the site of sulfide oxidation. In mine tailings, O_2 may become depleted from the soil gas at less than a meter below the surface and diffusive transport of O_2 becomes important (Andersen et al., 2001).

Retention of heavy metals in soils is affected directly or indirectly by pH. Direct effects of pH are (co)precipitation and dissolution phenomena of heavy metal-bearing minerals. Adsorption reactions are also pH-dependent. Therefore, element retention in soils will also be affected indirectly by changes in pH, e.g. hydrolyzed metal species ($MeOH^+$) are preferential adsorbed compared to free metal ions, the number of negative sites diminishes as pH decreases and metal cations and H^+

compete at low pH ($pH<4$) for the permanent adsorption sites (van Herreweghe et al., 2002). Calcite depletion is an important control on the timing of a possibly dramatic drop in drainage water pH (Strömberg and Banwart, 1999). When the acid neutralization capacity is exhausted, a breakthrough of dissolved metals to the groundwater has to be expected.

Zn and Pb are often found together in ore deposits, but the metals have different applications and biological effects. Zn is a physiologically essential element, whereas Pb has no known positive biological function and creates serious environmental and health hazards (Dudka and Adriano, 1997). Zn is a ubiquitous contaminant that imposes a hazard to a host of plants and animals – many aquatic organisms are particularly sensitive to this element. Although it is not a redox active species within soil or aquatic environments, oxidation and reduction reactions may nevertheless affect Zn partitioning. Zn sorbs strongly to Fe and Mn (hydr)oxides in aerated systems and to sulfide and carbonate phases in anoxic environments. Thus, changes in redox status may shift Zn partitioning (Bostick et al., 2001).

The aim of this study was the assessment of the environmental pollution caused by the weathering of sulfide bearing mine tailings. Especially we address in this section the dissolution of sphalerite in contrast to the well known dissolution processes of pyrite. The release of Zn and Pb from sulfide bearing flotation residues of a small scale mine in Western Germany is investigated with focus on metal transfer to soil solution. Beside total contents of the solid material, the soil solution was sampled with suction cups to study the release of Zn and Pb depending on redox and pH conditions. The influence of pH on leaching behavior was investigated with pH_{stat} tests. In addition, plant samples were analyzed to quantify metal uptake by plants. Isotopic analyzes were performed to assess the seepage velocity. These investigations and modeling of the soil solution provide an insight in current and future processes, which can cause environmental pollution.

5.2 Material and methods

5.2.1 Field site description

The studied field site is a former tailings pond with sulfide bearing flotation residues of a former ore mine (Figure 15). The site is located in northern Rhineland-Palatinate, Germany. Until 1961, Zn, Pb, and Ag have been mined at this site. To extract the ore, the material was crushed, ground, and subsequently processed in a flotation plant. For deposition, the tailings were pumped into an artificial lake in the narrow valley. Outlet discharge structures drained the clarified sewage of the tailings pond into the river (Herbst, 1962). The main part of the former tailings pond is now covered with coarse detritus. Only the rear area is directly accessible which is covered with different grasses and rush. In this part, the thickness of the fine grained flotation residues ranges from 3 to 7 m. Basis of the flotation dump is the former natural grown soil surface.

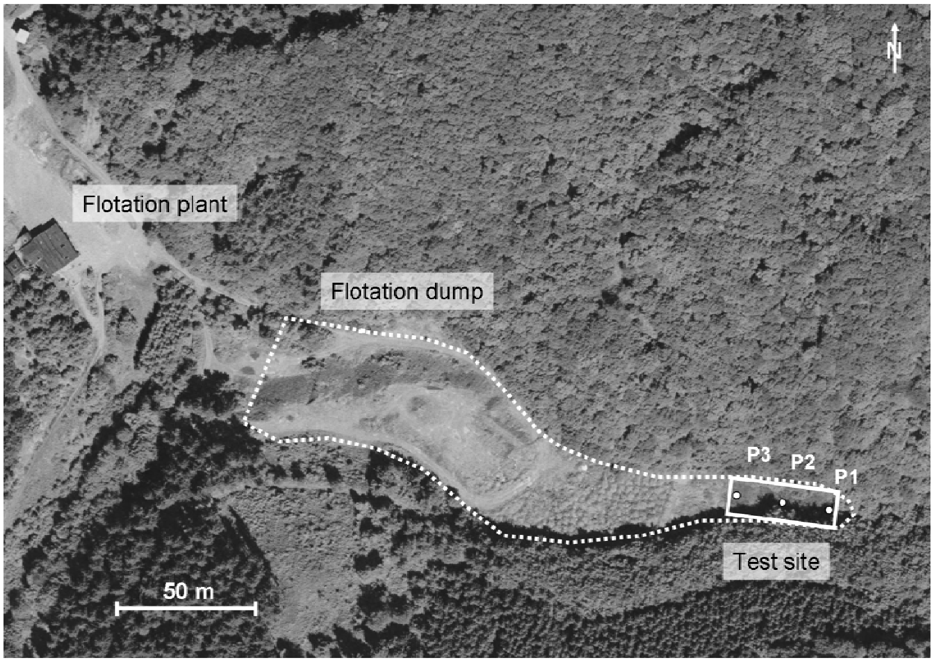

Figure 15: Orthophoto of the flotation plant, the flotation dump (dotted line) and the test site (solid line) in the rear part of the flotation dump with the position of the three sampling points (P1 to P3)

5.2.2 Soil sampling

Soil samples were taken from each vertical 30 cm section from three soil cores (P1 to P3, Figure 15) ranging in depths between 3 and 5 m. Total contents of major and trace elements were determined by X-ray fluorescence (XRF) (Philips, MagiXPro, Almelo, The Netherlands, Rh-tube) in finely ground samples (agate mortar). Total concentrations of C and S were measured using an CS elemental analyzer (LECO CS 225, St. Joseph, MI). Soil pH was determined in 0.01 M $CaCl_2$ solution (DIN ISO 10390, 1997).

5.2.3 Pore water sampling

Soil water accumulated in nylon suction cups (Ecotech) installed at 1, 2, and 3 m depth was collected every 2 to 4 weeks from September 2003 to October 2004 using a vacuum pump. If the seepage water is not in equilibrium with the soil and immobile water fractions, the applied vacuum may influence measured concentrations in suction cup water samples. For this reason the applied vacuum was varied between 600, 800, and 200 mbar. Electrical conductivity (EC), pH, E_h, and temperature were measured in the field in the soil water samples immediately after sampling. The solutions were passed through a 0.45 µm membrane filter and acidified for major cation and trace metal analysis with nitric acid p.a. Major anions were analyzed by ion chromatography (Metrohm, 761 Compact IC, column: Metrosep A SUPP5, Herisau, Switzerland). Major cations were analyzed by flame photometry (Eppendorf, ELEX 6361, Hamburg, Germany), heavy metals (Zn, Pb, Fe, Mn) and Mg by flame atomic absorption spectrometry (F-AAS) (Solar, Unicam 989, Cambridge, UK) and inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Elan 6100, Wellesley, MA), respectively.

Analyses for O and H stable isotopes and tritium of 3 samples from suction cups were performed for the evaluation of seepage velocities. This was done to assess the time frame of release processes. The tritium concentration can be used to estimate the mean residence time of the soil water (Allison, 1988). Stable O and H isotope ratios in soil water vary depending on seasonal temperature differences during precipitation and can be used to differentiate the residence time of young soil water from different depths (Allison, 1988). Tritium was analyzed by liquid scintillation counting (LSC) in Tritium Units ($1 TU = 0.119 Bq L^{-1}$). ^{18}O and ^{2}H were analyzed by isotope ratio mass spectrometry (ICP-MS). Results from ICP-MS analyzes were expressed as $\delta^{18}O$ and $\delta^{2}H$ per mil with respect to the Vienna Standard Mean Ocean Water (VSMOW) standard, with analytical precision of ± 0.15‰ and ± 1.5‰, respectively ($\delta^{18}O$: deviation of the $^{18}O/^{16}O$ ratio of the sample with respect to the standard, $\delta^{2}H$: deviation of the $^{2}H/^{1}H$ ratio of the sample with respect to the standard).

Solution speciation and mineral dissolution modeling was done with the hydrogeochemical computer model PHREEQC Interactive (USGS, Version 2.11, (released Febuary 7th, 2005) (Parkhurst and Appelo, 1999)). Saturation indices were calculated using the measured solution concentrations.

5.2.4 pH_{stat} tests

To assess the pH dependency of metal mobility, pH_{stat} tests were performed at four different pH values between 2 and 5. About 50 g of a field moist soil sample were stirred for 24 h with deionized water, resulting in a final liquid-to-solid-ratio of about 10. With an automatic titrator the pH was held constant at a given value by adding diluted nitric acid p.a. (0.1 - 0.5 mol L^{-1}, depending on target pH). With the amount of added acid and the dry mass of the sample, the acid neutralization capacity after 24 h (ANC_{24}) can be calculated as:

$$ANC_{24} = V_a * c_a * m_d^{-1} \qquad [7]$$

with V_a: volume of nitric acid [mL], c_a: acid concentration [mol L^{-1}], m_d: dry mass of the soil sample [kg], ANC_{24}: acid neutralization capacity after 24 h [mmol kg^{-1}].

After 24 h the solution was passed through a 0.45 µm membrane filter and acidified with diluted nitric acid to a pH value below 2 for metal analysis by flame atomic absorption spectrometry (F-AAS) (Solar, Unicam 989, Cambridge, UK).

5.2.5 Plant availability and uptake

To assess the plant availability of metals ammonium nitrate extractions of a sample from 0.13-0.16 m depth (P3-0.16) were carried out in six replicates inside a glove box under oxygen free atmosphere to prevent redistribution due to oxidation. Field moist sample corresponding to 8 g dry mass and 200 mL of 1 m NH_4NO_3 solution were weighed out into 400 mL air tight PE centrifuge tubes and shaken for 24 h. After 15 min of centrifugation at 20 °C and 2500 rpm, the liquid was decanted and filtered to a 0.45 µm membrane filter. The extracts were analyzed by flame photometry (Eppendorf, ELEX 6361, Hamburg, Germany) (Ca, K, Na) and by F-AAS (Solar, Unicam 989, Cambridge, UK) (Zn, Pb, Fe, Mn, Mg).

Four plant samples were taken and digested with concentrated nitric acid p.a. after oven drying for 48 h at 110 °C. The extracts were analyzed by ICP-MS (Perkin Elmer, Elan 6100, Wellesley, MA). Three were shoot samples and one a root sample of different plants growing at the former flotation dump nearby the soil core P3. The plants were identified as *Juncus conglomeratus* (whole shoots) and two grasses, which are likely to be *Poa trivialis* (whole shoots) and *Glyceria fluitans* (whole shoots and roots).

5.3 Results

5.3.1 Composition of soil samples

In Figure 16, the total contents of Zn, Pb, Fe, S, and C and soil pH of the samples from the three soil cores are shown. In general, the three soil cores show a relatively homogeneous distribution of trace and major elements. Below about 0.6 m depth, total elemental contents were rather constant. Total Zn contents of the soil samples averaged 10 g kg^{-1}, Pb contents averaged 2.5 g kg^{-1}, Fe 22 g kg^{-1}, S 8.0 g kg^{-1}, and total carbon 4.0 g kg^{-1}. In comparison to the subsoil, the topsoil samples contained smaller amounts of Zn and S, increasing amounts of Pb, and varying amounts of C. Only in soil core P2, Zn and Fe contents in the topsoil were higher than in the subsoil. This may be due to the fact that P2 is situated in a slightly lower terrain where the surface is more prone to water logging.

Below 2 m depth, soil samples had neutral pH values. Toward the surface, pH decreased down to pH 5.4 in P1 and P3, and to pH 5.9 in core P2, respectively.

In Table 5, results from carbon analyses of selected soil samples from core P3 are compiled. Inorganic carbon contents were relatively low in all samples. They increased with depth from 0.07% in the topsoil up to 0.28% in 4.5-4.8 m depth. In contrast, organic carbon contents were 2.4% at 4-6 cm depth and decreased to 0.1% in 4.5-4.8 m depth.

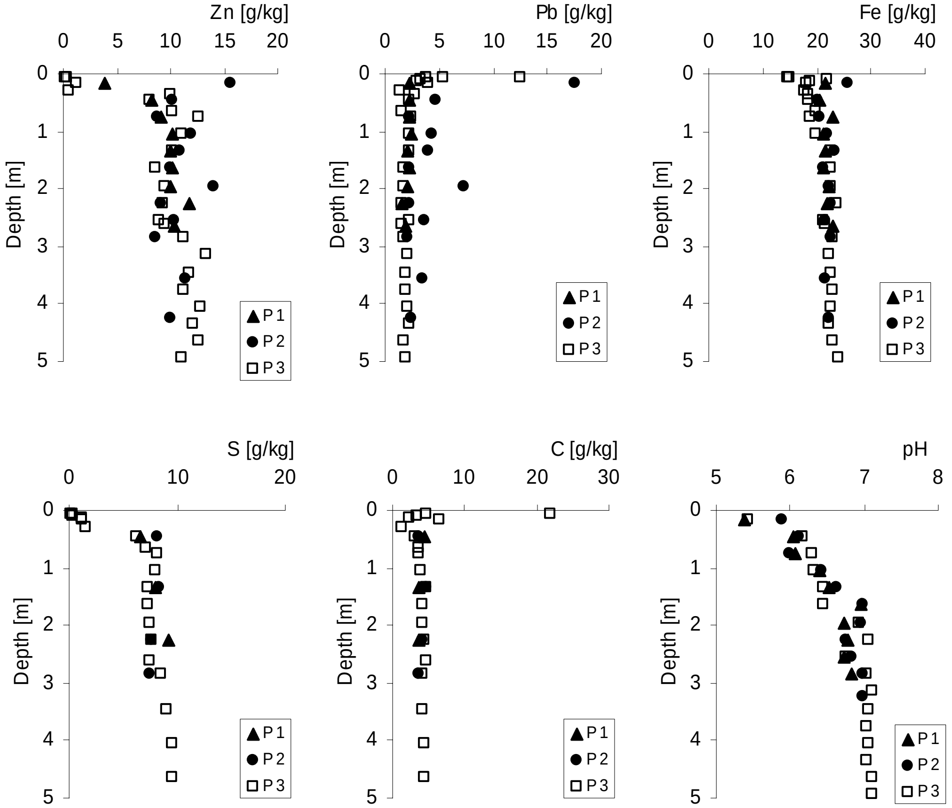

Figure 16: Total contents of Zn, Pb, Fe, S, C and soil pH of three different soil cores P1-P3

5.3.2 Characterization of soil water

Seasonal variations in EC, pH, T, Zn, and Pb concentration in the soil solution sampled by suction cups are shown in Figure 17. Average concentrations of major anions, major cations, and selected metals are compiled in Table 6. Dissolved contents of major ions (Mg, Ca, K, SO_4, and HCO_3) in the soil solution increased with depth (compare to EC). Metal concentrations (Fe, Mn, Zn) decreased with depth. Pb shows an erratic pattern of varying concentrations with depth and time up to 30 µg L^{-1}. The solution pH was neutral to slightly alkaline in deep samples and slightly acidic (pH 6) at 1 m depth. Seasonal variations were rather small. All parameters appeared to be independent from the applied vacuum (Figure 17) which indicates that the seepage water is in equilibrium with the soil and immobile water fractions. Calculation of saturation indices of calcite and dolomite showed that the saturation of the soil water with respect to carbonates increased with depth according to pH values. At 3 m depth, the soil water was in equilibrium with calcite and dolomite.

Table 5: Total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC) in the soil samples from soil core P3, TOC = TC-TIC

P3	depth	TC	TIC	TOC
	cm	%	%	%
P3-0.06	4-6	2.48	0.07	2.41
P3-0.1	6-10	0.47	0.09	0.38
P3-0.12	10-12	0.34	0.06	0.28
P3-0.16	13-16	0.12	0.06	0.06
P3-0.34	26-34	0.31	0.1	0.21
P3-0.7	60-70	0.31	0.18	0.14
P3-0.9	60-90	0.35	0.18	0.17
P3-3.0	230-300	0.46	0.26	0.2
P3-3.3	300-330	0.39	0.22	0.17
P3-4.8	450-480	0.42	0.28	0.14

Table 6: Average concentrations of selected elements in suction cup samples ± standard deviation in mmol(eq) L^{-1}

	sc 1 m	sc 2 m	sc 3 m
Mg	1.15 ± 0.16	1.21 ± 0.09	2.04 ± 0.26
Ca	0.97 ± 0.08	3.63 ± 0.16	4.36 ± 0.19
Na	0.08 ± 0.02	0.08 ± 0.01	0.15 ± 0.01
K	0.1 ± 0.08	0.12 ± 0.06	0.21 ± 0.14
SO_4	1.91 ± 0.14	2.31 ± 0.20	3.37 ± 0.33
HCO_3	0.83 ± 0.16	2.88 ± 0.42	3.34 ± 0.55
Fe	0.04 ± 0.07	< 0.004 ± 0.008	< 0.004 ± 0.004
Mn	0.08 ± 0.01	< 0.004 ± 0.002	< 0.004 ± 0.002
Zn	0.31 ± 0.05	< 0.003 ± 0.002	< 0.003 ± 0.002
Pb	$1.0e^{-5}$± $1.7e^{-5}$	$2.5e^{-5}$± $6.6e^{-5}$	$2.7e^{-5}$ ± $6.7e^{-5}$

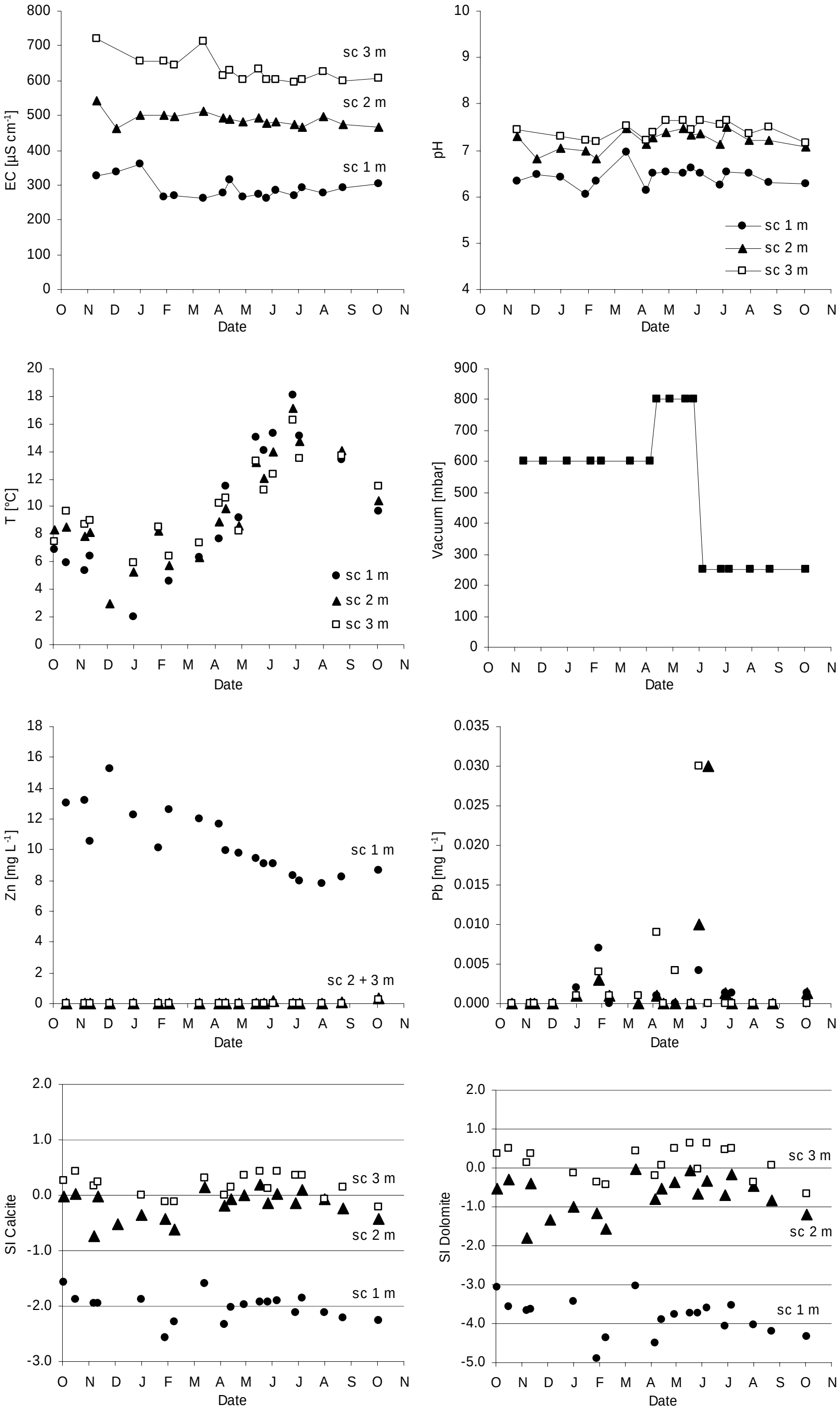

Figure 17: Results from soil water sampling by suction cups over one year. Suction cup samples from 1 m depth (solid circles), from 2 m depth (solid triangles) and from 3 m depth (open squares), SI: saturation index

Results of tritium analyses are compiled in Figure 18. The data indicate mean soil water travel times of less than 3 (maximum 5) years. Stable isotopes indicate different infiltration times of samples from different depth. The sample from 3 m depth with lighter $\delta^{18}O$ and $\delta^{2}H$ content was infiltrated at colder times than the shallower samples. It contains more winter precipitation. The samples plot on the global meteoric water line (Craig, 1961). This means that no influence of evaporation on the isotopic signature can be observed.

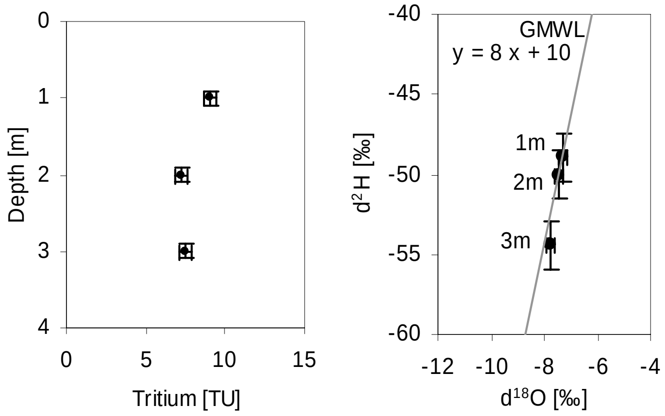

Figure 18: Isotope data from suction cup samples (sampling date 21.10.2003)

5.3.3 pH$_{stat}$ tests

The pH$_{stat}$ tests provide two kinds of information, the acid neutralization capacity after 24 h (ANC$_{24}$) and the release of metals depending on pH. Results are compiled in Figure 19. The ANC$_{24}$ increases linearly with decreasing pH (in a semi logarithmic plot) from about 50 mmol(eq) kg^{-1} at pH 5 to about 450 mmol(eq) kg^{-1} at pH 2. Zn and Fe release show a strong increase with decreasing pH to 126 and 142 mmol(eq) kg^{-1}, respectively, at pH 2. Pb release increases at pH < 4 and Mn release at pH < 5, both to about 10 mmol(eq) kg^{-1}.

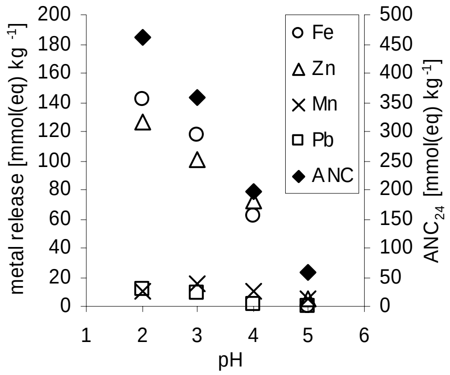

Figure 19: Results from pH$_{stat}$ tests, metal release and acid neutralization capacity after 24 h (ANC$_{24}$) in mmol(eq) kg^{-1} of sample P3-0.7 from 0.6-0.7 m depth

5.3.4 Plant availability and uptake

To investigate metal uptake by plants at the test site, four plant samples were taken and total contents were analyzed. Three were shoot samples and one a root sample of different plants growing at the former flotation dump nearby the soil core P3. Results and typical values (Bergmann, 1992; Bohn et al., 2001; Marschner, 1995) are compiled in Table 7. In addition, results from ammonium nitrate extractions are shown.

Analyses of plant samples show elevated heavy metal contents compared to typical values. Especially Pb contents are markedly elevated. Measured concentrations of Mn, Cu, Pb, and Zn are in or above the range of critical values above which toxic effects are to be expected (Kabata-Pendias and Pendias, 1992).

5.4 Discussion

The behavior of the different metals and their environmental impact depends on the different metal properties as well as on external conditions. To assess the future release of metals from the flotation dump it is therefore crucial to determine the main processes leading to acidification. Soil pH is a result from both, acid producing and buffering reactions. In agreement with this, soil pH determined in $CaCl_2$ shows an acidification of the topsoil down to values of approximately 5.5 where carbonate minerals are already depleted and increasing pH with depth (Figure 16). From 2 m on downwards, soil pH values are neutral and pH values of the soil solution lie in the range of the carbonate equilibrium (Figure 17). Table 5 shows a loss of inorganic carbon from the topsoil which averages approximately 200 mol m^{-2} (calculated per m^2 surface area of the flotation dump). This suggests an equal proton demand of the same amount.

Table 7: Contents of major elements and heavy metals of different plant samples and results from ammonium nitrate extractions

	K	Ca	Mg	Si	Al	Na	Fe	Mn	Cu	Pb	Zn
			[g kg^{-1}]						[mg kg^{-1}]		
Juncus shoots	19.9	3.7	2.8	0.8	0.2	9120	280	330	60	67	160
Poa shoots	20.4	7	3.9	6.7	1.2	2180	770	320	17	80	400
Gyceria shoots	81.8	3.5	2.9	5.9	1.7	830	1420	360	24	920	580
Glyceria roots	24.9	5.7	3.2	9.7	5.2	4080	7790	1700	78	450	800
typical values							50-200[a]	25-125[a]	4-15[b]	0.1-10[b]	15-80[a]
critical values[c]								300-500	20-100	30-300	100-400
NH_4NO_3	0.04	0.04	0.01	n.a	n.a.	n.a.	23	<4	n.a.	2751	62

[a] (Bergmann, 1992; Marschner, 1995), [b] (Bohn et al., 2001), [c] the critical values indicate the range above which toxic effects are to be expected, from Kabata-Pendias and Pendias 1992

The atmospheric deposition of protons in the last 40 years adds up to a maximum of 2 mol m^{-2}, assuming a rainwater pH not smaller than 4 and an infiltration rate not higher than 600 mm a^{-1}. Therefore, the oxidation of sulfide minerals has to be taken into account for the acidification of the topsoil.

Total contents of Zn and S (Figure 16) and in addition results from spectroscopic speciation investigations (compare to section 4) indicate that sphalerite is the dominating solid sulfide species. The direct oxidation of sphalerite does not release acid in itself (overall reactions):

$$ZnS + 2\ O_2 \rightarrow Zn^{2+} + SO_4^{2-} \qquad [8]$$

$$Zn^{2+} + H_2O \rightarrow Zn(OH)^{+} + H^{+} \qquad \text{pK: } 8.96 \qquad [9]$$

Subsequent hydrolysis of the Zn^{2+} ions releases protons and leads to pH values about 5.5 in unbuffered solutions (Banks et al., 1997) (eq. 3). However, due to several buffering mechanisms the influence on pH in the field is small, regarding the hydrolysis constant (pK). If the dissolution of sphalerite is mediated by Fe^{3+}, a reaction that is microbial-catalyzed by *Thiobacillus Ferrooxidans* (eq. 4 and 5), the acidification may be more serious, provided that Fe^{2+} is leached out with the soil water (Garcia et al., 1995).

$$ZnS + 2\ Fe^{3+} \rightarrow Zn^{2+} + S^{0} + 2\ Fe^{2+} \qquad [10]$$

$Zn^{2+} + S^0 + 4\ H_20 + 6\ Fe^{3+} \rightarrow Zn^{2+} + SO_4^{2-} + 6\ Fe^{+2} + 8\ H^+$ [11]

However, this reaction requires very low pH conditions (pH<3) to stabilize Fe^{3+} in soil solution (Moncur et al., 2005).

Therefore, the oxidation of pyrite is the most likely acid generation reaction (eq. 6, overall reaction (Rimstidt and Vaughan, 2003)). The estimated loss of inorganic carbon would correspond to an average amount of about 35 mmol kg^{-1} oxidized pyrite within the first 1.2 m of the soil core (according to eq. 12), which can be regarded as reasonable. Since sphalerite as well as galena has a lower rest potential than pyrite, the oxidation of pyrite is retarded (Kwong et al., 2003). The oxidation of pyrite usually causes far lower pH values in the soil water and produces acid mine drainage.

$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$ [12]

The influence of pH on metal mobilization was investigated by pH_{stat} tests (Figure 19, Table 8). In section 4 the same soil sample was investigated by sequential chemical extractions (SCE) (Table 9). A comparison between the results of pH_{stat} tests and SCE shows that the amount of Pb and Zn extracted in the first four steps (mobilizable fractions) of the SCE complies with the amount released by pH_{stat} tests at pH 2. These results indicate that oxidation reactions cause a redistribution of immobile species to mobilizable species, whereas a decrease in pH leads to a transfer of mobilizable species to the aqueous phase.

Table 8: Released amounts of pH_{stat} tests at different pH in mmol(eq) kg^{-1}

pH_{stat} tests mmol(eq) kg^{-1}	Zn	Pb	Fe	Mn	ANC_{24}
pH 5	5	0.1	<0.04	5	58
pH 4	72	1	62	10	195
pH 3	100	9	117	15	359
pH 2	126	12	142	11	461

Table 9: Released amounts of sequential chemical extractions in mmol(eq) kg^{-1}

SCE mmol(eq) kg^{-1}	Zn	Pb	Fe	Mn
1	56	0.2	0.1	5
1+2	87	2	23	8
1+2+3	122	12	217	22
1+2+3+4	123	14	244	22
1+2+3+4+5	308	15	637	23

Infiltrating rainwater interacts with the topsoil of the former flotation dump. Isotopic analyses indicate a vertical infiltration time of about 1-2 m per year (Figure 18). Soil water concentrations of major ions (Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}) increase with depth (Table 5, Table 6). This indicates the dissolution of carbonates and to some extent the dissolution of sulfides. Heavy metal concentrations in the soil water (Fe, Mn, Zn) decrease with depth. This is due to (1) lower E_H values in subsoil which decrease the solubility of sulfides and (2) the lower mobility of these metals at higher pH.

Zinc

With an average of 10 g kg^{-1}, this test site is highly enriched in Zn. In the oxidized topsoil, Zn concentrations are significantly lower than in the reduced subsoil (Figure 16). The distribution pattern of total Zn contents and soil pH values indicate that the topsoil, which is prone to oxidation and acidification, is already depleted in Zn. Oxidation of the sulfidic material leads to redistribution into mobilizable species. In addition, the mobility of Zn is highly depending on pH, as pH_{stat} tests show (Figure 19). High soil water concentrations (10 to 15 mg L) far beyond the statutory threshold can be found at acidic pH (Figure 17). Cela and Sumner (2002) investigated the influence of heavy metal loading of soils that do impair microbial mediated processes. Water-extractable Zn fraction was found to correlate best to nitrification inhibition limits (Cela and Sumner, 2002). Zn concentration in the acidified topsoil clearly lies in the range of complete inhibition (<0.5 mg L^{-1}). At neutral pH, Zn concentrations are below 0.001 µg L^{-1}. During the soil passage, the contaminated seepage water enters the reduced subsoil with pH buffering carbonates. Results indicate that Zn is immobilized there. However, when the acid neutralization capacity is exhausted, a breakthrough of dissolved Zn to the groundwater has to be expected.

Lead

Pb averages 2.5 g kg^{-1} inside the flotation dump. In contrast to Zn, the first centimeters of the oxidized topsoil with high TOC contents show higher Pb contents than the reduced subsoil (Figure 16). Since we have found high concentrations in plants growing on the test site (Table 7), the interaction with organic material may play a role for Pb distribution in the field. Ammonium nitrate extractions show that about 70% of total Pb in the oxidized topsoil can be regarded as easily mobilizable. In addition, these investigations have shown that about 80% of the cation exchange capacity in the topsoil is occupied by Pb. This means that plant uptake and bioavailability are questions of major concern regarding Pb. In contrast to Zn, Pb is not abundant as aqueous species at slightly acidic pH. Values lower than 4 are necessary to mobilize Pb in higher amounts (Alloway, 1999), as pH_{stat} experiments confirm (Table 8). This is why Pb is not expected to be leached out until the buffer capacity of the soil is exhausted. Anyhow, Pb concentrations up to 30 µg L^{-1} have been observed in the soil water (Figure 17).

5.5 Conclusions

The environmental fate and behavior of Pb and Zn in the flotation dump is strongly depending on pH and redox conditions. Oxidation of sphalerite leads to a transfer of Zn from immobile to easily mobilizable species. Sulfide oxidation leads to an acidification of the topsoil where the buffer capacity is already exhausted due to the leaching of carbonates. At acidic pH, Zn is transferred to the aqueous phase (soil water concentrations up to 15 mg L^{-1} are found in 1 m depth) and leached to the subsoil where soil pH is neutral. Electron supply and the buffer capacity of the material are found to be the main factors controlling the mobility of Zn. In contrast, the transfer of comparable amounts of Pb to the aqueous phase requires pH values < 4. Since Pb is enriched in the topsoil and accumulates in plants, not leaching to the groundwater but bioavailability is of major concern. If the acidification of the soil proceeds with the same rate than in the last 40 years, it will reach the bottom of the tailing in about 200 years and a breakthrough of metals to the groundwater has to be expected.

6 Conclusions

Heavy metal contaminations caused by mining activities are an environmental problem in many regions all over the world. Heavy metal release is a potential threat to soil and groundwater quality as well as plant and animal health. Therefore, the assessment of metal contaminations and their implications to the environment is an important task. Leaching tests and soil water sampling can be used to assess current metal concentrations in the soil water. To evaluate the long-term mobility of metals in the soil, weathering reactions and transfer processes have to be taken into account additionally.

Leaching tests can be a helpful tool for groundwater risk assessment in cases where it is not possible to investigate the seepage water and groundwater directly. However, the interpretation of leaching test results and the transfer to field conditions is difficult and requires expertise. It has to be regarded that it is not possible with any leaching test to entirely reflect natural conditions (and this was not the original intention during the development of batch leaching tests anyway). Several parameters distinctly deviate from natural conditions which complicates a transfer from leaching test results to the field.

Previous practical experience and fundamental research studies show that a conversion of leaching test results, as is proposed by the (already withdrawn) DIN19735, is impossible. Correlations between results obtained by different methods, regarding different kinds of materials and different sites, are not significant. This is due to different chemical/physical leaching processes. To simplify the performance of groundwater risk assessment with the help of leaching tests, several recommendations were published in section 2.

Common leaching tests were designed to investigate oxic material. If sulfide bearing anoxic material has to be investigated, particular attention has to be paid to possible artifacts. Oxidation of the samples during sampling, storage, and pretreatment leads to a transfer of sparingly soluble sulfides like sphalerite into more soluble species. pH value is lowered, which increases the metal mobility additionally. In S4 leaching tests with increasing sample storage time, an increase in the release of Zn with a slope of 6.0 mg kg^{-1} d^{-1} has been observed within the first 200 days. Zn release was doubled in 20 days of storage time. For this reason, a modification of the leaching tests is proposed where oxidation is prevented substantially. According to the results of this work, argon flushing does not improve results significantly. The performance of S4 tests inside a glovebox had no influence on the release of Zn. However, it has a significant influence on the release of Pb, which occurs in much lower concentrations in the investigated material compared to Zn, which has to be taken into account for the interpretation of leaching results. Compared to the tests without modification the overestimation of Pb release still seems to be tolerable, regarding that the results provide a conservative assessment. The performance of SSE inside a glove box still has to be investigated. Nevertheless, the modified SSE seems to be the only of the tested leaching procedures, which provides more or less realistic results to estimate current heavy metal release in the field. ANE is not suitable because a leachant is used which releases considerably higher amounts of cationic metals due to competing sorption. The S4 test usually underestimates concentrations due to the high L/S ratio, which leads to dilution effects. However, released amounts in mmol kg^{-1} dry mass are significantly overestimated by this method. Since there is no sufficient way to directly convert results from S4 tests and ANE to SSE the application of this two methods for the assessment of heavy metal release in the field can not be recommended.

The vertical distribution and speciation of Zn and Pb in sulfide bearing flotation residues was investigated to assess the weathering processes influencing their environmental impact. In this former flotation dump, the oxidation of sulfide minerals leads to an acidification of the topsoil with a soil pH of 5.5 where buffering carbonates are already depleted. In the subsoil the pH is buffered around 7. Spectroscopic analyses show that Zn in the parent material is mainly bound to sphalerite (ZnS). Oxidation of sphalerite in the topsoil and transition zone leads to a transformation into mobilizable species. A significant loss of 35% Zn and S from the topsoil has been observed. Proceeding acidification would lead to a significant release of Zn and sulfate and cause a substantial pollution of the groundwater. In contrast to Zn, Pb is enriched in the mobile fraction of the topsoil and 80% of the cation exchange capacity is occupied by Pb. This indicates that questions of bioavailability and plant uptake are of major concern.

It could be shown that the combination of SCE and EXAFS improved the assessment of Zn speciation in the soil profile of the flotation dump. SCE allowed a quantification of mobilizable species which are easily overlooked by spectroscopic methods and EXAFS analyzes enabled a determination of the residual Zn phases, which could not be differentiated by SCE.

To better assess the release of Zn and Pb from the flotation dump, soil water was sampled with suction cups and the seasonal variability of metal concentration in the soil water was investigated. Furthermore the influence of pH on the release of Zn and Pb was investigated with pH_{stat} test. Plant samples were analyzed to assess the potential risk of Zn and Pb entering the food chain and causing adverse affects on crops, livestock and man.

At acidic pH in the topsoil, Zn from mobilizable fractions is transferred to the aqueous phase (soil water concentrations up to 15 mg L^{-1} are found in 1 m depth). During the soil passage, the contaminated seepage water enters the reduced subsoil with pH buffering carbonates. Results indicate that Zn is immobilized there. However, when the acid neutralization capacity is exhausted, a breakthrough of dissolved Zn to the groundwater has to be expected. Electron supply and the buffer capacity of the material are found to be the main factors controlling the mobility of Zn. In contrast, the transfer of comparable amounts of Pb to the aqueous phase requires pH values < 4. Since Pb is enriched in the topsoil and accumulates in plants, not leaching to the groundwater but bioavailability and transfer along the food chain is for the short term of major concern. If the acidification of the soil proceeds with the same rate than in the last 40 years, it will reach the bottom of the tailing in about 200 years and a breakthrough of metals to the groundwater has to be expected.

Results from this study show that the assessment of metal release especially from sulfide bearing anoxic material requires an extensive comprehension of leaching mechanisms on the one hand and on weathering processes, which influence the speciation and the mobility of metals, on the other hand. Processes which may change redox and pH conditions in the future are often not addressed during the performance of groundwater risk assessment. This may impede sound decisions for soil protection and remediation.

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