Characterization of sediments in an abandoned mining area; a case study of Mansfeld region, Germany

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Abstract The distribution of selected heavy metals, including some radionuclides, metalloids and non-metals was determined in stream sediments in a region influenced by abandoned copper mining and ore processing activities. A considerable amount of the ore processing waste with a very complex composition and highly elevated concentrations of zinc, sulfur, lead, copper, arsenic, and a lot of other elements in the range between 100 and 1,000 mg/kg (Sb, Mn, Ni, Cr, Cd, Hg, and Ag) was piled up on mine dumps. The dispersion of the pollutants originating from this source and their environmental impact were investigated. Both, sediments and original waste material were studied to indicate the pathways and the mobilization behavior of different pollutants. For this purpose, the process of the elution of pollutants by application of different fractionation schemes was studied. The capabilities of different analytical techniques are shown for the analysis of solid samples (X-ray fluorescence spectrometry, Gamma-spectrometry) and liquid ones (ICP-atomic emission spectrometry, ICP-mass spectrometry and different techniques of atomic absorption). Additionally, the coupling of ion chromatography and ICP-MS detection was used to study the distribution of arsenic species in the sediment cores of a lake which acts as a natural sink for the region.

Keywords Heavy metals · Arsenic · Radionuclides · Sediment contamination · Ore processing residues

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Introduction

Pollution of surface water by heavy metals as an impact of mining and ore processing is a world-wide problem. The Mansfeld district (Saxony-Anhalt) is one of the regions in Germany that face serious pollution owing to more than 800 years of mining and smelting activities of Kupferschiefer, a metalliferrous Permian black shale formation. The ores were processed for copper, silver and several other non-ferrous metals. The processing generated large amounts of mining debris and processing wastes. Both were placed in settling ponds and also together with the mining debris on slag heaps. In this region approximately 50 million tons of slag from copper smelting and about 350 thousand tons of scrubber dust and sludge were dumped (Schreck 1997; Matheis and others 1999). The scrubber dust with a grain size of 1.55 μm (mean value) and a density of 2.92 g cm^{-3}, known as Theisen sludge, is an important source of environmental pollution in this region. It contains a variety of heavy metals in high concentration and substantial amounts of radioactive elements. Comparing the reported concentration values in the original Kupferschiefer samples (Hammer and others 1990), e.g. 0.09–12 g/kg of zinc, 0.09–21 g/kg of lead and 0.003–2 g/kg of arsenic, the enrichments of these elements are considerable in the Theisen sludge. Concentrations up

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to 240 g/kg Zn, 120 g/kg Pb, 10 g/kg As were determined. Elevated concentrations of sulfur (approx. 150 g/kg) and polyaromatic compounds - PAH's - with a higher boiling point (approx. 500 mg/kg) were also found. A physical and chemical description of this material was published several years ago (Weiss and others 1997). High concentrations of heavy metals have been released into the environment by airborne particles and via water discharge. The seepage waters have low pH-values caused by sulfide oxidation (Schubert and others 2003).

Sediments in such polluted areas represent one of the ultimate sinks for heavy metals discharged into the aquatic environment (Becker and others 2001). The sediments of streams and lakes at polluted areas are of interest for characterizing the degree of anthropogenic impacts and the environmental hazards which could be caused by remobilization (e.g. Rösner 1998; Singh and others 2000; May and others 2001; Marques and others 2001; Schäfer and Blanc 2002).

Analysis of sediments can be done under different aspects and takes also different protocols depending on the aim of the analysis. Traditionally, in most studies dealing with heavy metals and metalloids, the total concentration of relevant elements in the samples was considered. Due to the generally valid regulations the concentration range higher than 1 mg/kg and up to some % (w/w) is of importance. For these tasks one prefers methods of solid-state analysis, like X-ray fluorescence (XRF) and neutron activation analysis (INAA), or the total dissolution of the samples prior to the determination applying different techniques of atomic spectrometry. The maximum acid-soluble amount (leaching with hot aqua regia) and the water-leachable content of heavy metals and radionuclides are particularly used as characteristics. However, the mobility and bioavailability of inorganic pollutants depend strongly on their chemical form and type of binding. Consequently, the data on the total concentration of elements are quite insufficient to estimate the possible hazards caused by polluted sediments.

For understanding the chemistry of the heavy metals in their interaction with the matrices or to assess their mobility an usual approach is the partitioning using different chemical extraction, or after IUPAC (Templeton and others 2000), fractionation procedures. Sequential extraction schemes (to fractionate metals or other elements bound or associated in solid materials into several groups of different leachability) were employed to determine the distribution of these elements in different phases and are aimed to simulate various conditions whereby certain sediment components can be released (e.g. Schoer and Förstner 1987; Quevauviller and others 1998; Davidson and others 1998; Pueyo and others 2001; Fedotov and others 2002). Most of these procedures are based on the protocol proposed by Tessier and others 1979.

Because mobility, bioavailability, and (ultimately) the toxicity strongly depend upon the chemical form of an individual element, speciation studies are becoming increasingly important as a very useful and recognized tool in environmental investigations. One of the most interesting tasks is the determination of different arsenic species in environmental samples. Arsenic may be present in two main redox states, As(III) and As(V), in the sediments and in water too. Changes in solubility and mobility occur as a function of the redox potential as well as the pH conditions. Due to the different toxicity of the arsenic compounds and forms not only the total concentration of arsenic (Wong and others 1999; Williams 2001) and the sequentially extractable amount of this element (Wenzel and others 2001) but also the concentration of the different forms in aquatic and terrestrial systems have been the target of increasing attention in recent years (e.g. Brigth and others 1996; Kuehnelt and others 1997; Harrington and others 1998; Koch and others 1999; Mattusch and others 2000; Daus and others 2002; Kneebone and others 2002). Being able to determine different species of arsenic, it is important to specify their transport mechanism in the aquatic environment, toxicological risks, and interrelationships.

Depth profiles of selected elements, species and radionuclides of undisturbed sediment cores can be used to estimate the time dependence of pollution especially in lakes. It is possible to get information about differences of the load with anthropogenic pollutants by application of different methods of the trace element analysis in combination with such ones for the determination of radionuclides. Also a temporal reference of the load is available. Different statistical methods, e.g. Principal Component Analysis (PCA), could be applied to find similarities in the behavior of the analytes to recognize effects, e.g. the sedimentation of associated elements. Again, the PCA can be used to demonstrate the differences in the composition of the different layers of bore cores.

As mentioned above, an area in Saxony-Anhalt, Germany, polluted by former copper mining and ore processing was under investigation. The aim of these studies was also to demonstrate the capabilities of different analytical techniques for the characterization of such a highly polluted site. Both standard methods and methods, which are not common in environmental routine analysis, e.g. speciation analysis, gamma spectrometry should find application. With intention standardized analytical protocols were also used, to make the received results usable in the framework of authorities.

Site description

The area under investigation, the Mansfeld district, is located south-east of the Harz mountain in Saxony-Anhalt, Germany (Fig. 1). Substantial volumes of Theisen sludge have been dumped uncontrolled on the top of slag heaps which are located only a few hundred meters from site SB-HD ("Stadtborn Spring", Hergisdorf), where ground water and drainage waters feed the spring of the creek Boese Sieben. The sites B7-WB, B7-UR and B7-LD are 3.5, 8.5 and 11.5 km, respectively, downstream of the site SB-HD. Samples were also taken from the lake Suesser See, which is 5 km in length and approximately 1 km in width. The sites SS-EL1 and SS-EL2 (12.5 km from SB-HD) are

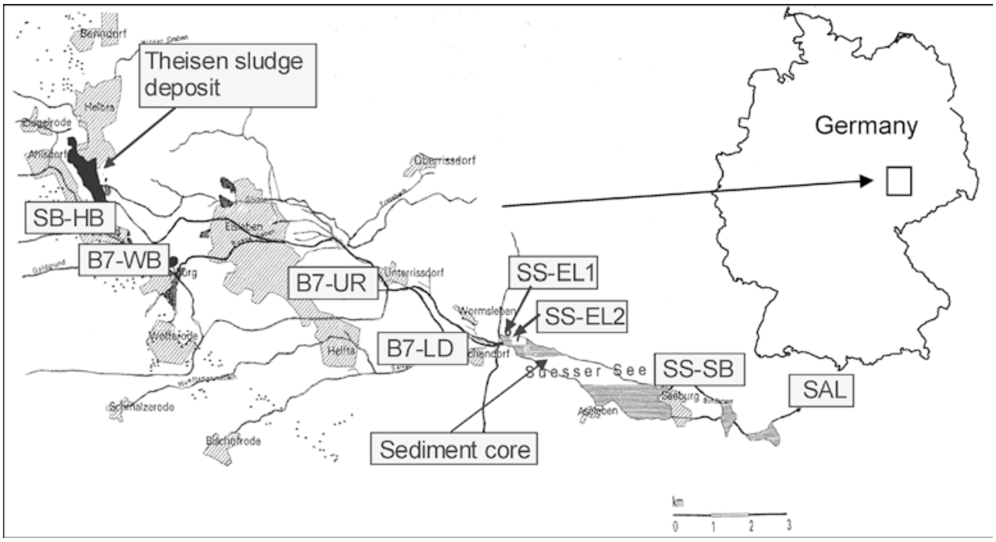

Fig. 1
Map of the sites

located in the mouth of the creek and the site SS-SB at the drain of the lake Suesser See. The lake is drained over the River Salza and afterwards the River Saale, a tributary of the River Elbe. The River Salza was sampled at site SAL which is 12 km downstream from the outlet of the lake Suesser See.

Material and methods

The sediment samples were collected at the eight sites as described above. Additionally several samples from the dumped Theisen sludge were taken. The results of the heavy element pattern with the depth inside a Theisen sludge deposit are reported by Schubert and others 2003.

Sampling

Theisen sludge samples were taken from different places, where this material was deposited. The sediments were collected within one day. The sediment samples (0–20 cm) were collected using an Ekman-Birge grab (HYDRO-BIOS Apparatebau, Kiel, Germany). The homogenized samples were divided into sub-samples. The material was air-dried for 48 hours. After drying the agglomerates were crushed and afterwards the samples were sieved on a 2.5 mm sieve (Retsch, Haan, Germany). The fraction <2.5 mm was ground in an agate mill (Retsch) to a grain size <100 µm. This fraction was used throughout in these studies. The samples were divided for X-ray fluorescence (additionally milled to a grain size <63 µm) and gamma- spectrometry's, and for the leaching procedures.
Additionally, sediment cores of approx. 0.5 m length were collected from the sediment of the lake Suesser See in an only little disturbed area which was approx. 2 km east from the sampling site SS-EL1, by A. Becker (University of Halle, Dept. Geological Sciences) in collaboration with a diver team. These samples were collected in polyethylene tubes (length 0.5 m, diameter 74 mm), sealed and stored at 4 °C in the dark. The original bore cores were divided into sub-samples of 1 cm thickness each.

Sample preparation

Solid materials

X-ray fluorescence

The total concentrations of selected elements were determined in additionally dried (105 °C) and ground material (<100 µm) using both wavelengths-disperse (WDXRF) and energy-dispersive X-ray fluorescence (EDXRF). The samples were mixed with stearine wax (Hoechst) as a binder in a ratio 80:20 w/w and subsequently pressed at 200 MPa to pellets (i.d. 32 mm). In addition discs were prepared by fusion of the samples with $Li_2B_4O_7$ (Merck) (1 g dried sample + 7 g $Li_2B_4O_7$) to improve the accuracy of the determination of the major compounds as well as several of the so-called "light elements" (atomic number <20).
For the quantitative analysis of samples which contain heavy metals that are out of the calibration range in available reference materials (Theisen sludge, SB-HD), the original material was diluted with SiO_2 powder (Riedel-de-Haen). Dilution factors of 5–10 reduce the concentrations of the elements of interest to a desired level and yield sample compositions which match the working range of calibrations performed by the EDXRF spectrometer (X-LAB2000, Spectro A.I.).

Eluates

Aqueous extracts

The German standard procedure DIN 38414 was varied a little. In all the experiments using sediment bulk samples 250 g of fresh material and 1,000 ml deionized water were used. After overhead shaking in polyethylene bottles (2 l) the supernatant was separated by centrifugation (9,000 rpm at 15 °C). After centrifugation each supernatant was divided. One part (10 ml) was directly used for the determination of sulfate, chloride, and nitrate. To another part (100 ml) 0.2 ml of suprapur nitric acid (65%, Merck) was added for stabilization. These acidified solutions were used for the determination of total element concentrations (ICP-AES, ICP-MS, and AAS).

For the determination of arsenic species in sediment samples from bore cores taken from the lake Suesser See 30 g of the wet material and 100 ml de-ionized water were overhead shaken at ambient temperature for 2 hours. The supernatant was separated by centrifugation (20 minutes at 4,500 min^{-1}). The dried mass was obtained by drying aliquots of the material at 105 °C.

Aqua regia extracts

Aqua regia extraction is commonly used to describe the maximum acid-soluble amount of heavy metal of solid samples. The aqua regia soluble content of metals was obtained according to DIN ISO 11466. Briefly, an amount of 3 g solid material is heated for 2 hours with 21 ml of hydrochloric acid and 7 ml nitric acid. The cooled extracts are centrifuged. The supernatant is diluted with deionized water to 100 ml and subsequently used for the determination of elements by atomic absorption and atomic emission and ICP-mass spectrometry.

Sequential extraction

For estimation of long-term impact on groundwater from Theisen sludge the established four stage sequential extraction by Schoer and Förstner was used. Briefly, the scheme was used to differentiate between the exchangeable fraction F1: soluble in 1 M NH_4COOCH_3, the reducible fraction F2: soluble in 0.4 M $(NH_4)_2C_2O_4$, the oxidable fraction F3: soluble in 30% v/v H_2O_2 at pH=2; afterwards extracted with NH_4COOCH_3 and the residual fraction F4: soluble in hot $HNO_{3\ conc}$.

Reference materials and standards

Analysis of solid samples

A set of different certified reference materials (CRM's) had been used in the XRF analysis for calibration. This includes geochemical materials 07402, 07406, 07407, 07409 (GBW series), SY2 (CANMET), sediments 07310 to 07312 (GBW series), NBS 2704, RM8407, RM8408 (all NIST), STSD-2, LKSD-4, PACS-1, CRM 277 (CANMET), soil samples SRM series 2709 to 2711 (NIST), city waste incineration ash BCR 176 (IRRM), sewage sludge's BCR 143R, BCR 146 (IRRM) and coal fly ashes ECO, ENO (IRANT, Slovakia), CTA (Poland).

For calibration of the gamma-spectrometry detector the CRM's IAEA-RGU-1, IAEA-RGTh-1 (International Atomic Energy Agency, Vienna) - and a radionuclides mixture NG1 (Physikalisch -Technische Bundesanstalt Braunschweig, Germany) were used.

Analysis of liquid samples

Suitable calibration solutions were prepared daily from stock solutions. Merck IV multi-element standard and single element standards of arsenic, sulfur and silicon (all Merck) were used in ICP-AES. Calibration solutions for ICP-MS were prepared by mixing multi-element standard solutions Merck VI and Spex 1, 2, 3, respectively, in nitric acid (0.2% m/v). Single element standards (Cd, As, Sb, Hg), all from Merck, were applied in flameless AAS. The stock solutions for IC-ICP-MS were prepared from arsenic trioxide (Fluka) arsenic standard [As(V)] (Merck).

Analytical techniques

X-ray fluorescence

The X-ray fluorescence measurements were carried out on both wavelength dispersive (SIEMENS SRS 3000) and energy-dispersive spectrometers (SPECTRO X-LAB 2000). The SRS 3000 is equipped with a 3 kW-Rh X-ray tube (125 μm Be window), 60 kV generator and eight-position crystal changer. The spectrometer operating conditions were vacuum, 34 mm collimator mask and the following analyzing crystals: OVO 55, Ge, LIF 100 and LIF 110 analyzing crystals. An outstanding high light of the SPECTRO X-LAB 2000 is the use of polarized X-rays for the excitation process, which yields lower detection limits compared with a wavelength dispersive device especially for the determination of heavy metals.

To use both the typical advantages of the wavelength dispersive spectrometer (high energy resolution, availability of a high performance X-ray tube) and the advanced technique of SRS 3000 was mainly applied to the determination of the light elements Na, Mg, Al, Si, P, S, K, Ca, Ti and Fe and to the heavy metals V, Cr, Mn, Co, Ni, As, Hg, Pb, and U, while the application of the X-LAB 2000 was focused to the determination of traces of Cu, Zn, Mo, Ag, Cd, Sn, Sb, and Ba which are commonly free from spectral line interferences.

For calculation of the concentration from the measured fluorescence intensities the software packages SPECTRA 3000 and X-LAB Pro 2.2 were used for the SRS 3000 and the X-LAB 2000, respectively. The measured data of standard reference materials were included in the evaluation routines to adjust the respective matrix correction algorithm based on the fundamental parameter method. Using such a calibration strategy it is possible to have a linear working range over more than four decades with limits of detection (LOD) lower than 10 mg/kg for most of the interesting heavy metals and metalloids. However, the detection limits of the "light" elements (atomic number 11 to 20) are approximately 100 mg/kg using $Li_2B_4O_7$ discs. As an example the recovery plot of arsenic (measured concentration versus certified values) in wax pellets to demonstrate the trueness of the method (Fig. 2).

Gamma-spectrometry

The measurements of the gamma activity of the bulk samples were carried out using HPGe coaxial low-energy

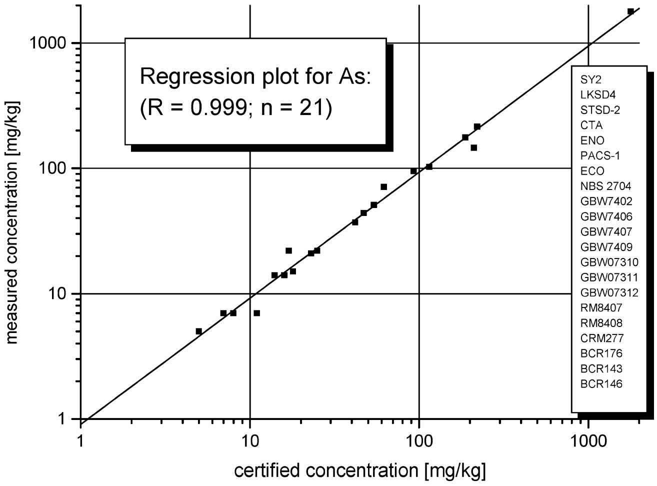

Fig. 2
Validation of trueness for the determination of As using WDXRF based on pellets prepared by mixing of geological SRM's and wax (1+4)

Table 1
γ-energies and abundances used for evaluation of γ-spectra

Radionuclides	γ-energy (keV)	abundance (%)
^{234}Th	63.3	4.1
^{226}Ra*) ^{214}Pb	295.2	18.7
	351.9	35.8
^{214}Bi	609.3	44.6
	1,120.3	14.7
^{210}Pb	46.5	4.05
^{228}Ac	911.1	29.0
	968.9	17.5
^{212}Pb	238.6	45.0
^{212}Bi	727.2	6.65
^{208}Tl	583.1	86.0
^{40}K	1,460.8	10.7
^{137}Cs	661.6	85.1

*) ^{226}Ra was determined on the understanding of radioactive equilibrium with its daughter nuclides ^{214}Pb and ^{214}Bi

Table 2
ICP-AES analytical capabilities using simultaneous measurements and compromise conditions, Plasma-Ar: 13 l min^{-1}, Auxiliary-Ar: 0.9 l min^{-1}, Nebulizer-Ar 0.9 l min^{-1} (cross flow), RF-Power: 1200 W, Sample delivery-rate: 1.5 ml min^{-1}

Analyte	Wavelength (nm)	Calibration range (mg l^{-1})	LOD* (mg l^{-1})
Al	308.215	0.05–100	0.022
As	189.042	0.05–10	0.03
Ba	455.403	0.01–10	0.01
Ca	396.847	0.05–10	0.02
Cd	226.502	0.05–10	0.03
Co	228.615	0.05–10	0.02
Cr	267.716	0.05–10	0.03
Cu	324.754	0.05–10	0.036
Fe	259.940	0.05–10	0.02
K	766.491	0.2–20	0.1
Mg	285.213	0.05–10	0.02
Mn	257.610	0.05–10	0.036
Ni	221.647	0.05–10	0.013
P	178.290	0.4–70	0.38
Pb	220.353	0.05–20	0.033
S	182.040	0.5–70	0.40
Zn	213.856	0.05–10	0.016

* LOD, limit of detection according to German Standards procedure DIN 32645 (in all cases the correlation coefficient was better than 0.999) calibration plots (n=9, each 5 measurements)

detectors (n-type) an active volume of 39 cm^3 and with a Be-window of 0.5 mm thickness (EG&G ORTEC, Oak Ridge, U.S.A.). The relative efficiency at 1.33 MeV (^{60}Co) is 25.9 %, the energy resolution at 122 keV (^{57}Co) amounts 570 eV. Passive shielding consists of 105 mm lead, 2 mm copper and 4 mm Plexiglas. The software GAMMAW (Dr. Westmeier Gesellschaft für Kernspektrometrie, Ebsdorfergrund, Germany) was used for the evaluation of the spectra. The calibration of the detector and the measuring geometry was done using CRM's. IAEA/RGU-1 (with 400 ± 2.1 mg/kg) of uranium and IAEA/RGTh-1 (with 800.2 ± 15.8 mg/kg) of thorium were used for the uranium and the thorium series, respectively.
The ^{40}K activity measurements were calibrated by CRM IAEA/RGK-1 [(44.8 ± 0.3)% potassium]. Using the radionuclides water solution NG1 a soil sample was prepared to calibrate the ^{137}Cs measurements. Table 1 contains the γ-energies used for the calculation of the specific activities of the determined radionuclides.

ICP atomic emission spectrometry

The leachable amounts of selected elements (see Table 2) were determined using an ICP-atomic emission spectrometer with cross-flow nebulization (Spectroflame P/M, Spectro A.I.). Depending on the composition of the matrix emission lines without interference's and positions for background correction had been selected. ICP-AES measurements were performed in undiluted and diluted samples because of the wide ranges in the concentration of the different analytes. Compromise conditions were used to reduce the time for determination. Both external calibration with matrix-matched samples and the standard addition technique were employed. The calibration range based on diluted ICP multi-element standard solution Merck IV, as well as single element standards for S and P (all Merck), was found to be between a few µg/l and 10 mg/l. That means the leachates had to be diluted to this concentration range if there are higher concentrations in the extracts. Using the given emission lines the limits of detection according to German Standards Procedure DIN 32645 are also listed in this table.

ICP mass spectrometry

For a survey analysis of trace elements in the concentration range below 0.1 mg/l ICP-(quadrupole) mass spectrometry was employed. All ICP-MS measurements (ELAN 5000, Perkin Elmer) were done by pneumatic nebulization (cross flow) using compromise parameters (Table 3). The aqueous samples were acidified with nitric acid (0.2 % m/v). The aqua regia extracts were diluted with de-ionized water. Because of the wide variety of elements in the Theisen sludge (amongst them are Be, Sc, Ge, Rh, Re and Rare Earth Elements (REE) which are often used as an

Table 3
ICP-MS (quadrupole) using cross-flow nebulization: analytical capabilities for the determination of selected elements in aqua regia solutions diluted (1:100) using compromise parameters Plasma-Ar: 15 l min^{-1}, Auxiliary-Ar: 0.80 l min^{-1}, Nebulizer-Ar: 0.9 l min^{-1}, RF-Power: 1000 W, Sample delivery-rate: 1.25 ml min^{-1}

Isotope	Calibration range (μg l^{-1})	LOD (μg l^{-1})	Isotope	Calibration range (μg l^{-1})	LOD (μg l^{-1})
^{51}V	10–100	0.015	^{118}Sn	2–20	0.036
^{59} Co	10–100	0.014	^{184}W	5–50	0.022
^{71} Ga	10–100	0.028	^{185}Re	5–50	0.017
^{74} Ge	10–100	0.05	^{209}Bi	10–100	0.008
^{82} Se	100–500	1	^{232}Th	5–50	0.007
^{95} Mo	5–50	0.062	^{238}U	10–100	0.006
^{109}Ag	10–100	0.024			

internal standard in ICP-MS), a method without an internal standard had to be used. The calculated detection limits and the working ranges for selected isotopes of interest were also listed. The calibration range was fitted to the concentration range of relevance for the aqueous samples under investigation.

Atomic absorption spectrometry

Arsenic and antimony were also analyzed after hydride generation and in situ trapping in a iridium-modified graphite furnace using a 4100 ZL atomic absorption spectrometer equipped with a FIAS-400 flow injection device (both Perkin-Elmer). This technique combines the advantages in the separation of the analyte from the matrix by hydride generation and the pre-concentration of As and Sb inside the graphite furnace. Briefly, the inorganic As and Sb species in the solution are reduced by potassium iodide (5% w/v) and ascorbic acid (5% w/v)) to As(III) and Sb(III), respectively. The solution is injected with a sample loop into a flow-injection device. There it is mixed with a reduction-solution ($NaBH_4$ 0.2 % w/v in 50 mM NaOH). The resulting gaseous hydrides are transferred into the permanent surface modified (40 μg iridium) heated graphite furnace of the atomizer (250 °C), where the hydrides are destroyed and the metalloids are sorbed. A temperature of 2,000 °C (4 s) was used for atomization and the absorbance measurements.

Solutions with low concentrations of Cd and Pb were simultaneously analyzed by the graphite furnace technique with a SIMAA 6000 (Perkin-Elmer) multi-elemental atomic absorption spectrometer. Working with Pd as modifier these two analytes were atomized at 2,000 °C. In all cases the standard addition technique was used.

Mercury was analyzed using the cold vapor technique (FIMS, Perkin-Elmer) with $NaBH_4$ for reduction of mercury ions.

The working ranges and the limits of detection of all the atomic absorption methods are listed in Table 4.

Coupling ion chromatography-ICP-MS

The binding of arsenic in the sediments, which was found in highly elevated concentration (some g/kg) in Theisen sludge, is of importance to estimate the potential eco-toxicological risk of this element. The determination of As species in aqueous extracts of sediments was performed as described in previous papers (Mattusch and Wennrich 1998; Mattusch and others 2000) using the coupling of ion chromatographic separation and ICP-MS detection. Briefly, the system consists of a binary HPLC-pump LC 250 (Perkin Elmer,), a pneumatic injection valve using a 200 μl sample loop (Dionex, Sunnyvale, USA) and an ICP-MS (ELAN 5000, Perkin Elmer Sciex,) as a high sensitive element-specific detector fixed on the m/z=75 (arsenic) channel. The two instruments were interfaced by a cross-flow nebulizer. The eluent was pumped isocratically at a flow rate of 1.0 ml/min. To determine the arsenic species a weakly anionic exchange column with a guard column (Ion Pac AS4A-SC and Ion Pac AG4A-SC, Dionex) together with an eluent containing 5 mM Na_2CO_3, 40 mM NaOH, and 4% (v/v) methanol (p.a., all supplied by Merck) had been applied. The instrumental conditions of the ICP-mass spectrometer were as follows: rf power: 1,000 W; plasma gas flow rate: 15 l/min, auxiliary flow rate: 0.80 l/min, nebulizer flow rate: 0.78 l/min; dwell time: 1 s; monitored: mass 75. The integration of the peaks after baseline correction was done by the computer program Microcal™

Table 4
Analytical capabilities using different AAS methods for the determination of As, Sb, Cd, Pb, and Hg

Analyte	Wavelength (nm)	Technique	Calibration range (μg l^{-1})	LOD* (μg l^{-1})
As	193.7	ETA with hydride generation and in situ pre-concentration[a]	1–10	0.99
As	193.7	ETA with hydride generation and in situ pre-concentration[b]	5–100	2.13
Sb	217.6	ETA with hydride generation and in situ pre-concentration[a]	1–10	0.43
Cd	228.8	ETA[c]	0.5–7.5	0.40
Pb	283.3	ETA[c]	5–100	4.14
Hg	253.7	Cold vapor[a]	0.5–10	0.36

FIA sampling loop: [a]500 μl, [b]200 μl; [c]sample volume 20 μl
LOD, limit of detection according to German Standards procedure DIN 32645

Origin™ (Version 4.10, Microcal Software Inc.). The precision of the calculation (n=4 at a level of 500 µg/l) of the concentration using this procedure was better than 0.8 % for each species. The calibration range was between 1 and 5,000 µg/l (LOD 0.4 µg/l).

Results and discussion

Direct analysis of solid material

X-ray fluorescence

All the solid samples analyzed by means of XRF based on calibrations done with CRM's. As summarized in Tables 5 and 6 there are significant differences in the concentration of either the main components (Si, Ca, Fe, S, Al) and of the heavy metals and arsenic in the materials investigated depending on the sampling site. Some limitations in the determination of trace elements in samples with extremely high concentrations of heavy metals, like Theisen sludge, have to be considered. On one hand, no certified reference materials with such a complex matrix are available for calibration. On the other hand, there are a lot of intensive lines in the fluorescence spectra leading to interference's. Based on the WDXRF results (Table 7) one can see the composition of the dumped Theisen sludge itself varied depending on the sampling site. These differences can result from the varying composition of the material deposed as well as from different leaching degree by alteration during open dumping over a period of several decades. Generally, a good agreement between XRF and the results analyzing aqua regia eluate was found. Exceptions were the extremely high amounts of Pb and also Mn, which form hardly soluble sulfates and oxides, respectively. The composition of the creek sediment at the site

Table 5
Main constituents (g/kg) of materials determined by WDXRF

Sample (site)	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
Theisen	n.d.*	2.5	9.4	~100	2.0	151	9.9	11.6	0.7	15.2
SB-HD	12.6	12.5	80.2	191	0.8	11.9	10.0	6.0	2.9	31.0
B7-WB	5.0	8.1	38.9	290	1.4	4.5	8.2	41.7	2.9	19.6
B7-UR	5.1	9.8	37.4	334	0.7	1.8	8.2	46.3	2.5	17.6
B7-LD	4.0	6.7	29.4	354	0.9	1.1	7.1	39.9	1.5	13.2
SS-EL1	5.6	7.3	42.0	288	1.8	7.8	8.7	33.8	3.2	21.1
SS-EL2	6.0	8.5	50.5	297	1.7	6.7	9.9	30.5	3.9	24.7
SS-SB	3.1	2.2	16.7	330	0.5	5.1	4.6	72.6	0.9	6.6
SAL	10.4	8.0	42.8	303	0.8	0.8	9.5	41.7	3.5	19.4

* Zn interference

Table 6
WDXRF data for selected heavy metals and metalloids (mg/kg)

Sample (site)	As	Sb	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Ba	U	Hg
Theisen	6,300	4,860	380	110	12,300	740	490	81,300	241,000	1,670	12	120
SB-HD	3,200	695	23	65	11,400	365	176	7,510	39,000	390	60	<5
B7-WB	33	4	7	54	754	739	38	780	1,890	510	4	<5
B7-UR	24	3	5	57	737	762	29	554	1,520	470	10	<5
B7-LD	18	6	4	26	360	562	19	179	940	330	10	<5
SS-EL1	120	13	7	55	724	616	31	605	2,150	460	3	<5
SS-EL2	35	2	5	74	448	508	30	350	1,750	510	4	<5
SS-SB	13	2	<2	13	92	647	10	57	580	280	<2	<5
SAL	12	<2	<2	54	25	423	22	36	80	410	3	<5

Table 7
Theisen sludge: comparison of the concentration in samples taken from different places of the heap (mg/kg)

Sample	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Mo	S	U	Ag
A_{XRF}	6,300	380	110	12,300	740	140	81,300	241,000	480	151,000	12	350
B_{XRF}	3,800	360	900	12,800	670	490	122,000	166,000	620	94,000	30	520
C_{XRF}	10,300	680	145	14,300	635	155	127,000	176,000	500	116,000	36	466
A_{aq}	5,800	330*	33	11,400	425	96	30,100	233,000	435*	167,000	17*	360*
B_{aq}	3,800	340*	890	12,000	490	500	36,000	170,000	640*	115,000	30*	520*
D_{aq}	5,570	360*	31	9,300	400	85	39,500	220,000	515*	146,000	20*	

$_{aq}$ aqua regia soluble: ICP-AES and ICP-MS (*) values

SB-HD shows clearly the influence of the dumped Theisen sludge. The concentration of As, S and the heavy metals (Zn, Pb, and Cu) in the stream sediments decreases with increasing distance from the source SB-HD, as expected. Obviously, the lake sediments act as a sink for heavy metals and metalloids. Particularly, the concentration of Fe, As, Pb and Zn were significantly higher in the lake-sediments, taken at the sites SS-EL1 and SS-EL 2, than in the stream sediments. Within the lake strong differences exist regarding the heavy metal concentrations in the sediment between the high concentrations at the mouth of creek Boese Sieben and those in the area of the discharge (site SS-SB), i.e. over a distance of approx. 5 km.

Results of gamma spectrometry

The results for the determination of selected radioactive isotopes (^{232}Th and ^{238}U series) in the solid materials by the gamma spectrometry are summarized in Table 8.
The high concentration of the ^{210}Pb in the dumped Theisen sludge with gamma activities in the kBq kg^{-1} range is a result of the processing of the ores whereby especially Pb and Zn were enriched in the flue dust. This is in accordance with the very high concentrations of Pb (and Zn) determined by WDXRF.
Comparing the uranium concentration calculated from the gamma activities and the WDXRF results a good agreement was found at elevated concentrations. The gamma spectrometry is a more suitable technique than the WDXRF (LOD: 2 mg/kg) for samples with a uranium concentration less than 10 mg/kg.
There is also a high precipitation of ^{238}U (^{234}Th), which had been leached out of the Theisen sludge, by forming poorly soluble compounds in the sediments in the drain of the sludge heap (site SB-HD).
The concentration of ^{238}U (^{234}Th) and ^{210}Pb decreased with increasing distance from the site SB-HD, but were still detectable. That means that a considerable portion of the sediments within the pathway is influenced by the dumped Theisen sludge, confirming the results obtained by WDXRF analysis.

Analysis of leachates of the solid samples

Different extraction procedures in combination with analytical methods were used for the characterization of the leaching behavior of selected elements from sediment samples.

Aqua regia extracts

As shown in Tables 5 and 6 (WDXRF-data) the main components in the sediments are Si, S, Fe, Al, Ca, and Mg. The concentrations of elements classified as particularly environmentally relevant, U, Cu, Ni, Pb, Zn, and As varied in a broad range between a few mg/kg and some g/kg. That means they are at levels that are of interest to estimate the

Table 8
Results of gamma spectrometric analysis (^{238}U decay chain) ^{234}Th: concentration of selected isotopes in sediment samples (Bq kg^{-1}) and the calculated concentrations of U and Th (mg/kg)

Sample	^{234}Th	^{226}Ra	^{210}Pb	^{228}Ac	^{212}Pb	^{212}Bi	^{208}Tl	^{40}K	U[a]	Th[b]
	(Bq/kg)								(mg/kg)	
Theisen	115±16	159±15	3481±80	<5	8±1	8±2	3±0.5	246±20	9.3±1.6	<1.2
SB-HD	718±44	55±3	883±24	40±3	43±1	42±2	15±1	674±12	58.1±3.6	9.9±0.7
B7-WB	117±10	95±6	130±7	35±6	37±2	32±4	13±2	497±25	9.5±0.8	8.7±1.5
B7-UR	142±16	147±6	122±9	28±2	30±1	34±2	11±1	508±10	11,5±1,3	6,9±0,5
B7-LD	131±25	122±6	106±10	24±4	22±1	22±3	8±1	442±17	10.6±2.0	5.9±1.0
SS-EL1	90±12	60±5	120±5	38±5	38±2	44±4	14±1	533±32	7.3±1	9.4±1.2
SS-EL2	77±8	43±3	82±3	40±4	42±1	42±5	14±1	572±13	6.2±0.6	9.9±1
SS-SB	65±9	17±2	22±1	12±2	13±1	11±1	4±1	278±15	5.3±0.7	3.7±0.5
SAL	45±4	30±3	31±2	35±3	35±1	36±3	12±1	572±40	3.6±0.3	8.7±0.7

[a]calculated from the ^{234}Th decay [b]calculated from the ^{228}Ac decay

Table 9
Aqua regia soluble amount of selected main constituents (mg/kg) by ICP-atomic emission spectrometry

Sample (site)	Concentration (mg/kg)										
	Cu	Zn	Pb	As	Mg	Al	P	S	K	Ca	Fe
Theisen	11,400	234,000	30,100	5,800	2,620	6,950	720	170,000	8,750	7,250	11,100
SB-HD	12,000	38,600	6,900	3,100	9.2	48.5	0.7	10.6	9.8	5.3	26.8
B7-WB	630	1,630	630	30	6.1	14.8	1.1	3.2	4.3	33.4	15.2
B7-UR	540	1,240	390	11	7.4	14.5	0.5	01.0	4.8	38.2	13.4
B7-LD	360	810	150	17	5.4	12.8	0.7	1.3	4.6	33.2	10.7
SS-EL1	600	1,850	490	85	5.4	15.3	1.4	5.4	3.8	26.3	16.9
SS-EL2	380	1,580	270	23	6.6	18.7	1.3	4.2	4.5	25.2	19.3
SS-SB	100	460	57	8	1.9	5.6	0.4	3.7	1.0	62.1	4.9
SAL	20	64	30	9	6.5	15.2	0.6	0.7	3.9	34.4	15.4

Table 10
Aqua regia soluble amount of selected heavy metals and metalloids (mg/kg)

Sample (site)	Concentration (mg/kg)																			
	Ba[a]	Cr[a]	Mn[a]	Ni[a]	Cd[b]	Hg[b]	Sb[b]	V[c]	Co[c]	Ga[c]	Ge[c]	Se[c]	Mo[c]	Ag[c]	Sn[c]	W[c]	Re[c]	Bi[c]	Th[c]	U[c]
Theisen	30	33	420	95	340	105	2,040	123	78	44	31	720	435	363	9,990	22	63	390	0.8	17
SB-HD	130	33	260	100	14	0.6	540	109	27	9.1	14	48	990	16	150	14	4.3	4	5.7	55
B7-WB	250	25	350	24	7	1.3	3	86	17	4.8	0.5	4.6	17	5	13	0.4	0.07	0.6	2.8	5.3
B7-UR	210	24	510	18	5	0.2	3	52	9	5.7	0.3	5.2	5	4	11	0.2	0.07	0.7	4.4	2.5
B7-LD	140	21	430	17	4	0.1	2	84	10	3.1	0.3	1.1	13	2	14	0.3	0.03	0.1	3.1	5.8
SS-EL1	170	138	440	36	7	0.9	10	88	12	5.6	0.8	7.4	9	7	24	0.5	0.17	2	4.1	4.0
SS-EL2	160	27	360	23	4	0.5	2	113	12	3.8	0.2	1.8	22	5	7.9	0.3	0.04	0.2	4.1	9.1
SS-SB	90	14	470	42	2	0.1	1	18	4	1.5	0.2	2.6	38	0.2	4.2	0.4	0.11	0.1	1.4	4.6
SAL	100	21	280	16	1	0.2	1	28	6	4.6	0.1	1.3	1	0.1	2	0.1	n.d.	0.1	0.9	0.9

[a] ICP-AES
[b] AAS
[c] ICP-MS values

Table 11
Comparison of the total (WDXRF) and the aqua regia leachable concentration of elements in a sediment sample at different sites (ICP-AES or AAS* values) ratio aqua regia: WDXRF

Analyte	SB-HD	B7-WB	B7-LD	SS-EL1	SS-Sb
Ca	0.88	0.80	0.83	0.78	0.86
Al	0.60	0.38	0.43	0.36	0.28
Fe	0.86	0.78	0.81	0.80	0.74
S	0.90	0.72	1.15	0.68	0.72
Zn	0.99	0.86	0.86	0.86	0.79
P	0.90	0.77	0.77	0.75	0.77
Mn	0.73	0.77	0.77	0.72	0.72
Cu	1.05	0.84	1.01	0.83	1.06
Pb	0.92	0.81	0.81	0.81	1.00
As*	0.97	0.90	0.93	0.71	0.64
Cd*	0.61	0.71	0.93	0.71	n.d.
Co	0.68	0.73	0.92	0.69	n.d.
Cr	0.51	0.46	0.81	0.36	1

environmental risk by mobilization and translocation of this material. Both ICP-AES and ICP-MS were used for the determination of the aqua regia extractable concentration of these elements. The results of selected elements are summarized in Tables 9 and 10. As shown in Table 11 there are significant differences in the leaching behavior of the elements. The amount extracted strongly varied for aluminum (28%–60%) and for zinc, calcium, lead, iron, copper >80% of the total content analyzed by WDXRF/ EDXRF in most of the sediment samples investigated. There are also significant differences in the leaching behavior depending on the sampling site indicating differences of analyte binding in the sediment samples under investigation. (An assertion for recoveries higher than 100% may be caused by sample inhomogeneities.).

Sequential extraction of Theisen sludge

Figure 3 (log scale) compares results of the single extraction steps, the sum (F1–F4) of concentration eluted in the different sequential extraction steps and the total concentration in the solid material (XRF data). Most of the tested elements (with the exception of vanadium) are mobilized within this four-step procedure more than 70% by weight. In the exchangeable fraction relatively high amounts of sulfur (11%), nickel (12%), manganese (14%) and lead (9%) are soluble. After step F3 81% of sulfur, 84% of lead and 93% of cadmium were removed from the original material. That means there is a high risk to mobilize these elements under environmental conditions. On the other hand the mobilization of As (20%), V (14%), Cu (4%), and Mo (3%) are relatively low. These elements are mainly soluble only by nitric acid (Step F4).

Aqueous extracts

A method, which is frequently used for risk estimation of sediments, is leaching the sediments with de-ionized water, like that described in German Standard procedure DIN 38414 S4. This scheme simulates the initial contact of solid material with de-ionized water only. This procedure does not reflect the circumstances in reality. On one hand, a static process is simulated, but there are dynamic processes in the environment. On the other hand, de-ionized

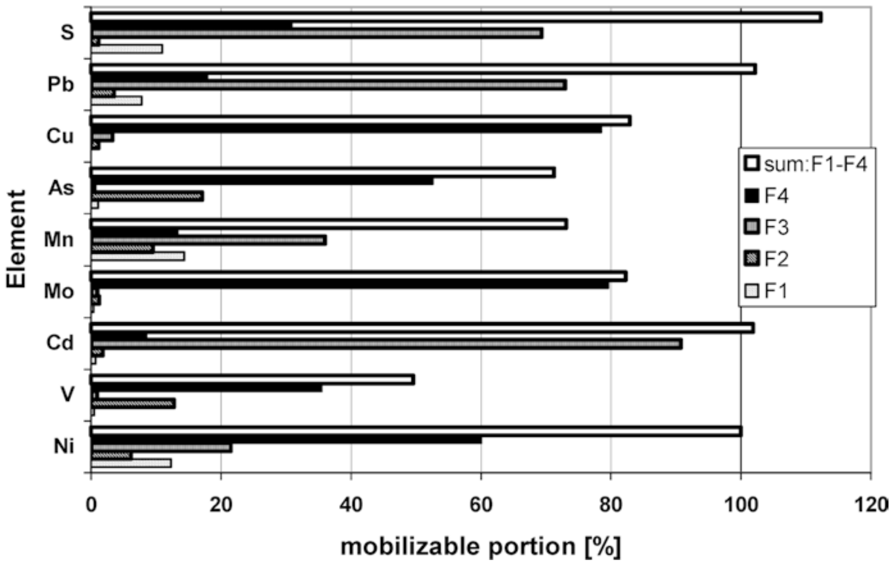

Fig. 3
Partitioning of selected elements in Theisen sludge using sequential extraction (Schoer and Förstner 1987)

water is used for extraction. In the aquatic environment however, the water that affects the samples is characterized partially by strongly varying pH-values, different salt concentrations, and organic substances, like humic acids. Despite its limitations, this scheme is in widespread use in regulations for the characterization of the mobilization rate of inorganic and organic compounds from solid wastes in the environment.

Thus shaking of solid materials with de-ionized water was used to estimate the mobilization of heavy metals out of the dumped materials and sediments. As shown in Table 12 distinct amounts of As, Cd, Cu, Mn, Ni, Pb, Zn and SO_4^{2-} are mobilized out of the sediment (precipitate) at the spring, site SB-HD. The concentration of most of the elements in this aqueous extract are however substantially smaller (with the exception of lead) than in the surface and the pore waters. This is indicative of the fact that already at the spring a considerable portion of the heavy metals forms quite stable precipitates under contact with air.

The behavior of the heavy metals in the samples from the other sampling sites is different. Despite partially high concentrations of Cu, Pb and Zn in the sediments, the concentrations of these elements are very small in the aqueous extracts. They are lower than the attainable detection limits of ICP-AES. That means that rather stable sediments had been formed.

Analysis of bore core materials

Depth profiles of selected elements, species and radionuclides of undisturbed sediment cores can be used to estimate the time dependence of pollution especially in lakes. It is possible to get information concerning differences of the load with anthropogenic pollutants by application of different methods of the trace element analysis in combination with methods for the determination of radionuclides. Also a temporal reference of the load is available.

Total concentration of heavy metals and radioactive isotopes

Bore cores taken from the bottom of the lake Suesser See had been divided into sub-samples (see experimental section). In these the total concentrations of some main components (Al, Si, Fe, Ca, K, and Ti), selected metals and metalloids (Ag, Ba, Cd, Cu, Mn, Mo, Pb, Sn, V, Zn, As, Sb) representative of the Theisen sludge were analyzed employing WDXRF. Selected values were plotted in Fig. 4. A similar pattern for all the elements included in the figure is evident. The highest concentrations of these metals were found between 11 and 25 cm depth. There are only minor deviations in the pattern of Pb, As, Sn, Mo, Ag, Cd and Sb compared with Cu and Mn. The behavior of vanadium seems to be slightly different in comparison with these two groups. The highest concentrations for V (Table 13) were found in the region, in which also As, Mo, Pb and Sn are most enriched. As shown in Fig. 5 the highest concentration values of uranium were also found between 11 and 25 cm with a maximum in 12 cm depth. One can also see good agreement between the WDXRF data and the values calculated from the γ-activities.

The ^{210}Pb dating method has been applied to the measurement of sedimentation rates in lakes, estuaries and coastal marine sediments (Shukla 1993). The age of different horizons in a sediment core can be calculated by the radioactive decay law

$$C = C_0 e^{-\lambda t} \qquad (1)$$

where λ is the decay constant of ^{210}Pb (0.0311 y^{-1}), C_0 the activity concentration of unsupported ^{210}Pb (^{210}Pb-excess=^{210}Pb–^{226}Ra) of the time of deposition, and C the ^{210}Pb-excess measured at time t, assuming that ^{210}Pb and ^{222}Rn are immobile in the core. This method assumes that the ^{210}Pb-excess remains constant with time at a particular location. Then, the difference in age between the surface sediment and sediment in depth n is given by

Table 12
Results of the analysis of aqueous extracts of sediments from investigated sites (all values in mg l^{-1})

Analyte	SB-HD	B7-WB	SS-EL1
Na	45	11	35
Ca	141	105	115
Mg	39	16	26
K	132	11	22
Al	4.7	<0.02	<0.02
As*	0.008	0.02	0.065
Cd	0.64	<0.03	<0.03
Cu	1.34	<0.04	<0.04
Fe	<0.02	<0.02	<0.02
Mn	5.39	<0.04	<0.04
Ni	0.42	<0.02	<0.02
Pb	1.23	<0.03	<0.03
Zn	440	<0.02	<0.02
SO_4^{2-IC}	1180	141	265
Cl^{-IC}	62	6.3	37
NO_3^{-IC}	19	2.7	0.3

*AAS values ^{IC}ion chromatography

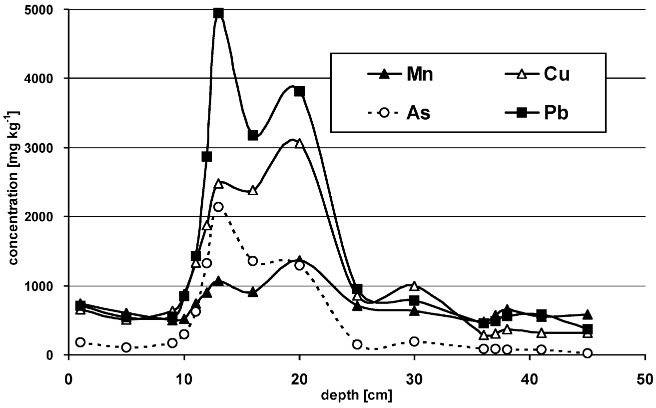

Fig. 4
Variation of the total concentration of selected elements (mg/kg) with the depth of a sediment core (lake Suesser See) using WDXRF

$$t_n = \ln\left[\left({}^{210}\mathrm{Pb} - \mathrm{excess}\right)_0 / \left({}^{210}\mathrm{Pb} - \mathrm{excess}\right)_n\right]\lambda \qquad (2)$$

^{137}Cs in the environment results above all firstly from the fallout of the atmospheric nuclear weapons tests till 1963 and secondly due to the Chernobyl accident in 1986. The fallout collected on the Earth's surface through both dry and wet deposition; and entered sediments mainly through erosion. The depth distribution of ^{137}Cs frequently shows two maxima which correspond with the years 1963 and 1986. In the bore core the ^{137}Cs depth distribution (Fig. 6) shows one maximum only at a depth of 7 cm which is correlated to the year 1986. Considering the sample date the mean sedimentation rate between 1986 and 1998 is about 6 mm per year.

The evaluation of the depth distribution of ^{210}Pb-excess in the bore (Fig. 6) core was based on the Constant Initial Concentration (CIC) model (Robbins and Edgington 1975; Durham and Joshi 1980). For the calculation of the mean sedimentation rate only the core depth sections 0–8 cm

Table 13
Concentration of selected elements (mg/kg) within a sediment bore depending on the depth (XRF-results)

Depth (cm)	Concentration (mg/kg)																	
	Al	Si	K	Ca	Ti	Fe	V	Mn	Cu	Zn	As	Pb	U	Mo	Ag	Cd	Sn	Sb	Ba
1	41,400	209,000	17,000	81,100	3,180	21,200	68	746	658	4,710	185	705	4	13	5	11	39	9	447
5	40,800	205,000	15,900	83,300	2,880	19,200	56	599	513	3,650	105	536	9	8	4	10	30	6	425
9	45,900	235,000	18,700	51100	3,120	20,600	78	501	638	4,080	168	555	11	11	5	10	40	10	456
10	47,700	227,000	18,800	56,200	3,300	22,500	106	517	875	5,700	292	850	12	17	7	14	62	19	474
11	48,300	215,000	19,700	59,300	3,360	24,600	150	739	1,330	9,470	627	1,440	16	39	13	23	100	39	528
12	47,800	203,000	18,000	58,500	3,180	27,100	284	905	1,880	16,900	1,330	2,870	25	100	24	40	158	67	599
13	49,000	191,000	15,600	55,000	3,060	29,700	442	1,080	2,480	24,900	2,140	4,950	33	177	38	60	239	85	702
16	59,300	213,000	22,400	38,300	3,720	35,600	338	913	2,380	17,000	1,360	3,180	21	138	23	38	132	45	650
20	50,000	179,000	17,500	56,400	3,240	29,900	238	1,370	3,070	40,600	1,290	3,810	20	141	25	55	160	74	701
25	59,500	225,000	22,000	34,000	3720	32,500	84	708	859	5,530	147	950	7	18	6	14	26	10	572
30	60,500	231,000	22,700	42,900	3,960	32,400	80	632	992	6,000	193	787	3	13	5	13	13	8	551
36	57,500	240,000	23100	37,400	3,780	29,000	74	476	287	1,820	80	456	9	12	2	6	8	4	492
37	57,400	232,000	22,300	41,500	4,080	30,300	78	571	303	2150	82	488	5	11	2	8	9	4	506
38	59,000	229,000	23,100	45,400	3,540	31,500	76	660	366	2,500	77	558	10	13	2	9	8	3	498
41	58,590	230,000	23,300	42,900	3,900	31,600	80	548	319	3,180	70	585	7	10	2	10	8	4	510
45	62,000	228,000	24,700	45,400	4,080	33,400	86	587	323	1470	20	366	6	7	-2	5	7	3	503

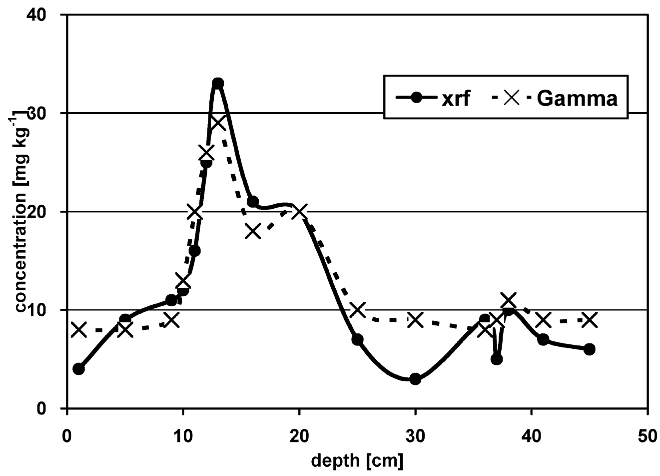

Fig. 5
Variation of the total concentration of uranium with the depth of a sediment core (lake Suesser See): comparison of the results of WDXRF and gamma activity analysis

and 37–50 cm were used. The part between 8 and 37 cm is disturbed by high lead content of the sediment material (see Table 13 and Fig. 4). On the basis of the CIC model the mean sedimentation rate is about 8 mm per year. Taking into consideration the high uncertainties of the activity values measured in consequence of the low mass of sample material and the high contamination by lead the two calculated values of sedimentation rate are in good agreement. Consequently, the maximum values of the heavy metals and metalloids were deposited in the 1950s. Based on another bore core and the WDXRF data set containing the concentration of 19 elements (Al, Si, K, Ca, Ti, Fe, V, Mn, Cu, Zn, As, Pb, U, Mo, Ag, Cd, Sn, Sb, Ba) in 16 depths of the core (Table 13) different statistical methods (Program Statistica 6.0) were applied to find similarities in the behavior of the analytes and also in the sediment layers and thus to recognize effects, e.g. the sedimentation of associated elements. The results of the Principal Component Analysis (PCA), see Fig. 7, demonstrate the significant differences in the behavior of the anthropogenic elements (V, Mn, Cu, Zn, As, Pb, U, Mo, Ag, Cd, Sn, Sb) resulting from the Theisen sludge pollution and the geogene ones (Si, K, Ti, Al, Fe, Ca, Ba). The PCA can also be used to demonstrate the differences in the composition of the different layers of the bore core. Factor 1 is dominated by high concentrations of heavy metals of anthropogenic origin at a depth of 12–20 cm.

As shown in Fig. 8 a large similarity of the composition of the sediment sampled between 30 and 45 cm in depth was determined. Obviously, these samples differ relatively strongly from the remaining samples according to their composition.

There is a high correlation between Cu, Zn, As, and Pb within the core (Pearson correlation coefficients varied from $r_{Zn,As}$=0.84 to $r_{As,Pb}$=0.99). The Canonical Correlation Analysis results in a highly significant correlation between the main elements Pb, As, Cu, Zn as one group (originated from the Theisen sludge) compared with the geogene ones Al, Si, K, Ca, Ti, Fe, and Ba (Table 14).

Concentration of selected elements in aqueous extracts

The capabilities for the mobilization of selected elements by water in different depths of the bore core were studied. As one can clearly see in Fig. 9, the highest concentrations of the interesting heavy metals in the water extracts from sediment samples, which were taken between 20 and 35 cm depth, were received. Comparing this with the total contents (Table 13), a correlation with the total content of the analytes is recognizable.

Arsenic species in aqueous extracts

Depending on the redox conditions in the different depths of the sediment core, one can find different redox species of elements. The arsenic species were investigated in dependence of the depth to get a more detailed picture of this element. Arsenic species in the water extract were found out in five of ten core samples applying the coupling of ion chromatographic separation and ICP-MS detection.

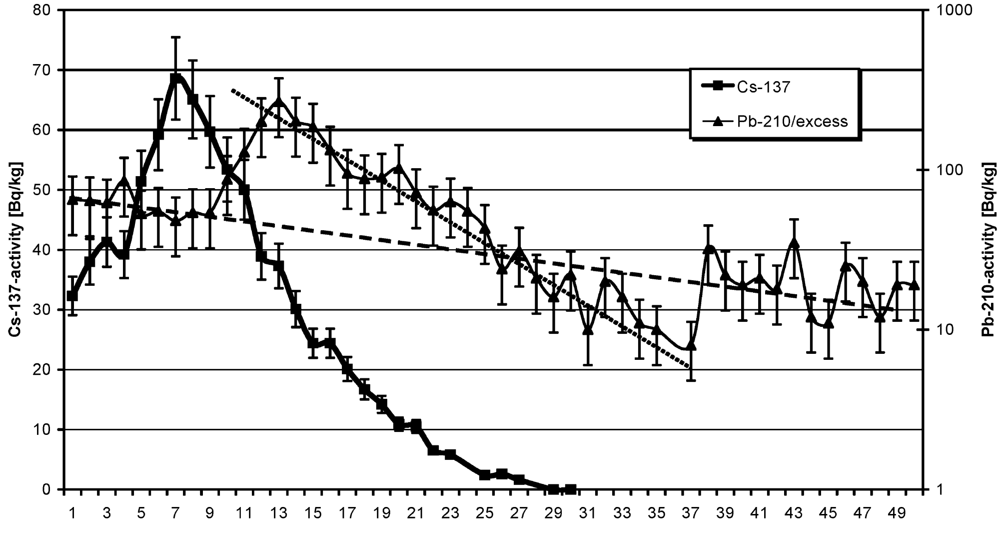

Fig. 6
Depth distribution of ^{137}Cs (linear) and ^{210}Pb-excess (exponential) in the bore core

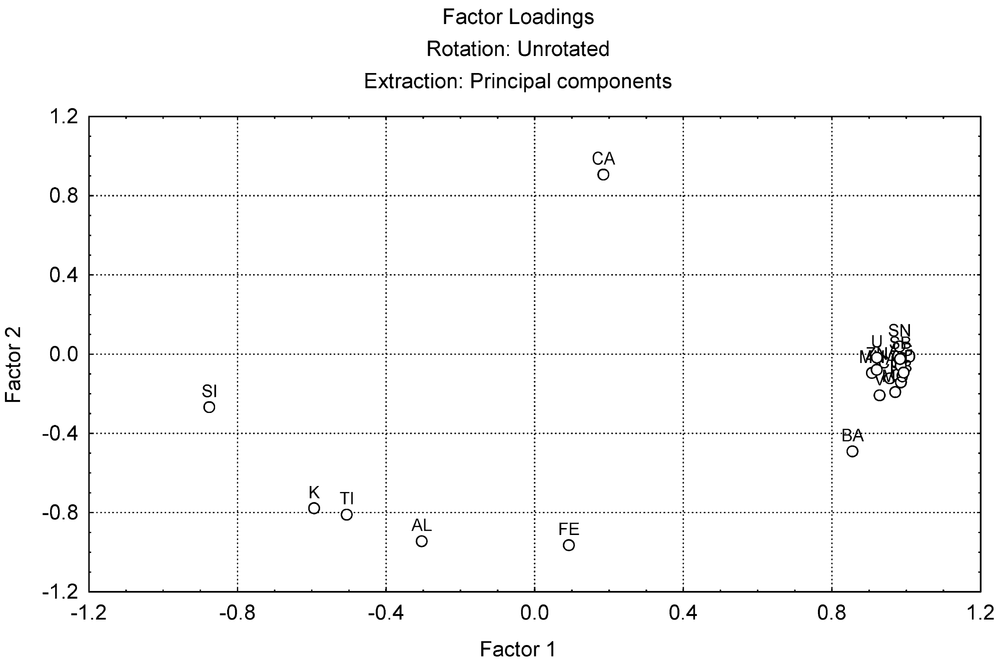

Fig. 7
Results of the Principal Component Analysis (PCA): factor loadings of anthropogenic elements (V, Mn, Cu, Zn, As, Pb, U, Mo, Ag, Cd, Sn, Sb) and the geogene ones (Si, K, Ti, Al, Fe, Ca, Ba) within a sediment bore sampled in lake Suesser See (total concentration)

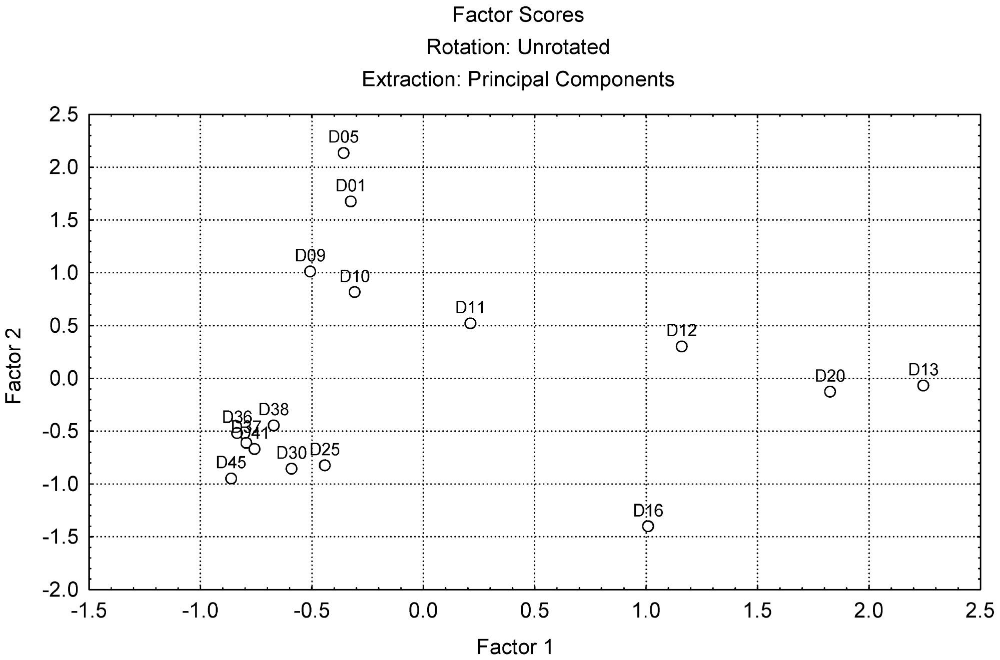

Fig. 8
Results of the Principal Component Analysis (PCA): differences in the composition of the different layers of the bore core in lake Suesser See (total concentration)

In the other samples the concentrations of As(III) and As(V) were lower than the limit of detection (0.4 μg l^{-1}). As illustrated in Figs. 10 and 11, only As(III) and As(V) were identified and quantified. It is shown in the sediment samples that As(III) is predominantly retained. An additional small peak can be seen, which cannot be assigned to arsenic-organic compounds. It is assumed that it concerns an adsorbate of As(V) to iron (As_xFe_yOH). This adsorbate was also found in seepage water samples from tailings material of the tin ore processing (Wennrich and others 1997). In Fig. 11 one can also detect clear differences in the concentration of arsenic species as a function of the sampling depth. There was a good correlation between the total concentration of arsenic measured by hydride generation AAS and the sum of the arsenic species determined by the hyphenated technique (IC-ICP-MS).

Conclusion

Analysis of sediments from a creek system indicated contamination from various elements associated with former copper mining and ore processing by the water pathway over a distance of more than 20 km. The importance of dumped Theisen sludge becomes particularly clear. Because of the very complex composition of this material and a multiplicity of inorganic species, which are of importance under toxicological and ecotoxicological aspect, a multiplicity of different analytical methods was used for the description of the source of contamination as well as the pathways of the pollutants. The results show that different XRF techniques can be used for the simultaneous determination of the total concentration of the majority of heavy metals and metalloids within the range of a few mg/kg up to 30% w/w in solid samples (Theisen sludge, sediment, drill core material). Thereby the choice of suitable solid reference materials, the correct sample preparation and a qualified matrix adjustment for samples with high concentrations of heavy metals and metalloids are of special importance for the traceability of the results. In order to be able to determine very low concentrations of naturally occurring radionuclides in the solids, gamma spectrometry is the method of choice. To derive information concerning the history of pollution, the distribution analysis of heavy metals and radionuclides within lake sediment cores are a suitable

Table 14
Results of Canonical Correlation Analysis: difference between the main elements Pb, As, Cu, Zn as group (originated from the Theisen sludge) compared with geogene ones Al, Si, K, Ca, Ti, Fe, and Ba

Stat. canon. analysis	Canonical analysis summary, canon. r: .9942, chi2(28)=65.23 p=.00008	
N=16	1. Set	2. Set
No. of variables	7	4
Variance extracted	87.36%	100.00%
Total redundancy	47.28%	96.02%
Variables:		
1	Al	Cu
2	Si	Zn
3	K	As
4	Ca	Pb
5	Ti	
6	Fe	
7	Ba	

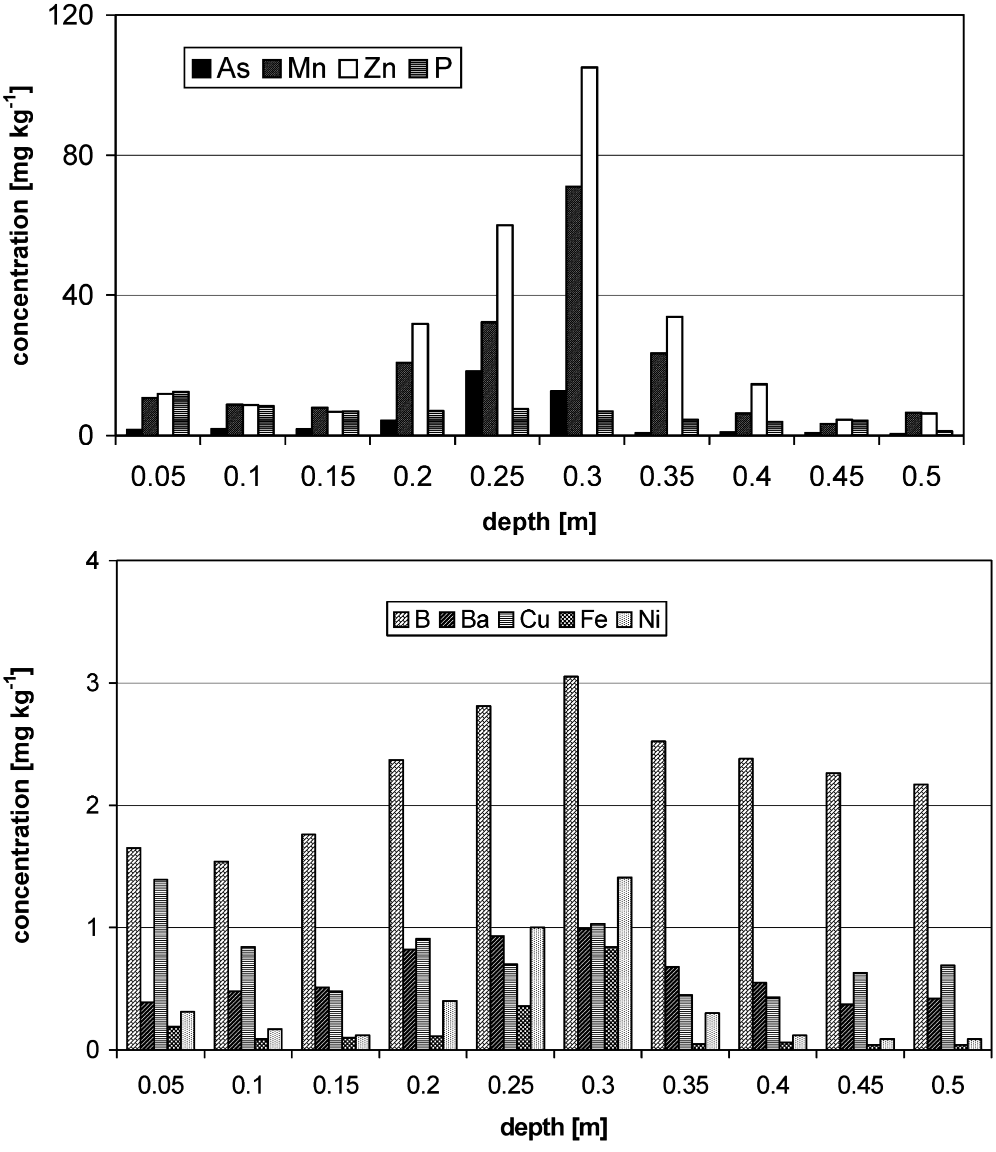

Fig. 9
Variation of the concentration As, Mn, Zn, P (in water extracts) with the depth of a sediment core

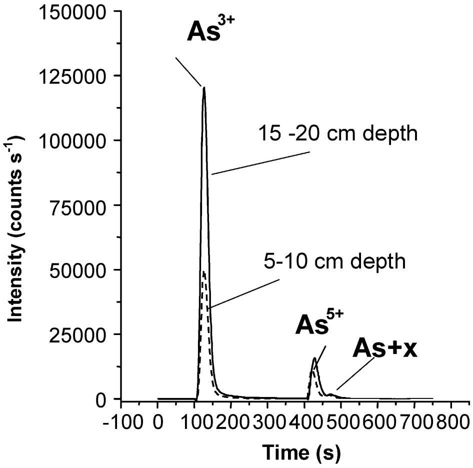

Fig. 10
Results of IC-ICP-MS: arsenic species in water extracts of lake sediments depending on depth (*dotted line*: sample taken between 5 and 10 cm; *continuous line* 15–20 cm)

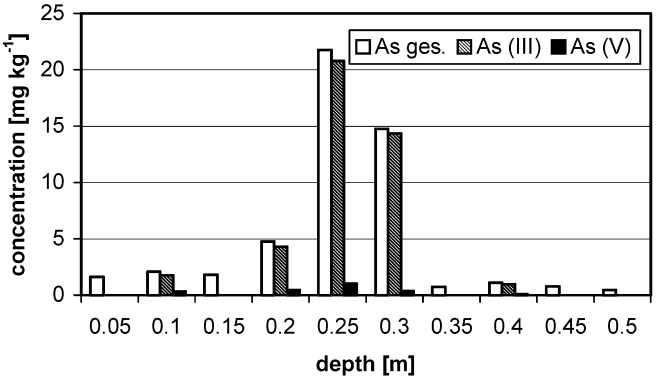

Fig. 11
Variation of the concentration (in water extracts) with the depth of a sediment core: As_{total} and arsenic species

tool. Based on XRF multielement analysis and the application of statistical methodologies it was possible to recognize periods with similar pollution. Also predicates about similarities of different elements were possible regarding their transport and sedimentation with this methodology. The determination of the isotopes ^{137}Cs and ^{210}Pb is an advantageous methodology for the determination of the age in sediment drill cores and thus for a dating of the deposits of heavy metals. The analysis of the surface water and suspended matter (both were done in an additional study) is of importance for the current description of transport of the relevant heavy metals and metalloids. It is also of interest for a modeling of precipitation processes and bioavailability to analyze the pore water. Depending on the elements of interest one has to apply different techniques, as demonstrated here.

A suitable tool for estimation of the ecological risk posed by primary inorganic waste deposits and polluted sediments is the application of different approaches for operationally defined fractionation as demonstrated here by sequential extraction of Theisen sludge or the leaching of sediment samples by aqua regia and water. For further investigation one has to look for dynamic leaching procedures to achieve more realistic data to describe the long-term behavior of deposed material under natural conditions.

As also shown in the results presented here, the coupling of ion chromatographic separation and ICP-MS detection is a very suitable analytical method in order to receive information about the binding of harmful metalloid species, particularly about the redox forms of arsenic. Data from these studies would help to formulate a more accurate ecological risk assessment for the area under investigation. On the other hand the presented methodology (including standard protocols) could be helpful in planning a strategy for investigations in highly polluted mining areas.

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