

Multi-metal contaminated stream sediment in the Mansfeld mining district: metal provenance and source detection

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ABSTRACT: In metal mining districts, element and radionuclide patterns in contaminated stream sediment can be used as tracers to detect and track the sources of pollution, and to distinguish geogenic from anthropogenic input, a prerequisite for rehabilitation planning. An example is given from the Mansfeld mining district in central Germany, where mining of 'Kupferschiefer' was conducted for over 800 years and led to extensive environmental pollution, considered to be mainly of geogenic origin. In consequence, only emergency measures have been implemented. The aim of the present study was to identify the metal sources in the mining district and to assess the range of pollutant migration. In combining conventional geochemistry, mineralogy and radiometry, it was shown that most of the multi-metal pollution in the Mansfeld mining district is of anthropogenic origin. The major sources of metals are low-grade ore, metalliferous flue dust and slag. Conventional geochemistry provided information on the spread of contamination in the rivers of the mining district. Mineralogy and microchemistry added data on the composition of the source material and pointed to the potential sources of contamination. Finally, the fraction of these sources in environmental pollution was estimated by gamma-spectroscopy.

KEYWORDS: *Kupferschiefer, stream sediment, environmental pollution, source detection*

INTRODUCTION

Conventional stream sediment and heavy mineral sampling are common techniques in mineral and metal exploration that have led to the discovery of major ore deposits world-wide. In recent years, stream sediment sampling has developed into an essential tool for geochemical mapping, and is also used in Europe and Germany (Plant *et al.* 1997; Birke & Rauch 1993; 1997; Fauth *et al.* 1985), where exploration targets are more limited. In particular, in environmental monitoring, stream sediment sampling is gaining increasing importance. Central applications are in the assessment of regional contamination in rivers and lakes, in tracing the development and range of former mining activities, and in risk analysis to assess the potential remobilization of pollutants.

While based on similar sampling techniques and analytical procedures in exploration and in environmental monitoring, the sample processing can be different. Exploration and environmental surveys frequently apply incomplete digestion (aqua regia) of stream sediment, followed by ICP-AES and AAS analysis. X-ray fluorescence (XRF) analysis is applied when total contents are required. In addition, grain size plays a different role in both kinds of survey. In exploration and in geochemical mapping, the sampled sediment is coarse-grained and often includes the <180 µm (<80 mesh) fraction. FOREGS (Forum of European Geological Surveys) recommends that one collects <150 µm sediment samples for geochemical mapping (Salminen *et al.* 1998). In environmental monitoring in Germany, the preferred sediment fraction is <63 or even

<20 µm (BfG 1994). Given these differences, data obtained in exploration campaigns are not fully applicable to environmental monitoring. Consequently, many conclusions drawn from conventional geochemical exploration data about the environmental impact of contaminations are not suitable for the identification and tracing of the sources of pollution.

In view of these limitations, the major aims of our study were to develop effective tools to depict pollution by metals in rivers of a mining district, to determine the range of pollutant migration spreading from point sources of different origin, and to trace and detect unambiguously the sources of pollution by means of stream sediment analyses. One focal point was to differentiate geogenic from anthropogenic sources of pollution, a prerequisite for the proper planning of restoration measures. On the analytical side, the idea was to combine methods from three independent fields of research: conventional geochemistry, mineralogy and radiometry. The results of this study should contribute to a successful development of rehabilitation measures in a metal mining district after the cessation of mining and smelting.

The well-known Mansfeld mining district in central Germany was selected as the target area for research. Here, over an area of c. 750 km², mining and smelting of base metals and precious metals took place for almost 800 years. This region suffers from the legacy of mining, being characterized by numerous heaps made of radionuclide-containing mining and smelting waste, large-scale subsidence and salinization of the ground water even in densely populated areas, and metal contamination of soils and water.



Fig. 1. Location map of the study area.

STUDY AREA

Physiography

The Mansfeld mining district is situated in central Germany, east of the Harz Mountains and west of the town of Halle (Fig. 1). The local climate is characterized by a low precipitation rate (average 450 mm/a) and only a few, but heavy, rainfall events that cause torrential floods and an enormous redeposition of sediment. The rivers in the study area flow into the Saale and Elbe rivers, and finally into the North Sea.

Mining and smelting

Mining of 'Kupferschiefer', a bituminous marlstone of Permian age (average: 1.5% Cu; 1% Pb; 1% Zn), was carried out from the late twelfth century but ceased in 1990 for geological and economic reasons. Ore treatment was performed in two smelters close to Eisleben and produced matte ('copper stone': Cu, Ag, Au, Pt, Pd), slag and metalliferous flue dust. Both by-products, slag and flue dust, were used as secondary resources, the first for the production of cobblestones and the second to recover Zn, Pb, Sn, Re, Se, Ge, and Cd. However, after 1978, the reprocessing of metalliferous flue dust stopped and the

residue was stored in open basins on mining waste heaps (Matheis *et al.* 1999) in the surroundings of the smelters.

Environmental contamination in the mining district

The Mansfeld mining district is affected by extensive pollution. Soils close to the former smelters show significant metal enrichments in the upper 20 cm, attributed to the emission of fumes during ore smelting and to wind-drifted flue dust. The surface water chemistry is characterized by increased contents of sulphate and zinc, caused by the inflow of leachate from mining waste heaps (Strauch *et al.* 2001; Schubert *et al.* 2003). Water from abandoned adits shows extremely high contents of dissolved salt and metals, mainly Zn, Cu and Pb (Spilker *et al.* 1999). Sediment in the Mansfeld lakes contains up to 5% Zn, 0.5% Pb and 0.45% Cu, and has accumulated *c.* 4500 tons of Zn, 560 tons of Pb, and 500 tons of Cu during the last 50 years (Becker *et al.* 2001).

Different sources of metals were held responsible for this extensive contamination. One is outcropping Kupferschiefer ore, which occurs along the margins of the Mansfeld mining district (Fig. 2) and is subject to fluvial erosion. Another source for metals is waste from medieval and pre-industrial mining (wall rock, low-grade ores), piled up in *c.* 2000 heaps of different size and forming a belt almost 3 km in width, that follows the outcropping Kupferschiefer ore (Fig. 2). Some of these heaps, which are up to 30 m high, are situated along rivers (Fig. 3a), and pluvial and fluvial erosion of metalliferous particles may occur. A third type of potential source for metals is the smelting by-products, in particular slag and metalliferous flue dust. Slag heaps are of tabular shape and up to 50 m high (Fig. 3b), containing *c.* 50×10^6 tons of slag. A part of the slag is mined as a secondary resource, in particular for road construction. The flue dust has been stored in open basins on slag- and mining-waste heaps (Fig. 3c). In total, 450 000 tons of flue dust have been deposited at the sites of the former smelters, the major part of it in a 14–18 m deep basin, embedded in a flattened mine dump 25 m in height (Schreck 1997). Since these basins are not lined, flue dust may have infiltrated the heaps (Schubert *et al.* 2001). Flue dust consists of agglomerates of inorganic particles embedded in a matrix of various polyaromatics. Such agglomerates have a median diameter of only 1.25 μm , but range in size up to 100 μm . The inorganic particles, mainly complex solid solutions of Pb, Zn, Cu, and Fe sulphides, are of sub-micrometre size. Flue dust is easily leachable by water (Schreck 2001; Paschke *et al.* 2001). Metalliferous seepage water at the base of heaps, affected by the weathering of the flue dust, contains up to 2 g/l of zinc and *c.* 6 g/l of sulphate at neutral pH (Schreck & Glaesser 1998; Schubert *et al.* 2003).

Since the abandonment of mining in 1990, various rehabilitation concepts for the former smelters and several metallurgical facilities have been developed. However, to date, only

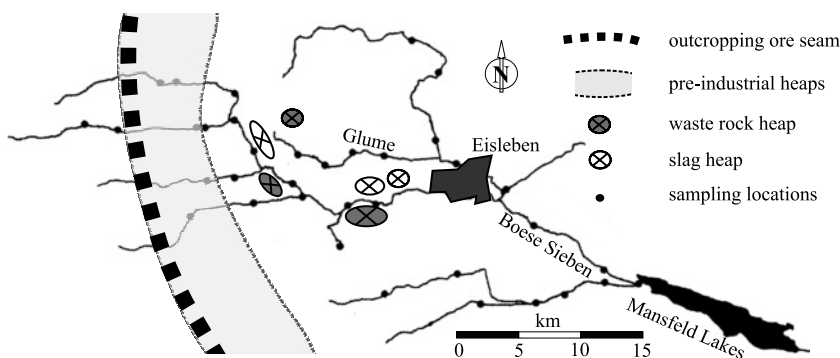


Fig. 2. Drainage system and major sources of pollution in the centre of the mining district.



Fig. 3. Mining and smelting waste: (a) low-grade ore heaps along a brook; (b) tabular slag heaps near Eisleben; (c) flue dust deposit, partly redeposited.

immediate measures have been implemented, while long-term concepts were left out of consideration. This development is due to budgetary constraints and is based on the prevailing opinion that most of the contaminating metals are of geogenic origin, in particular stemming from the erosion of the outcropping Kupferschiefer ore.

METHODS

Sampling

From summer 1998 to spring 1999, 116 stream sediment samples were collected from all rivers of the Mansfeld mining district. In the reconnaissance phase of the campaign, one sample per 3 km was taken, in the follow-up phase the intervals were reduced to one sample per kilometre. At each sampling site a distance of 20 m (10 m to a side) was marked and 5 to 10 subsamples were taken from the upper 10 cm of sediment accumulation with PVC shovels. All the samples were collected from sediment accumulations close to the river banks, preferably from the inner banks of the river bends. The subsamples of 5 to 10 kg were collected on a plastic pad, homogenized, reduced to 2 kg each, and placed into two PVC containers. One of these containers was for geochemical and mineralogical analyses, the second for gamma-spectroscopy. In early 2000, ten of the most contaminated sites were resampled, following the same procedure.

Sample preparation

All samples for geochemical and mineralogical analyses were kept for 48 hours at 60°C in a drying cabinet. About 500 g of each sample was dry- and wet-screened to separate the grain fractions >2 mm, 2 mm–630 µm, 630–200 µm, 200–63 µm, and <63 µm. Aliquots of these five fractions were ground down in an agate-lined ball mill for powder X-ray diffraction (XRD) and for XRF pellet preparation. Pellets for XRF analyses (trace elements) were manufactured by mixing 4 g of sample powder, 0.9 g of cellulose and then compressing the mix in a hydraulic press for 3 min at 300 MPa. XRF analyses for the major elements were carried out using a glassy melt, produced by borate fusion.

Samples for gamma-spectroscopy were made from the original sediment by drying and screening it to <250 µm, with subsequent storage in cylindrical capsules of 108 cm³.

Analytical methods

Bulk geochemistry. Total analyses (XRF) of stream sediment samples were required for estimating the range of pollutant migration. XRF analyses of both powder pellets and fusion pellets were carried out by a wavelength dispersive Siemens SRS

3000 spectrometer. The system has been calibrated using 20 different reference materials. Instrument precision (σ) is typically \approx 0.5% (0.2–1.1%) for major elements and 1.2% (0.4–2.9%) for the trace elements As, Co, Cr, Cu, Ni, Pb, Zn, and V. The detection limits for the major elements are \approx 0.01% and for the trace elements \approx 10 ppm. Duplicate analyses of samples from individual locations yielded variations in concentration of \approx 10% (1.8–21.9%) for the major elements and \approx 12.3% (0.2–24.6%) for the trace elements.

Mineralogy. Petrographical and mineralogical research included methods such as powder XRD analysis, optical microscopy in polarized and reflecting light, and electron microprobe analysis (EPMA) of separated grain fractions and mineral concentrates. For XRD analysis a Seifert diffractometer, model XRD 7, using Cu radiation, was employed. The detection limit for mineral phases is 5 vol%. For optical identification, mineral concentrates from different grain fractions of metalliferous sediment samples were obtained by Na-Polywolframate density separation ($\rho=2.75$ g/cm³). The mineral concentrates for microscopy were either embedded in Meltmount® or prepared as polished thin sections. EPMA was carried out on both kinds of samples using an ESMA SX 100 instrument from Cameca.

Gamma-spectroscopy. Activity measurements of sediment samples were carried out by low-level gamma-spectroscopy using coaxial low-energy HPGe detectors, n-type (ORTEC) with an active volume of 39 cm³ and 0.5 mm Be window. The detector and the measuring geometry were calibrated using certified reference material IAEA RGU-1. The solid samples were measured for about 12 h in a cylindrical capsule of 108 cm³. The mean standard deviation is 20% for ²³⁸U (²³⁴Th), 10% for ²²⁶Ra and 9% for ²¹⁰Pb.

RESULTS

Conventional geochemistry

The results of the conventional geochemical survey on stream sediment samples show that metals such as Fe, Ni, and Zn are very heterogeneously distributed over the mining district (Table 1). In agricultural areas, remote from any mining and smelting activities, this metal concentration is low and does not exceed the non-mining background values. In the centre of the mining district, around the former smelters and close to the historical mining and smelting sites, distinct enrichments of all metals in stream sediments were found. In particular, Fe, Cr, Ni, As and Zn are enriched downstream of the outcropping ore seam. In the neighbourhood of the smelters, where different sources are present in close proximity, As, Cu, Pb and Zn are anomalously accumulated in stream sediment. However, bulk chemistry

Table 1. Chemical analyses of stream sediment samples (trace elements) from different environments (mg/kg).

Sample	Environment	Fe	As	Cr	Cu	Ni	Pb	V	Zn
ML 69	Upstream ore seam	14827	9	57	201	20	214	052	397
ML 21	Downstream ore seam	39166	36	153	247	110	31	113	4427
ML 2	Downstream smelter 1	51406	487	121	198	0	567	128	6429
ML 15	Downstream smelter 2	28885	56	92	1054	56	1034	122	3796
ML 75	Agricultural area	18045	6	66	27	19	37	39	119
NMBG	Non-mining background	17462	4	65	38	26	54	48	165

Smelter 1=Helbra; smelter 2=Eisleben.

NMBG=non-mining background values calculated from nine stream sediment samples, collected in unpolluted river sections.

alone does not help to identify single sources of pollution, and additional methods have to be applied to resolve the picture in detail.

Another attempt to identify the sources of pollution was by comparing the chemical composition of the different grain size fractions in stream sediment samples (Table 2). In most of the samples two peaks in metal enrichment occurred: (1) the coarse-grained fraction of >630 µm and (2) the fine-grained fraction of <200 µm. Differing from this trend, samples taken downstream from a smelter show distinct metal enrichments only in the <200 µm fraction sample. The general trend in metal enrichment can be explained either by different metal sources (coarse-grained slag; fine-grained clay minerals) or by adding medium-grained, non-metalliferous sediment from surface erosion. However, close to the smelters, extremely fine-grained flue dust may become perceptible in stream sediment.

To trace the sources of pollution 'marker elements' were used, pointing to either flue dust, slag or the outcropping ore. For example, by comparing the chemical compositions of Kupferschiefer and metalliferous flue dust, one finds that flue dust is extremely enriched in volatile elements such as Sn, Bi, As, Sb and Tl (Fig. 4; Wennrich *et al.* 2001). These 'marker elements' are components of the smelter's flue gas and have been enriched in the flue dust by more than a factor of 50 compared to the crude ore. By detecting above-average concentrations of these 'marker elements' (mainly As) in stream sediment, it was possible to prove, at least semiquantitatively, that there was a portion of flue dust in metal contamination of several river sections (Table 3). However, more detailed information could not be obtained from the analytical data, because

many marker elements, in particular As, are extremely mobile under neutral to alkaline conditions (formation of arsenate ions), and co-precipitate with iron hydroxides. The crusts and coatings so-formed on mineral grains (see the following section) may well occur in river sections remote from the smelters.

Mineralogy and microchemistry

X-ray diffraction. Mineral identification and microchemical analyses of metalliferous grains in stream sediment open up further possibilities for source identification. The first task was to identify the metal-containing minerals. Bulk analyses of original stream sediment samples by XRD did not fully explain the sediment mineralogy (detection limit of 5%), displayed only light minerals such as quartz, calcite and feldspar, and were not able to quantify the amount of slag (mostly amorphous) in the samples, which make up to 30 vol% of the sediment in some river sections. After heavy mineral concentration by density separation, which included all the slag particles, XRD was successful in detecting pyroxenes, a constituent part of crystalline slag, hematite, goethite, mica and dolomite. However, no primary minerals from the Kupferschiefer ore could be found.

Optical microscopy and EPMA analysis. By means of optical microscopy it was shown that slag particles contain sulphidic inclusions ('droplets'), similar to chalcopyrite. These inclusions are a product of an incomplete segregation of slag and matte in the blast furnace and make up 1% of the slag volume. In reflected light, grains of covellite, a primary ore mineral, were identified. Other opaque minerals such as ilmenite or

Table 2. Trace element concentration in different grain size fractions of stream sediments (mg/kg).

Sample	Environment	Fraction	Fe	As	Pb	Cu	Zn
2	Historical smelting	>2 mm	17 485	9	776	1617	1756
		2 mm–630 µm	18 045	9	634	1257	1594
		630 µm–200 µm	14 198	0	619	911	1336
		200 µm–63 µm	14 967	0	671	1071	1672
		<63 µm	19 513	2	811	1233	1868
5	Downstream smelter 1	>2 mm	40 985	105	122	125	2548
		2 mm–630 µm	43 922	130	279	102	4147
		630 µm–200 µm	40 355	162	389	200	5677
		200 µm–63 µm	33 501	187	649	298	5348
		>2 mm	26 927	23	160	400	2077
7	Total drain mining district	2 mm–630 µm	14 617	8	268	564	1608
		630 µm–200 µm	8 183	12	100	299	902
		200 µm–63 µm	13 359	9	263	391	1310
		<63 µm	24 059	28	224	572	2431

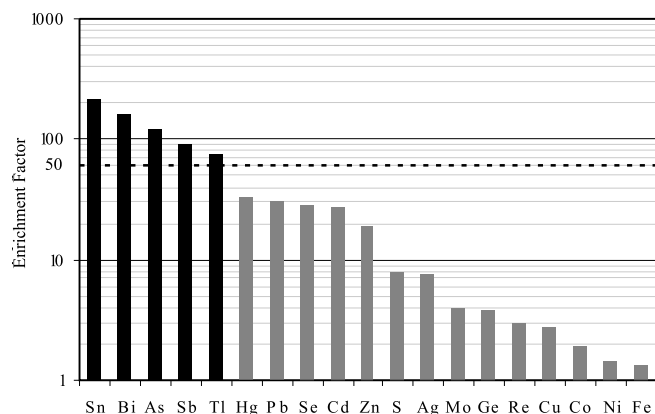


Fig. 4. Element enrichment factors in flue dust (fresh) versus Kupferschiefer. Marker elements for flue dust displayed in black. Data from Jahn *et al.* (1997) and Wennrich *et al.* (2001).

hematite are thought to be detritus from the erosion of the non-mineralized bed rock.

The most powerful tool in mineral identification is EPMA analysis. Three different kinds of metalliferous particles were detected in the sediment samples and analysed in detail: primary Kupferschiefer ore minerals; smelting products and aquatic precipitates; and agglomerates of secondary origin. Primary ore minerals, 50 to 100 μm in diameter, are covellite (Fig. 5a), chalcopyrite and sphalerite. Ore smelting contributed slag from different technical processes (blast furnace slag, converter slag; Fig. 5b), fragments of furnace refractories, and metalliferous

flue dust. The slag particles range in grain size from $\approx 200 \mu\text{m}$ to more than 2 mm. Single flue dust particles are of sub-micrometre size and form agglomerates of 1–100 μm in diameter. Finally, precipitates of iron hydroxides (Fig. 5c), containing Zn, Pb, Mn, As, P and Si, and metalliferous coatings (Fe, Mn) on mineral grains, have been detected. These very fine-grained precipitates form by the mixing of river water with Fe-rich leachates from weathering. EPMA analysis of sphalerite grains in stream sediment contributed to understanding their provenance. Sphalerite from Kupferschiefer ore is made up of almost pure ZnS , while sphalerite from flue dust includes Fe, Pb and Cu, pointing to high-temperature mineral formation during smelting.

Gamma-spectroscopy

The third method applied was gamma-spectroscopy. This method is based on the fact that all the potential source materials for metals contain radionuclides, but show a different status in radioactive disequilibrium. This feature can be used as a marker for source detection in stream sediment. In unprocessed rock, including low-grade ore, ^{238}U , ^{226}Ra and ^{210}Pb are in radioactive equilibrium. Ore smelting leads to a shift in radionuclide distribution and causes an enrichment of U and Ra in the slag, while flue dust is extremely enriched in radioactive Pb (Table 4). The average activities and key radionuclide distribution patterns ($^{238}\text{U}/^{226}\text{Ra}/^{210}\text{Pb}$ in Bq/kg) in Kupferschiefer are 451 Bq/kg (150/167/134), in copper slag 1621 Bq/kg (651/770/200), and in flue dust 8593 Bq/kg (192/196/8205) with peaks up to 23 kBq/kg. Hence, gamma-spectroscopy is a source of information on the share of low-grade ore, slag and flue dust in stream sediment.

When plotting the radionuclide activities of all analysed stream sediment samples in a normalized triangular diagram with $^{238}\text{U} + ^{226}\text{Ra} + ^{210}\text{Pb} = 100\%$, the values are arranged in three different fields (Fig. 6). The majority of the samples display radioactive equilibrium and fall into the field of 'low-grade ore'; $\approx 10\%$ of the samples are dominated by slag; and another 14% are influenced by flue dust. These results imply that low-grade ore is present in $\approx 75\%$ of all analysed samples and so can be regarded as a major source for metals in stream sediments.

DISCUSSION

Stream sediment sampling and analyses may lead to incorrect interpretations when the riverine dynamics, including precipitation and discharge, are not taken into consideration. Ideally, a constant input and transport of pollutants is required for source detection. In the Mansfeld region, stream sediment accumulates for several months in areas of low turbulence in rivers and is then flushed downstream by torrential floods that occur five to

Table 3. Marker elements (in bold type) for Kupferschiefer, slag, and flue dust (mg/kg).

Element	Kupferschiefer ^a	Slag ^a	Flue dust (fresh) ^b	Flue dust (weathered) ^a
Fe	9337	13 708	12 700	14 722
Mn	1461	2340	930	938
Cr	<4	233	130	201
Cu	4763	1636	13 200	10 117
Pb	4713	172	143 000	95 772
Zn	10 151	2788	193 000	83 182
Cd	52	1	435	451
As	27	3	3800	6674
Sb	16	10	1470	2050
Bi	1	<1	165	212
Sn	54	68	11 600	7672
Tl	3	<2.5	n.a.	137

n.a., not analysed.

^{aa} Data from Jahn *et al.* 1997 (XRF).

^{bb} Data from Wennrich *et al.* 2001 (XRF, ICP-AES).

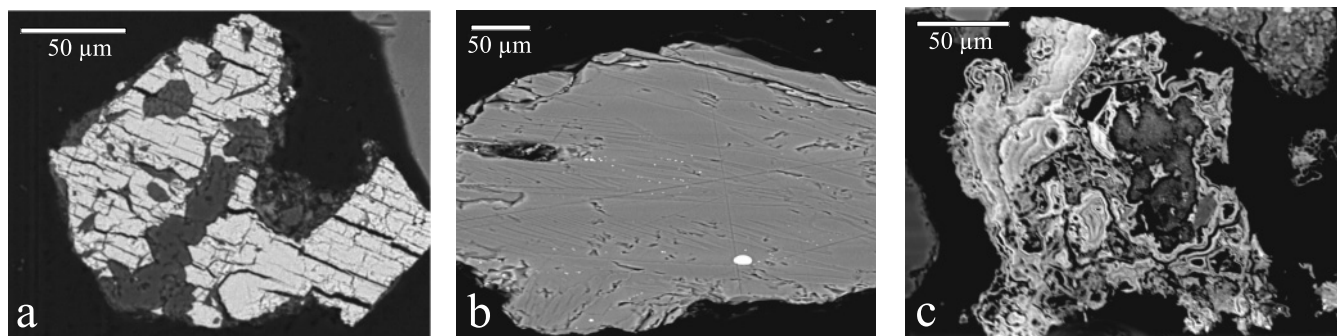


Fig. 5. Metalliferous particles in stream sediment: (a) detrital covellite (CuS); (b) recrystallized slag with inclusions of matte (white); (c) concretionary precipitate of Fe-hydroxides, containing heavy metals.

Table 4. Total radioactivity and radionuclide distribution of the source material and in selected stream sediment samples.

Source material / sample	Total radioactivity (Bq/kg)	^{238}U (Bq/kg)	^{226}Ra (Bq/kg)	^{210}Pb (Bq/kg)	Provenance
Low grade ore (n=3)	451	150	167	134	
Slag (n=3)	1621	651	770	200	
Flue dust (n=6)	8593	192	196	8205	
ML 1	258	47	58	153	F
ML 4	73	34	16	23	L
ML 14	408	157	159	92	S
ML 15	423	151	154	118	S
ML 19	537	198	203	136	S
ML 21	100	42	32	26	L
ML 28	206	48	31	127	F
ML 35	110	42	37	31	L
ML 38	504	85	91	328	F
ML 53	92	30	37	25	L

Provenance: L=low grade ore; S=slag; F=flue dust.

ten times a year (Schreck 2001). Consequently, the sediment from different river sections is repeatedly mixed, is much less sorted by grain size and density than under more continuous discharge conditions, and is affected by all available metal sources of the river catchment area. Nevertheless, source detection is still possible but is less reliable than under more continuous discharge conditions.

This study has shown that one can distinguish between most of the different metal sources by combining geochemical, mineralogical and radiometric methods. Gamma-spectroscopy gives the first quantitative results on the fractions of the different source materials in stream sediment. Furthermore, gamma-spectroscopy provided information on the range of pollutant migration in the mining district. Stream sediment with above-average contents in ^{210}Pb (radioactive disequilibrium) was found over a distance of ≈ 15 km downstream of the smelters, reaching as far as the Mansfeld lakes (Fig. 2) and was even detected in lake sediment. At several adit openings, up to 30 km from the mines, sediment with enrichments in ^{210}Pb occurs, pointing to the improper disposal of flue dust in abandoned mining galleries, which were flooded after the cessation of mining.

Sediment mineralogy and geochemistry revealed that metal-liferous particles from all available sources contribute to the pollution of the rivers in the mining district. In particular, the anthropogenic input seems to be highly significant for the metal load of stream sediment. The results did not allow a precise

quantification of the fractions of metals in stream sediment from geogenic and from anthropogenic sources. However, preliminary evaluation concerning the environmental impact of these sources can be given. Slag contains $\approx 1\%$ of metal sulphides but is, at least in the short term, of no significance to the environment because the sulphidic minerals are embedded in a glassy matrix, resistant to weathering under neutral to moderate alkaline conditions.

The fractions of outcropping Kupferschiefer and low-grade ore (mining waste) in stream sediment are difficult to distinguish. Both materials are similar in geochemistry, mineralogy and in radionuclide distribution. By comparing the local occurrence of both source materials in the mining district, an evaluation of their possible environmental impacts was made. Outcropping Kupferschiefer ore, 20–40 cm thick, occurs at the western margin of the mining district (Fig. 2) and is eroded by four partly drained rivulets in a totally vegetated environment. These rivulets are dry during the summer season. The total surface of the ore seam available for fluvial erosion is 200 m². Low-grade ore from pre-industrial mining is piled in three major heaps situated directly along the streams. These heaps are 150–800 m long and up to 30 m high, the slope angle is $\approx 60^\circ$ (Fig. 3a). The surface of just these three heaps that is available for pluvial erosion is 40 000 m², which is a factor 200-times larger than the surface of the outcropping Kupferschiefer. Thus, the Kupferschiefer plays only a minor role as a source of pollutants.

Stream sediment, which contains residues from ore smelting, shows element contents that cannot be derived from the local ore but that may serve as marker elements for industrial metal discharge. One example for such an ‘external’ element is Sn in smelting waste from the Mansfeld mining district, which is clearly enriched in flue dust (Fig. 4). In this case, Sn was a component of scrap from the electronics industry (solder), which was processed as a secondary resource for Cu. Another ground for ‘external’ elements being found in smelting waste is from the processing of imported ores of different types.

CONCLUSIONS

By combining three different, independent methods of stream sediment analysis, it was possible to unambiguously determine the sources of metal pollution in the Mansfeld mining district and to estimate their significance for the environment. In decreasing order of importance, these sources are: (1) low-grade ore from mining; (2) metalliferous flue dust and slag from smelting; and (3) outcropping Kupferschiefer ore. Conventional

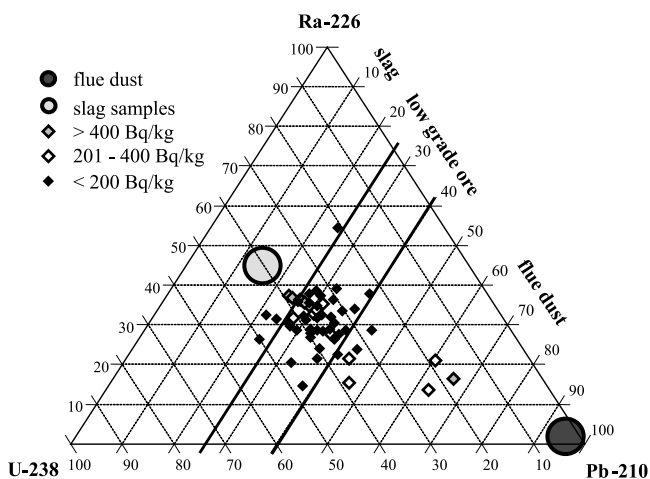


Fig. 6. Triangular plot of radionuclide ratios in stream sediment samples and in source material.

geochemistry provided information on the lateral extent of contamination in the rivers of the mining district and helped to derive marker elements that pointed to the source materials. Mineralogy and microchemistry added data on the composition of the ore minerals and their formation, and contributed to allow differentiation of mining waste from pyrometallurgic waste products. Finally, the fractions of these sources in environmental pollution were estimated quantitatively by gamma-spectroscopy.

The range of pollutant migration from the different source materials over the mining district varies considerably. Emissions of flue dust are restricted to the area of the former smelters and flue dust deposits, and could not be tracked for more than 15 km downstream (exception: adits). Particles from low-grade ore and slag have spread all over the region and could be identified in stream sediment samples at the mouth of the rivers, even 30 km away from their source. Such pollutants include particles from mining waste (slag and low-grade ore) that were used as a secondary resource for constructional purposes.

The results of this study are of importance for the redevelopment of the former mining district. Early rehabilitation concepts were based on the assumption that most of the metals in the region are of geogenic origin and only emergency measures have to be taken to contain mining and smelting residues. More recent concepts are focused on the covering and sealing of contaminated industrial areas. Identification of widespread distribution of anthropogenic contaminants by the methods described here makes it clear that these measures alone will not stop the steady release, by natural erosion, of metals from the pre-industrial heaps. A first step in the right direction would be to flatten the steep slopes of the heaps, to plant the heaps with vegetation and to avoid any secondary mining of heap material for construction.

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