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Heavy Metal Pollution Downstream of Old Mining Camps as a Result of Flood Events: an Example from the Mulde River System, Eastern Part of Germany

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ABSTRACT

Floods occurring as a consequence of very heavy rainfall in the southeastern part of Germany resulted in the erosion of waste dumps and tailings along the Mulde river system. Components derived from these sources, e.g., slags and charcoal, can clearly be recognized downstream in the flood sediments. As a consequence, the flood sediments contain in part extreme concentrations of heavy metals (up to 14,000 ppm Pb), As (up to 8,000 ppm), and U (up to 47 ppm) in the clay fraction. However, due to the origin of the contaminants, coarser grain fractions likewise contain extreme, though generally lower, concentrations of toxic elements. Initial leaching experiments show, that the toxic elements are readily leached from both, the clay fraction and from coarser fraction. Hence flood sediments contaminated by material derived from waste dumps and tailings constitute a considerable risk for land use.

(Key words: Flood events, Tailings, Environmental geochemistry, Toxic elements, Pb, Cd, As, U)

1. INTRODUCTION

One of the predicted consequences of the global climate change is the increased occurrence of heavy rainfall and resulting flood events in particular in the temperate area of the earth (e.g., Easterling et al. 2000). Such floods may lead to significant erosion and hence

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mobilization and redistribution of large amounts of material within the affected areas. Where erosion affects the remains of mining activity (tailings, waste dumps) or river sediments polluted by such activity, heavy metals (as well as As, U) pollution may be spread over large areas. In this way, the effects of flood events resemble failure of tailing ponds, though in the latter case, the contamination is usually more intense, but also more restricted to the immediate vicinity of the riverbed. The areal restriction of the effects of flood events to river beds and adjacent lowlands distinguishes the environmental affects from those brought about for example by volcanism, where ash fall affects much larger areas (e.g., Andal et al. 2005).

These processes of redistribution of contaminated materials could be studied in detail after the August 2002 floods that affected the catchment area of the river Elbe and its tributaries in the Czech Republic and in the eastern part of Germany. The Mulde river system, which comprises the Freiberger Mulde and the Zwickauer Mulde, which join downstream to form the Vereinigte Mulde ('United Mulde'), drains the area of several former mining camps. As the release of heavy metals and, in particular, As (Freiberger Mulde) and U (Zwickauer Mulde) from tailings, waste dumps and from mines (acid mine drainage) had been studied in the years 1991-1993 (Beuge et al. 1999), a baseline existed against which the changes resulting from the flood events could be evaluated. These earlier studies have indicated heavy pollution of the Mulde river system waters and river sediments at that time. Furthermore, it was predicted that flood events would remobilise pollutants already contained in river sediments.

In the following paragraphs, we will briefly present some results of a study, carried out in the aftermath after the August 2002 floods to address the following questions:
* What is the composition of the flood sediments?
* What are the main sources of the contaminants?
* How quickly will pre-flood conditions be re-established?
* Are there any lessons to be learned that can be generalized?

In the present contribution we will focus largely on the flood sediments; details of the subsequent changes in river sediment composition and water compositions will be presented elsewhere. In addition, we cannot at this stage answer the question concerning the reestablishment of pre-flood conditions (work in progress: Klemm et al. 2004; Broekaert et al. 2004). A discussion of the local implications of the data is beyond the scope of this paper.

2. THE MULDE RIVER SYSTEM

The Mulde river system is one of the main tributaries of the Elbe River. Its catchment area covers the gentle northern slopes of the Erzgebirge (Ore Mountains), which to the south steeply decents into the Eger Graben. The Freiberger Mulde originates at an elevation of 825 m above sea level and has a length of 124 km before joining the Zwickauer Mulde to form the Vereinigte Mulde ('United Mulde') at an elevation of 137 m corresponding to a gradient of 5.5 per mil. The source of the Zwickauer Mulde is located at 759 m above sea level and the river has a length of 166 km. Hence its is shallower, i.e., the gradient is 4 per mil. The Vereinigte Mulde has a length of 121 km at which point it flows into the Elbe River at 56 m above sea level. The gradient of the Vereinigte Mulde is only 0.7 per mil (Fig. 1).

The catchment areas of the Freiberger, Zwickauer, and Vereinigte Mulde, respectively, cover about 3000, 2400, and 2100 km^2. The upper reaches of Freiberger and Zwickauer Mulde are characterized by high rates of precipitation (800 - 1100 mm yr^{-1}), whereas at the confluence of these rivers, the precipitation is on average less than 600 mm (data compiled from various sources by Beuge et al. 1999).

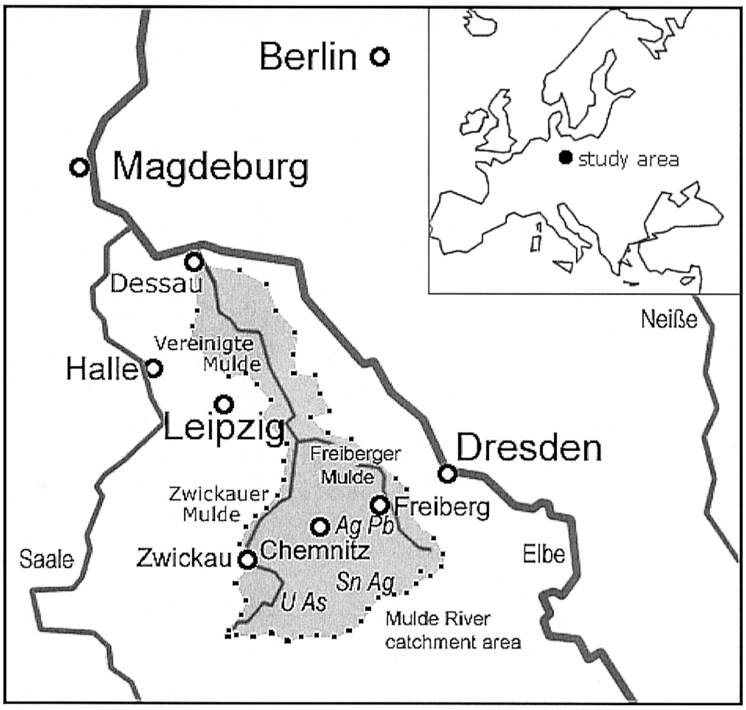

Fig. 1. Map of the study area, inset shows the location of the area within Europe.

3. GEOLOGIC SETTING OF THE CATCHMENT AREA

The Mulde rivers drain an area of about 7600 km^2 covering part of the northern slopes of the Ore Mountains (Erzgebirge) in the south and the plains of the Northern Saxony Lowlands to the south. The catchment areas of the Mulde rivers are underlain by different lithologies that host different types of mineralization.

The catchment area of the Freiberger Mulde, covering the south-eastern part of the study area, is largely underlain by gneisses and less abundant mica schists and granulites that host vein-type Pb-Zn-Ag mineralization in the Freiberg area and Sn-W-mineralization (greisens) along tributaries. A significant minor element in all these mineralizations is As, whereas the host rocks appear to be depleted in this element. Another element associated with all types of mineralzation is Cd. Some of these mineralizations have been mined more or less continuously for about 800 years (e.g., Beuge et al. 1999, Baacke et al. 1999).

The catchment area of the Zwickauer Mulde occupies the south-western part of the study area. It is underlain largely by phyllites, mica schists, as well as some granite, gneiss and Permian sediments (red sandstone). These rocks host widely distributed, very low-grade Sn mineralization and significant Bi-Co-Ni-U-Ag mineralization, that has been the target of extensive mining in the Aue-Schneeberg area (Hösel et al. 1997).

The catchment area of the Vereinigte Mulde, which comprises the northern part of the study area, is mostly underlain by Cenozoic sediments largely devoid of mineralzation.

The presence of abundant and diverse mineralizations in the catchment area of the Mulde river system has lead to a natural enrichment of toxic elements (heavy metals, Cd and As) in both soils and river sediments. This contamination was augmented since the early days of mining (e.g., Baacke et al. 1999) due to the influx of elements released from mine workings, waste dumps and tailing.

4. THE AUGUST 2002 FLOODS

In the area studied, the floods started on August 12, 2002 after heavy rainfalls during the night. In the Freiberg area, precipitation was about 200 - 250 mm within 24 hours and higher values, up to 312 mm, were observed at higher elevations. The highest tide was reached in the night of August 13th and lasted for several hours. After another 24 hours, on August 14, it was just a 'normal' flood, as occurs occasionally during the snow melting.

Within the catchment area of the Mulde river system, large areas were flooded, in particular in the catchment area of the Vereinigte Mulde (10800 ha) and to lesser extends in the catchment areas of the Freiberger Mulde (4600 ha) and the Zwickauer Mulde (2300 ha) (LFUG 2003). The flooded areas largely comprise agricultural land, both arable land and pasture, hence deposition of contaminated sediments could be of consequence for land use.

5. FLOOD SEDIMENTS

Flood sediments were collected between September 25 and October 16, 2002, i.e., between 6 and 10 weeks after the flood event. Sediments were collected close to sampling locations selected for the 1991 - 93 study. At the same time, river sediment and water samples were taken at the locations sampled in 1991 - 1993 (some results are already published by Klemm et al. 2003). All investigations were restricted to gain fractions < 20 μm and < 2 mm to obtain results compatible with those obtained by other groups studying the same flood event. It should be noted, that studies of river sediments typically are restricted to the analysis of sediment fractions < 20 μm as that fraction is considered to contain most contaminants (e.g., Müller 1999). In Table 1, the results of the grain size analysis of a few selected samples are given. These data suggest that neither the clay fraction nor the coarse fraction is abundant in the samples. The lack of large amounts of the clay fraction probably reflects the high energy regime prevailing during sediment deposition.

5.1 Mineralogy

The mineralogical composition of the grain fractions < 20 μm and 0.02 - 2.0 mm were determined by quantitatively XRD using methods outlined by Kleeberg and Bergmann (2002). The fraction < 20 μm was obtained by dry sieving and is an aliquot of the sample used for chemical analysis. In contrast, the fraction 0.02 - 2.0 mm was obtained by wet sieving of an aliquot of the < 2 mm fraction used for the chemical analysis. Hence, the fraction 0.02 - 2.0 mm used for XRD analysis does not correspond to the fraction < 2 mm used in the chemical analyses. This allowed to determine the composition of the coarser fraction more precisely where the samples contained larger amounts of very fine grained sediment (for example in sample FM03, Table 1). Furthermore, a significant amount of the organic material (lighter than water) was removed by this procedure.

Table 1. Results of the grain size analysis of selected samples (wet sieving).

Sample	1-2 mm [%]	0.2-1 mm [%]	0.02-0.2 mm [%]	<0.02 mm [%]
FM 19 BE	14	47	28	11
FM 17 HI	2	53	43	2
FM 10 RÄ	3	40	48	8
FM 03 WK	2	11	18	70
ZM 13 CR	1	54	45	1
ZM 19 KE	3	78	14	4

Since previous work had shown the Mulde river sediments to contain significant amounts of X-ray-amorphous material, e.g., glassy slags, Fe-hydroxides and organic material (charcoal), 10% of ZnO were added to all samples as internal standard. This procedure allows to determine the amounts of X-ray-amorphous material as the difference between the sum of the minerals and 100%.

The investigated flood sediments of the Freiberger Mulde exhibit significant compositional variation both between sampling stations and between grain size fractions (Table 2). In general, the fine grained fractions contain more x-ray-amorphous material (21 - 36%) than the coarse fractions (17 - 30%, excluding one sample). Microscopic studies showed that the x-ray-amorphous substances are mostly glassy slags. These slags vary in colour (mostly black, occasionally blue) and vesicularity, suggesting multiple sources.

The most abundant mineral is quartz (25 - 38% in the fraction < 20 μm and 20 - 55% in the fraction 0.02 - 2 mm). Other minerals found in all samples are plagioclase, orthoclase, muscovite, chlorite, and rutile. Kaolinite is present in the clay fractions of all samples but is usually absent in the coarser fractions. Its low abundance in the clay fractions (3 - 7%) and the low abundance of the < 20 μm fraction in the < 2 mm fraction of the samples (1 - 11% with

Table 2. Selected mineralogical data for the flood sediments as determined by quantitative XRD [Rietveld method, Kleeberg and Bergmann (2002)] (2σ errors in bracket below the data).

Sample (river km)	amorph.	quartz	plagiocl.	orthocl.	muscov.	illite	chlorite	biotite	hematite	rutile	kaolinite	others
Freiberger Mulde												
FM19 (<20 μm)	33.3	30.4	7.8	6.2	8.0	-	6.7	-	-	1.1	4.5	2.1[1)]
34.4 km	(2.3)	(1.0)	(0.8)	(0.7)	(0.9)	-	(0.9)	-	-	(0.3)	(0.9)	(0.5)
(0.02-2 mm)	17.4	43.5	12.8	14.3	8.0	-	3.8	-	-	0.2	-	-
	(3.0)	(1.3)	(1.1)	(2.0)	(1.0)	-	(0.8)	-	-	(0.2)	-	-
FM17A (<20 μm)	31.7	29.3	6.8	9.0	9.0	4.5	4.7	-	1.4	0.6	3.1	-
42.5 km	(2.5)	(1.0)	(0.8)	(1.3)	(1.0)	(1.0)	(1.1)	-	(0.3)	(0.3)	(0.8)	-
(0.02-2 mm)	20.2	55.4	5.7	8.0	3.8	-	1.8	0.2	-	-	-	5.0[1)]
	(2.1)	(1.2)	(0.6)	(1.3)	(0.7)	-	(0.7)	(0.3)	-	-	-	(0.4)
FM10 (<20 μm)	25.8	37.7	5.6	8.9	9.7	4.9	3.1	-	1.1[4)]	0.7	1.6	2.0[2)]
71.5 km	(2.8)	(1.1)	(1.0)	(1.2)	(0.9)	(0.9)	(1.0)	-	(0.2)	(0.3)	(0.9)	(0.8)
(0.02-2 mm)	30.2	31.7	7.6	7.2	11.9	-	5.4	-	-	0.8	-	3.5[2)]
	(2.4)	(1.0)	(0.7)	(1.1)	(0.9)	-	(0.9)	-	-	(0.2)	-	(1.1)
FM03 (<20 μm)	35.9	25.3	6.5	6.9	13.6	-	6.3	-	-	0.9	4.5	-
105.7 km	(2.3)	(1.0)	(0.8)	(1.2)	(1.0)	-	(1.0)	-	-	(0.3)	(0.9)	-
(0.02-2 mm)	40.4	20.8	5.6	6.2	14.2	-	6.5	-	-	0.9	5.6	-
	(2.2)	(0.9)	(0.8)	(1.1)	(0.9)	-	(1.0)	-	-	(0.2)	(0.9)	-
Zwickauer Mulde												
ZM19 (<20 μm)	23.7	29.6	5.5	6.9	20.3	-	6.4	1.2	0.8	0.9	4.7	-
109 km	(2.5)	(1.0)	(0.8)	(1.0)	(1.1)	-	(1.0)	(0.6)	(0.3)	(0.3)	(0.9)	-
(0.02-2 mm)	11.8	52.3	8.1	12.5	8.8	-	3.8	-	-	0.4	2.5	-
	(2.8)	(1.5)	(1.1)	(1.3)	(1.1)	-	(0.9)	-	-	(0.3)	(0.8)	-
ZM13 (<20 μm)	22.5	32.2	7.8	6.9	19.3	-	5.1	-	0.8	1.1	-	-
87.5 km	(2.7)	(1.1)	(0.8)	(1.4)	(1.2)	-	(1.0)	-	(0.3)	(0.3)	-	-
(0.02-2 mm)	16.9	41.2	8.6	12.1	13.0	-	3.6	(2.1)	-	0.3	2.2	-
	(2.9)	(1.2)	(0.9)	(1.1)	(1.4)	-	(1.1)	(0.7)	-	(0.3)	(1.1)	-
Vereinigte Mulde												
VM02 (<20 μm)	27.7	36.7	6.4	8.8	11.3	1.8	4.0	-	0.5	0.6	3.1	-
	(2.5)	(1.1)	(0.8)	(0.9)	(0.9)	(0.8)	(0.9)	-	(0.3)	(0.3)	(0.9)	-
(0.02-2 mm)	19.4	49.2	7.2	11.2	7.2	-	3.4	-	-	0.3	2.2	-
	(2.5)	(1.2)	(0.9)	(1.3)	(0.9)	-	(0.8)	-	-	(0.2)	(1.0)	-

[1)] calcite [2)] kyanite

amorph. = amorphous material, plagiocl. = plagioclase, othocl. = K-feldspar (mostly orthoclase), muscov. = muscovite one exception) reflects the high energy regime during the transport and deposition of the flood sediments. Only in one sample, taken close to the confluence of Freiberger and Zwickauer Mulde, both grain fractions studied have almost identical compositions. The microscopic study of this sample reveals, that the coarser grains are composed of smaller grains, i.e., they are indurated river sediments, hence their similar mineralogical and chemical composition (see below).

Only two samples from the Zwickauer Mulde were analysed by XRD. Both samples are rather similar and the main difference between these samples and those of the Freiberger Mulde are a higher muscovite contents in the former (ca. 20% vs. < 13%). In all, they appear to contain less amorphous material and less quartz (Table 2).

A comparison of these results with those of previous studies is not straightforward, because during the campaign in the nineties only river sediments with the grain fraction < 20 μm had been investigated (Beuge et al. 1999). It is however notable, that the flood sediments contain about twice as much quartz as the river sediments studied in 1991 - 1993 (25 - 38% versus ca. 15%). Plagioclase and orthoclase have about the same abundance in both types of samples (6 - 9%) whereas illite, composing 26 - 36 of the clay fraction of the river sediments is subordinate or absent in the clay fraction of the flood sediments. These differences indicate that the flood sediments are dominated to a larger extent by detritical components and components of anthropogenic origin, whereas the river sediments studied in 1991 - 1993 are dominated by minerals formed in the sedimentary cycle (in particular illite). In addition, the differences suggest that the flood sediments are not simple reworked river sediments, but contain at least an additional component.

5.2 Geochemistry

The chemical composition of the grain fractions < 20 μm and < 2 mm are given in Table 3 (note that the fraction < 2 mm also includes the fraction < 20 μm, which however is < 12 weight % in most samples, except for FM03, where the fraction < 20 μm makes up 70% of the sample, see Table 1).

The composition of the flood sediments along the rivers is shown for selected elements in Figs. 2, 3. The first two samples (km 34.4) taken along the Freiberger Mulde represent largely uncontaminated sediments upstream of the mining and smelting places of Muldenhütten and Freiberg. As river sediments taken upstream in 1991 - 1993 showed variable and generally increasing values downstream it is suggested that even our first two samples do not really represent completely uncontaminated samples.

Almost all elements analysed show a dramatic increase at the next station (km 42.5). Exceptions are Co, Cr and Ni which exhibit largely constant values along the whole river (10 - 34 ppm Co, 35 - 75 ppm Cr, 17 - 58 ppm Ni). The element concentrations of As, Sb, Sn and Pb increase 35 to 75 fold, concentrations of Cd, Cu and Tl increase by one magnitude. The reason for this is the erosion of dumps of the smelters at Muldenhütten. The effect of erosion of the old dumps can be seen in the field as well as in the microscopic study of the flood sediments.

Downstream, the metal concentrations decrease relatively rapidly though they never fall

Table 3. Chemical composition of the flood sediments (concentrations in ppm).

Sample	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Sn	Tl	U	Zn
Freiberger Mulde																
FM 19 <20 µm	2.0	150	3.9	13	52	75	34200	0.5	888	28	335	6.7	14	0.5	3.6	456
FM 19 <2 mm	1.4	102	2.7	10	35	48	26000	<0.25	737	19	229	4.2	<10	0.4	2.4	305
FM 19A <20 µm	1.3	159	6.2	17	41	115	37700	0.9	1330	25	418	5.8	10	0.5	3.0	838
FM 19A <2 mm	0.8	114	4.7	15	26	68	31300	<0.25	1040	17	232	3.7	<10	0.3	1.8	549
FM 17 <20 µm	30.6	8360	73.6	27	45	963	78600	2.8	959	63	14400	485	580	6.9	9.4	3400
FM 17 <2 mm	19.6	4080	47.2	34	28	813	78300	2.7	831	55	7120	337	518	3.8	5.4	3270
FM 17A <20 µm	12.2	2840	48.8	21	52	509	54100	3.6	1100	47	6800	234	222	2.9	6.4	2540
FM 17A <2 mm	12.7	1820	40.5	23	47	739	45000	3.4	910	48	5090	168	213	2.1	4.9	2250
FM 16 <20 µm	17.4	2440	43.1	22	45	711	70500	1.5	1470	39	4720	97	168	2.0	7.2	3460
FM 16 <2 mm	8.8	1230	24.8	12	24	421	32600	0.6	846	20	2260	37.9	77	1.0	3.4	2330
FM 15 <20 µm	29.3	2960	32.6	22	44	736	59700	6.4	1180	46	7370	157	202	2.4	10.0	3580
FM 15 <2 mm	18.9	1610	26.7	17	36	564	42400	6.8	964	29	3840	79	100	2.1	7.5	2920
FM 15A <20 µm	29.1	2530	30.0	19	41	718	70600	6.3	1390	34	6160	101	135	2.4	8.8	2920
FM 15A <2 mm	16.4	1530	27.7	15	30	507	40400	3.7	931	23	3760	68.4	101	2.0	5.7	3060
FM 14 <20 µm	31.3	2910	29.3	22	48	744	73000	11.0	1500	41	6900	132	196	2.5	9.8	3290
FM 14 <2 mm	15.9	1340	19.8	15	31	442	39400	5.4	1040	24	3240	62	73	1.6	5.1	2300
FM 11 <20 µm	21.8	1440	19.9	16	53	362	40500	3.2	1350	36	3370	53	72	1.8	5.8	1840
FM 11 <2 mm	19.0	979	17.2	13	44	313	32100	2.7	1140	29	2170	39	45	2.0	4.1	1600
FM 10 <20 µm	28.4	1730	22.9	19	56	427	56800	4.9	1560	39	3510	64	86	2.4	5.9	2040
FM 10 <2 mm	12.9	751	12.3	12	34	229	26500	1.5	834	23	1450	29	30	1.4	2.5	1160
FM 06 <20 µm	22.1	1190	22.3	16	57	320	36500	3.2	1280	41	2470	54	55	1.6	5.3	1690
FM 06 <2 mm	17.4	969	18.8	15	60	282	33800	2.8	1260	39	1990	42	44	1.9	4.0	1720
FM 03 <20 µm	6.1	431	13.0	23	77	196	40100	1.4	1300	64	738	13	35	0.9	8.8	1120
FM 03 <2 mm	6.6	396	14.2	22	75	196	38100	1.3	1360	58	685	12	31	1.0	8.8	1060
FM 3A <20 µm	7.7	443	11.2	15	57	144	39100	1.2	946	43	786	17	26	0.9	5.4	966
FM 3A <2 mm	7.2	384	11.4	14	57	140	28700	1.2	1050	40	732	16	21	0.9	4.9	903
FM 01 <20 µm	7.1	430	8.4	13	41	134	25600	1.3	916	33	886	15	24	0.6	3.7	963
FM 01 <2 mm	8.0	370	9.7	13	43	136	25900	1.2	932	32	784	14	21	0.9	3.6	939
Zwickauer Mulde																
ZM 05 <20 µm	0.5	164	1.6	21	23	78	31400	0.6	1650	26	135	5.8	43	1.6	34.4	171
ZM 05 <2 mm	0.2	65	1.6	11	12	39	20000	<0.25	1090	13	49	2.1	25	1.7	13.4	105
ZM 81 <20 µm	1.5	245	3.7	36	49	150	60900	0.8	1510	119	197	10.0	43	1.1	25.2	507
ZM 81 <2 mm	1.0	169	2.9	30	41	132	38700	1.0	1340	111	125	6.2	32	1.2	19.8	410
ZM 13 <20 µm	1.0	146	4.4	36	50	129	61400	1.2	1280	107	129	7.3	39	0.8	28.9	473
ZM 13 <2 mm	0.4	63	2.0	19	25	69	26200	<0.25	634	52	54	3.8	19	0.6	12.8	297
ZM 16 <20 µm	1.0	160	4.1	30	42	124	42200	0.6	1110	82	132	5.6	28	0.7	37.2	488
ZM 16 <2 mm	0.4	59	2.1	16	22	79	22800	<0.25	625	43	50	2.3	21	0.6	19.3	275
ZM 19 <20 µm	1.3	181	10.8	34	47	151	41700	0.6	1160	93	148	6.6	29	1.0	47.4	678
ZM 19 <2 mm	0.5	58	5.0	14	21	62	20900	<0.25	585	41	47	2.3	<10	0.5	17.0	282
Vereinigte Mulde																
VM 02 <20 µm	3.3	253	3.2	17	52	103	39800	1.3	1030	36	436	10	28	0.8	6.5	410
VM 02 <2 mm	2.0	139	1.8	12	31	57	20400	0.5	787	23	248	5	14	0.5	8.6	261

to values observed initially at km 34.4. In lognormal plots (concentration versus river length) most elements shown parallel patterns (Figs. 2, 3) suggesting that all elements are related to one component that is diluted downstream.

The < 20 μm fractions of flood sediments of the Zwickauer show altogether much less variation compared to the Freiberger Mulde. For a number of elements concentrations are of the same magnitude as the background values for the Freiberger Mulde. A major exception is Uranium, which is more enriched in all samples than in any one from the Freiberger Mulde and this is true even for the samples taken upstream of the uranium-mining camps at Aue. For some elements, a significant increase has been observed between km 40 and 60 (enrichment factors are: Zn: 3; Cd: 2.2; Ni: 4.6; Ag: 2.9). In contrast to the conditions in the Freiberger Mulde, these concentrations do not decrease significantly downstream.

5.3 Metal Distribution between Fine (< 20 μm) and Coarse (< 2 mm) Grain Fractions

It is commonly assumed, that metals incorporated into sediments reside largely in the fine grain fraction, bound to clay minerals, Fe-hydroxides, and organic matter. As shown in Fig. 4, this appears to be true for the Zwickauer Mulde, where the < 20 mm fractions contain 1.5 to more than 3 times more Pb, Zn and As than the coarse fraction (which also includes the fine

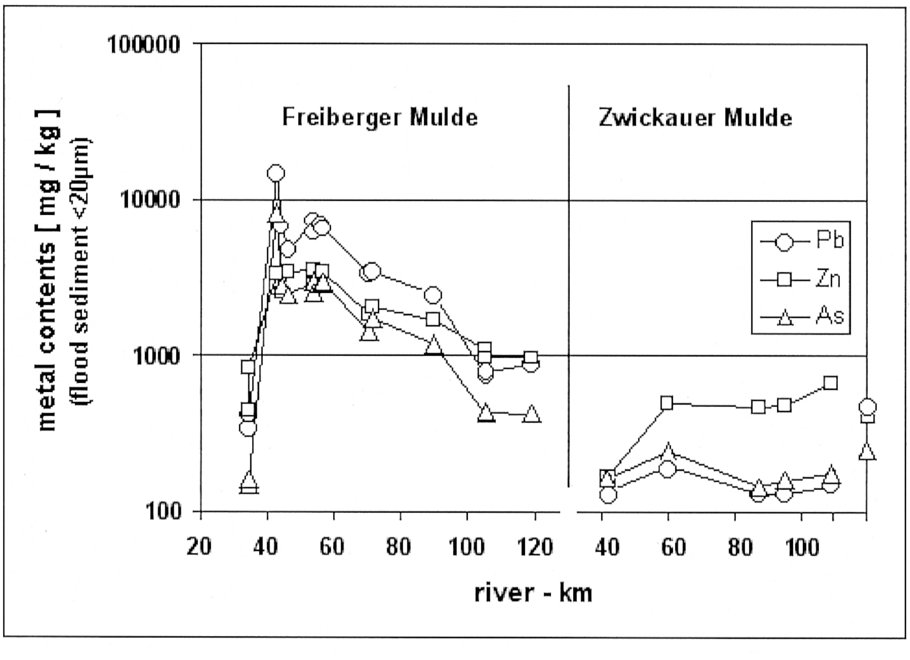

Fig. 2. As, Pb and Zn concentrations in the < 20 μm fraction of flood sediments along the length of the Freiberger Mulde and Zwickauer Mulde. Symbols at the right border of the graph refer to the United Mulde, about 2 kilometres downstream of the confluence.

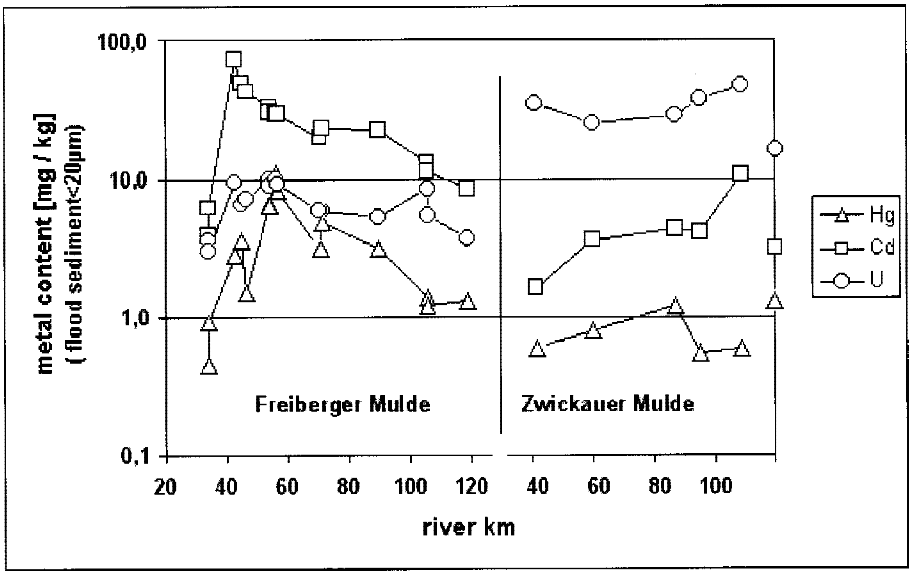

Fig. 3. Hg, Cd, and U concentrations in the < 20 μm fraction of flood sediments along the length of the Freiberger Mulde and Zwickauer Mulde. Symbols at the right border of the graph refer to the United Mulde, about 2 kilometres downstream of the confluence.

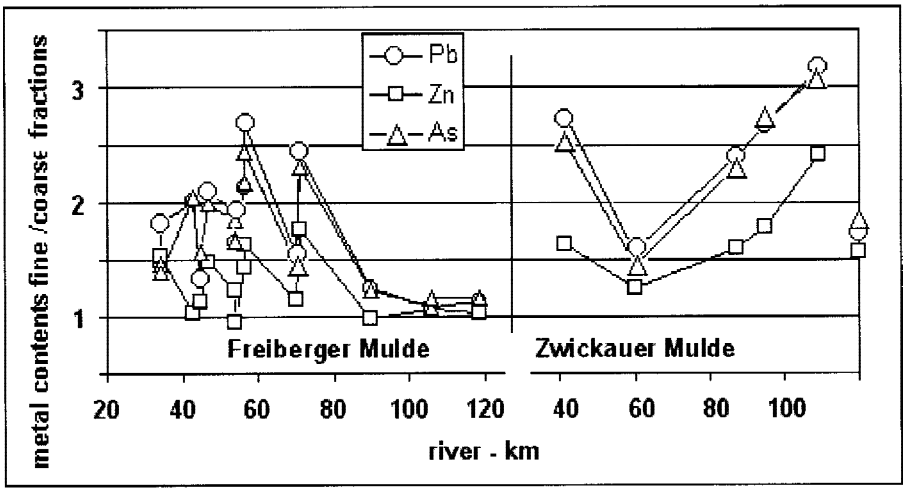

Fig. 4. Enrichment factors of Pb, Zn, and As in fine grained (< 20 μm) flood sediments relative to coarse grained (< 2 mm) flood sediments (note that the < 2 mm fraction contains also the (< 20 μm) fraction as explained in the text.

fraction). For the Freiberger Mulde this is not true: close to the area, where waste dumps were eroded and close to the confluence with the Zwickauer Mulde, the relationship is close to unity. This may have two different explanations:

* Either the grain fraction < 20 μm overwhelms the fraction < 2 mm because it is the most abundant fraction in the < 2 mm sample. This, however, is not the case as shown by grain size analysis, showing that the fraction < 20 mm is less than 11% of the total < 2 mm fraction (with the exception, FM03, where it makes up 70%). However, the microscopic study of the coarser grains shows that in the samples taken close to the confluence of Freiberger and Zwickauer Mulde that they consist of cemented smaller grains, i.e., they constitute indurated river sediments. Hence, the coarse fraction is largely identical with the fine grained fraction.
* Alternatively, both fine and coarse grain fractions could contain a contaminated component, which may or may not be a common component. This is the case close to the industrial area of Muldenhütten and Freiberg, where waste dumps were eroded that obviously contributed fine to coarse material to the flood sediments. The fact that in the log-normal plots the patterns for different elements run roughly parallel strongly argues for a common, or for well mixed components.

5.4 Element Distribution in Different Sequential Extraction Fractions

The thickness of the flood deposits was in the range of less than 1 cm and more than 10 cm. Hence the total addition of toxic elements to the soil was moderate to insignificant, in particular since the soil in the catchment areas of the Mulde Rivers are generally characterized by already high background values.

In order to evaluate, whether leaching of elements from the flood sediments may effect the hydrosphere and biosphere, some sediment samples were leached sequentially. This included

Extract A: leaching with acetic acid (0.11 mol l^{-1})
Extract B: hydroxyl amine hydraulic chlorite (0.5 mol l^{-1})
Extract C: hydrogen peroxide (30%)
Extract D: aqua regia

In the first fraction (Extract A), already 72% Cd; 41% Zn; 44% Mn and 10% Pb were found. Of the elements present in lower concentrations, Ni (44%), Co (34%), and Cu (31%) showed significant mobilization. This "easy" mobilization of toxic elements suggests that further mass balance calculations, as well as monitoring in the field are required to evaluate the effect on soils, plants, and groundwater.

6. CONCLUSIONS

The current study has yielded several results that may be not only of local, but of more general interest:

1. It is common practice to evaluate the contamination of rivers by analysing water samples and the < 20 μm fraction of river sediments. However, this may not provide an accu-

rate picture in the case of flood sediments as these may also contain coarse components that are highly contaminated. Such coarse material may be derived from old waste dumps. In particular, because of the high energy environment of floods, coarse material may be more abundant than fine grained material and hence be the main carrier of toxic elements. Where such coarse material is significantly contaminated and easily leached, such material may significantly contribute to the pollution of soils and groundwater.

2. It appears necessary to carry out mineralogical studies as well as chemical studies in order to interpret element fluxes. In the present study, two cases were found, where the different grain fractions analysed contained similar abundances of metals. Close to the source of heavy contamination by erosion of waste deposits, both coarse and fine grained fractions contained abundant slags. In the second case, the similarity was "artificial", i.e., the coarse grain fraction consisted of indurated, reworked older river sediments, that were already contaminated.
3. On a more general level, the study shows that flood events may spread contaminants over large areas, where tailings and waste dumps are not sufficiently protected from erosion. Where these tailings contain abundant glassy components, e.g., slags, which are easily leached, toxic elements may quickly enter the biosphere, hence it may be necessary to either remove such sediments from agriculturally used land (as was done for example in a garden area on the banks of the Freiberger Mulde close to Freiberg) or to dilute the contaminants by deep ploughing to mix the flood sediments with the underlying soil.

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