HEAVY METALS IN SURFACE SOILS AND STREAMBED SEDIMENTS IN THE WALLAPAI MINING DISTRICT, NORTHWESTERN ARIZONA, A HISTORIC MINING DISTRICT IN A SEMIARID REGION

by

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ABSTRACT

Even today heavy metals from the widely distributed remnants of historic mining in the Wallapai Mining District (Mohave County, Arizona) can contaminate the environment. This investigation focused on the spatial distribution of metals in streambed sediments and surface soils and on the potential environmental hazard they represent under the prevailing semiarid conditions.

Generally speaking, the metal concentrations decrease sharply within a short distance of the source of pollution. In the streambeds this is due to the rapid precipitation and sedimentation of dissolved metals. Moreover, there is limited sediment transport because in the ephemeral watercourses water flows only sporadically and only for short distances. From the distribution pattern of the heavy metals and the particle size distribution in the surface soils it is obvious that the wind does not move large amounts of contaminated sediments over any great distances. Thin surface crusts, which protect particularly the finer grained surfaces of tailings from deflation, play an important role in protecting the surface soils from wind erosion. The solubility of the heavy metals appears to be very limited in the investigated soils and sediments. The main reasons for this are the adsorption of the metals to iron and manganese oxides, the soil moisture deficit for most of the year and the relatively high pH values.

Judging from the distribution and potential mobility of the heavy metals and from the results of recent groundwater and vegetation studies, the environmental hazard in this region remains at a tolerable level.

1 INTRODUCTION

Beginning in the mid-1860s the southwestern US experienced a mining boom, and a large number of mines were developed. They went through alternating phases of economic upswing and decline, but by the end of the 1940s most of the smaller mines had been abandoned for good (Woznicki 1987, Beck and Haase 1989). Nevertheless, their tailings, waste rock dumps and acid mine drainage still represent an environmental hazard because of the heavy metals released from them (Young and Clark 1978, Marcus 1987, Rampe and Runnels 1989, Rösner 1995a, 1996, 1998, Graf et al. 1991, Hyde 1994, Lind and Hem 1993).

The metals can either be leached directly into the groundwater and the surface water (Young and Clark 1978, Lind and Hem 1993) or accumulate in soils and sediments (Brümmer et al. 1986, Bradley 1989, Moore and Luoma 1990, Schachtschabel et al. 1992). Under certain circumstances they can be redissolved and become available to plants or enter the groundwater with the percolation water

(Young and Clark 1978, Bergmann 1989, Herms 1989, Sauerbeck 1989). This article will deal only with heavy metals in fluvial sediments and in soils; the contamination of water and vegetation in the study area (cf. below) was dealt with in recent publications (Rösner 1995b, 1996, 1998).

Most studies of the distribution and transport of heavy metals in fluvial systems have been done in humid regions (e.g. Wolfenden and Lewin 1978, Chase and Wainwright 1983, Bradley 1989, Schmidt et al. 1992, Gatzweiler and Mager 1993, Hiller 1994, Taylor 1996). There are comparatively few studies dealing with drylands (e.g., Harres et al. 1987, Marcus 1987, Rampe and Runnels 1989, Graf et al. 1991, Lind and Hem 1993). Although in the perennial rivers of the humid temperate zones pollutants are transported by means of contaminated sediments (Wolfenden and Lewin 1978), transport in dissolved phase and in suspension additionally plays an important role in distributing pollutants (Symander 1978, Symander and Herrmann 1979, Bradley 1989, Schmidt et al. 1992). In contrast, in the perennial streams of semiarid regions the dissolved heavy metals precipitate rapidly, contaminating the streambed sediments (Rampe and Runnels 1989). In ephemeral streams the distribution pattern of heavy metals seems to be related to the physical mixing of contaminated and uncontaminated sediments (Marcus 1987, Graf et al. 1991).

Surface soils can be contaminated either directly by flue dust released when the ore is smelted (Moore and Luoma 1990) or indirectly due to deflation of tailings and waste rock dumps (Harres et al. 1987). The latter plays a subordinate role in humid latitudes and is therefore usually mentioned only incidentally (e.g., Gatzweiler and Mager 1993).

As far as the mobility of heavy metals is concerned, the investigations of Graf et al. (1991) indicated that in arid regions the fixation of the metals is more stable than in humid latitudes.

Evidently it is not possible to automatically transfer our knowledge of the distribution and chemical mobility of heavy metals in soils and sediments in humid regions, and the ensuing environmental hazard, to semiarid or arid regions. To better understand the relevant processes in drylands, we need to ask three fundamental questions: how far does the contamination extend in fluvial sediments and soils in arid or semiarid regions? What are the transport mechanisms underlying the spatial distribution pattern? How mobile are the heavy metals in soils and fluvial sediments? The objective of this study was to describe the distribution, transport and environmental significance of heavy metals in the vicinity of former mining sites, so that the impact of historic mining on the environment in arid climates can be better assessed. For this a representative example, the Wallapai Mining District in northwestern Arizona, was chosen.

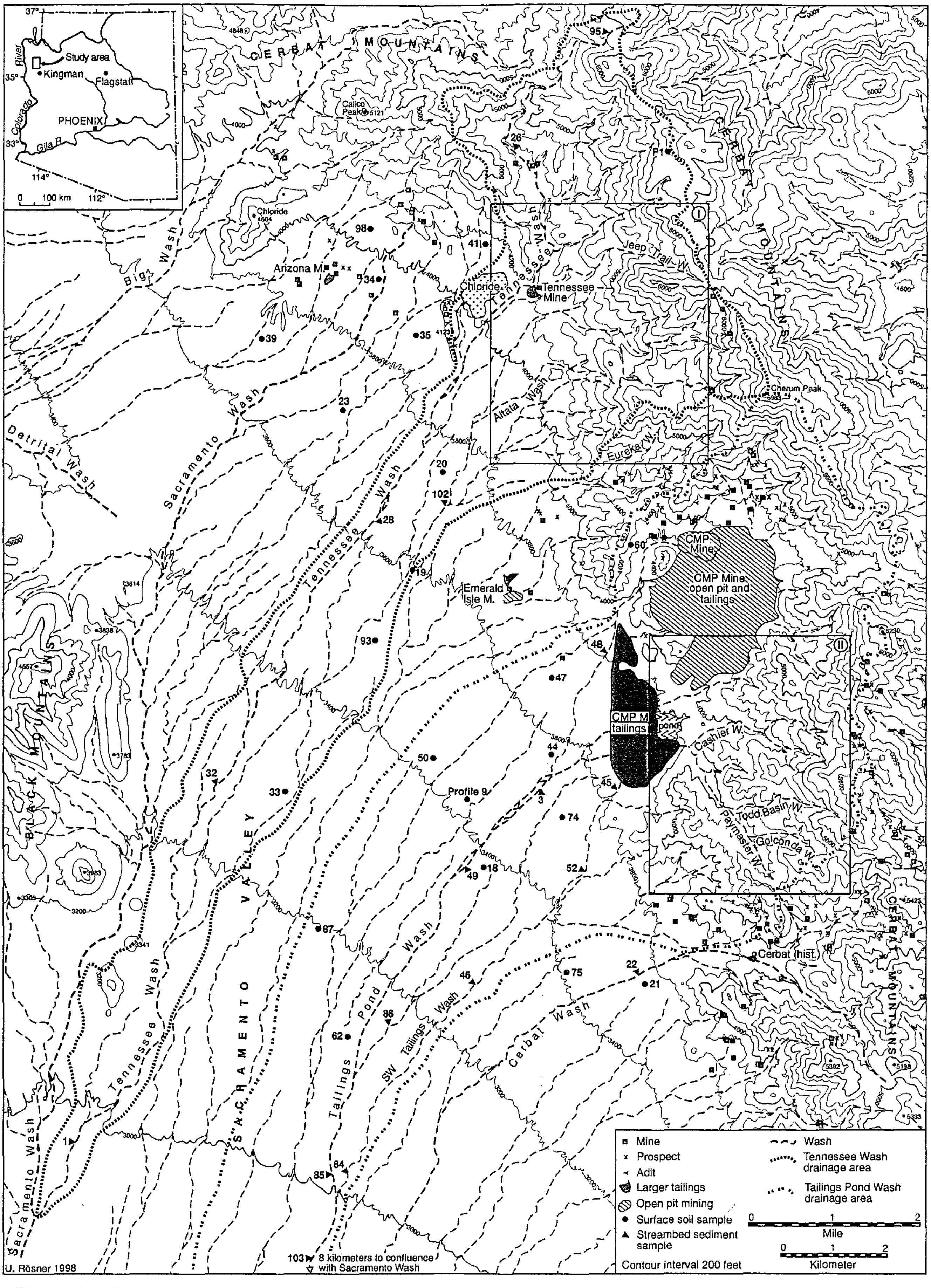


Figure 1: The study area in the Wallapai Mining District with the locations of the sampling sites. The sampling sites and the mines in the central Chloride Mining District (detail I) and the Mineral Park and Cerbat Mining Districts (detail II) are shown in Figure 2.

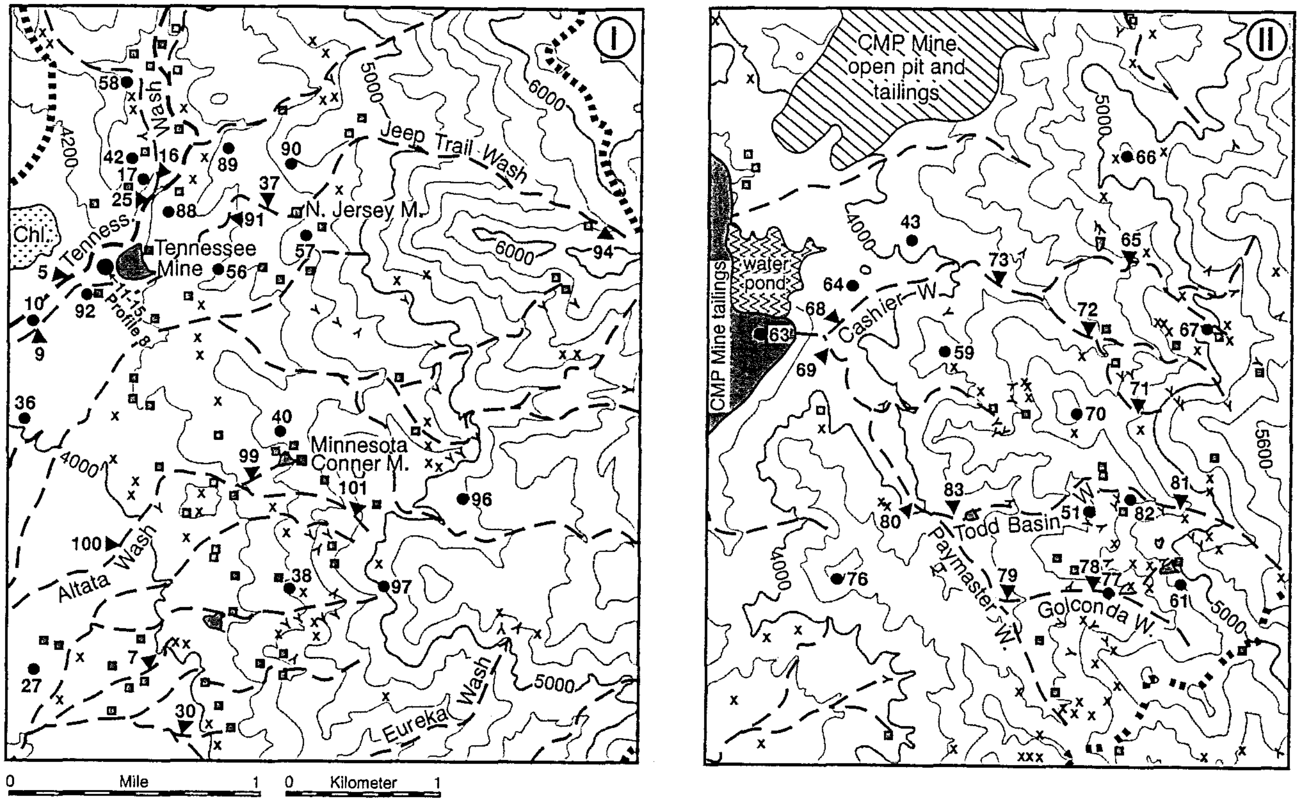


Figure 2: Sampling sites and mines in the central Chloride Mining District (detail I of Figure 1) and the Mineral Park and Cerbat Mining Districts (detail II of Figure 1).

2 THE STUDY AREA

The Wallapai Mining District (Figures 1 and 2) encompasses the central part of the Cerbat Mountains, which extend in a NW-SE direction north of Kingman and are flanked to the west by the Sacramento Valley (Dings, 1951: plate 18). According to Schrader (1909) it is divided into four districts, three of which are relevant for this study: the Chloride Mining District, the Mineral Park Mining District and the Cerbat Mining District. The Chloride Mining District encompasses essentially the northeastern part of the drainage area of the Tennessee Wash and the mines located west of Chloride. The Mineral Park Mining District adjoins the Chloride Mining District to the south and extends approximately to the southern boundary of the drainage area of the Tailings Pond Wash; south of it follows the Cerbat Mining District. Because of their close proximity the latter two will be dealt with together. For the investigation of fluvial sediments the two largest drainage areas were chosen, that of the Tennessee Wash (57 km^2) and that of the Tailings Pond Wash (93 km^2) [because the topographic maps show only the names of the Tennessee, Sacramento and Cerbat Washes, all other washes mentioned here were given names of their own].

The Cerbat Mountains are composed predominantly of Precambrian crystalline rocks. Granite gneiss, mica schist, porphyritic granite and gneiss are the rocks with the widest distribution (Thomas 1953). For mining purposes two large granitic intrusions, one north of Chloride and one south of the site of the Cyprus Mineral Park Mine (in the following abbreviated as CMP Mine) were particularly important, as were widely distributed younger dikes of granite porphyry, pegmatite, aplite and lamprophyre (Dings 1951, Thomas 1953). The minable ores (cf. below) occur primarily in veins (Dings 1951).

The climate is semiarid to arid with average annual precipitation rates of 150-260 mm per year at the foot of the Cerbat Mountains and around 350 mm at elevations above 1200 m. The interannual variation is high (more than 24%) (Sellers and Hill 1974, Bureau of Land Management 1978, Western Regional Climate Center 1996). Approx. 60% of the precipitation falls in winter. 83% of the days with rain have low intensities of 0.25-12.7 mm (calculated according to data from the Western Regional Climate Center 1996). The mean July temperature ranges from 21 °C to 29 °C, depending on the elevation; the January temperature between -4 °C and 7 °C (Richmond and Richardson 1974). The mean relative humidity ranges from 27% to 39% (Sellers and Hill 1974: 288). The stream flow varies, in correspondence with the altitudinal differences in climate. At higher elevations it is intermittent, while at lower elevations it is ephemeral.

The soils are shallow to moderately deep, have a sandy and sandy loamy texture, are rich in skeletal material, and are covered by a desert pavement consisting of rock fragments ranging in size from pebbles to cobbles (Richmond and Richardson 1974).

Most of the mines were discovered between 1863 and 1900 by prospectors searching for gold and silver; later mainly lead and zinc were mined (Dings 1951: Table 1). In the first half of this century comparatively little copper was produced, but copper production increased greatly when the Emerald Isle Mine (Figure 1) expanded operations in the early 1940s (Dings 1951: 149 and Table 1). The acme of copper production in Mohave County was reached in 1961, when the Duval Corporation began to operate its Copper and Molybdenum Mine and a large concentrator. Today the mine belongs to the Cyprus Mineral Park Corporation (Cyprus Mineral Park Corporation signboard, 1995). Mining activities had practically ceased in the Wallapai Mining District by the end of the 1940s (Malach 1977); only the CMP Mine is still operating today. Nevertheless, even today a characteristic feature of the canyons of the Cerbat Mountains is old tailings and waste rock dumps, lined up one after the other, unprotected from fluvial and aeolian erosion.

Larger mines, such as the Tennessee Mine east of Chloride (Figures 1 and 2), processed ore on site. It was crushed, ground down to a size of 0.5 to 1 mm and then leached, usually with sulfuric acid, later also with cyanide (personal communication, Roland L. Gittings, Historical Society of Chloride). The remaining slurry of water and fine solids was piped to the tailings and allowed to deposit. Which heavy metals will get into the fluvial sediments and the soils is determined to a large extent by the mineralogical composition of the tailings and waste rock dumps, and it in turn depends on the ores that were mined (Dings 1951). In the area of the Tennessee Mine and the Tennessee Canyon E and NE of Chloride the principal metallic minerals are sphalerite (α-ZnS), galena (PbS) and pyrite (FeS_2), and in lesser amounts arsenopyrite (FeAsS) and chalcopyrite ($CuFeS_2$). Most of the mines also produced gold and silver ores [cerargyrite (AgCl), native silver (Ag), native gold (Au), argentite (Ag_2S)]. Southeast of Chloride chalcopyrite-rich ores were mined for copper, whereas farther to the S the Emerald Isle Mine mined chrysocolla ($Cu_4H_4[(OH)_8 \mid Si_4O_{10}]$) bearing alluvium for copper. Die CMP Mine operated open pit mines for malachite ($Cu_2[(OH)_2 \mid CO_3]$), azurite ($Cu_3[OH \mid CO_3]_2$), chalcocite (Cu_2S), turquoise ($CuAl_6[(OH)_2 \mid PO_4]_4 * 4H_2O$) and molybdenite ($MoS_2$). In the region of the Todd Basin gold and silver ores were also mined. They, however, always occur in connection with chalcopyrite, sphalerite, pyrite and galena (Schrader 1909, Dings 1953; geochemical formulas according to Watzenauer 1982).

At the old mines no attempts were made to protect the tailings from fluvial erosion, deflation or tailings seepage. In 1993, however, a dam was constructed around the large CMP Mine tailings to prevent seepage. Additionally, in 1995 the slopes of these tailings were leveled and covered with soil so that they could be revegetated.

3 METHODS

A total of 40 samples of streambed sediments and 60 samples of surface soils were taken at varying distances from the old mines. For the background samples sites were chosen that were essentially unaffected by mining. All samples were taken at a depth of 2.5-7.5 cm, because previous experience has shown that the metal concentrations are highest near the surface (Chase and Wainwright 1983). At 11 sites two samples were taken to test current aeolian influence, one at a depth of 0-1 cm and one at 2.5-7.5 cm. Two soil profiles were investigated as examples of the vertical displacement tendencies of heavy metals in this region. Additionally, eight samples from tailings represented the sources of contamination. The locations of all sites are shown in Figures 1 and 2.

The sediment properties were analyzed in the laboratory of the Department of Geography in Erlangen. Here we determined the particle size distribution (wet sieving and pipette analysis according to Köhn 1928, with particle size fractions defined according to the customary German grades: clay: $< 2 \mu m$, silt: 2-63 μm, sand: 63-2000 μm), $CaCO_3$ content (by gas volume using a Scheibler apparatus), pH (H_2O) and pH ($CaCl_2$) (using a Knick model 751 pH meter), electrical conductivity (EC) (using a WTW model LF 318 conductivity meter in a 1:5 extract) and organic matter (by loss on ignition technique) (cf. Kretzschmar 1994, Schlichting et al. 1995).

All samples were submitted to McKenzie Laboratories, Phoenix, Arizona, for analysis of the heavy metal contents. Samples 1-30 were analyzed for 12 different heavy metals (As, Ag, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, Fe, Mn). Ag, Hg and Se lay almost without exception below the detection limit; consequently they were not measured in the other samples and are not included in the following discussion. For preparation, 2 g of ground fine soil was digested in concentrated nitric acid and 30% hydrogen peroxide. The digestate was then refluxed with hydrochloric acid for the analyses by ICP (inductively coupled argon plasma spectroscopy) and with nitric acid for the furnace AAS (atomic absorption spectroscopy supplemented by graphite furnace) (McKenzie Laboratories 1992, 1994). The metals were first measured by ICP. If the metal concentration was very low, the material was additionally analyzed by graphite furnace AAS. For quality control replicate samples were processed with each analytical batch or every 20 samples, whichever was greater. All listed heavy metal concentrations represent the average of three measurements.

The absolute metal concentrations were converted to enrichment factors, which make it possible to evaluate the contamination of soils or sediments in relation to the geogenic background levels. The enrichment factor is the ratio between the metal concentration of a sample and the mean concentration in uncontaminated samples from the same region. For those heavy metal concentrations below the detection limit the value was set equal to half the detection limit for the calculation. The linear dependence between soil parameters and heavy metals was tested by means of Pearson's correlation coefficient (calculated with Microsoft Excel 5.0).

4 RESULTS

4.1 Material Properties and Background Values

Table 1 shows the general characteristics of the surface soils, streambed sediments and tailings materials in the Wallapai Mining District. The samples used to calculate the mean values were all taken outside of the central mining areas, so as to minimize their influence on pH, organic matter and electrical conductivity.

	pH	pH	$C_{org.}$	EC	$CaCO_3$	Clay*	Silt*				Sand*			
	(H_2O)	($CaCl_2$)	(%)	(µS/cm)	(%)	< 2	2 - 6.3	6.3 - 20	20 - 63	total	63 - 200	200 - 630	630 - 2000	total
Streambed sediments														
Mean	**7.6**	**6.9**	**0.7**	**52**	**0.3**	**2.7**	**1.2**	**1.6**	**3.4**	**6.1**	**18.6**	**48.3**	**24.4**	**91.2**
Maximum	9.0	7.9	1.5	114	1.1	8.7	3.9	7.4	13.0	17.5	44.9	68.9	53.9	97.5
Minimum	4.3	3.8	0.4	12	0.0	0.8	0.0	0.1	0.1	0.9	4.4	30.2	1.5	73.8
SD	1.4	1.3	0.3	31	0.4	1.9	1.1	1.6	2.9	4.7	9.4	10.7	11.9	6.3
n	21	21	21	21	21	21	21	21	21	21	21	21	21	21
Surface soils														
Mean	**7.4**	**6.6**	**1.8**	**66**	**1.7**	**9.1**	**3.4**	**4.7**	**12.8**	**20.9**	**23.9**	**24.6**	**21.6**	**70.0**
Maximum	8.7	8.0	3.1	175	18.9	16.5	10.4	9.1	22.0	33.7	49.6	32.6	42.9	81.7
Minimum	5.7	5.3	1.0	17	0.0	4.9	1.3	1.6	6.4	10.4	14.9	14.5	5.6	54.6
SD	0.7	0.8	0.5	39	4.2	2.8	1.8	1.5	4.0	5.4	7.6	4.4	7.1	6.9
n	39	39	39	39	39	39	39	39	39	39	39	39	39	39
Tailings materials														
Mean	**4.2**	**4.2**	**3.0**	**2080**	**0.0**	**19.4**	**8.5**	**12.3**	**16.5**	**37.3**	**27.9**	**8.9**	**6.4**	**43.2**
Maximum	6.9	6.9	5.2	3150	0.0	46.1	17.6	26.1	21.3	60.0	52.2	14.5	13.9	69.5
Minimum	2.3	2.2	1.1	1370	0.0	3.6	1.6	5.0	5.1	26.9	4.8	1.7	0.0	16.8
SD	2.0	2.0	1.8	554	0.0	13.6	6.1	6.7	5.9	11.3	18.8	5.6	5.7	19.2
n	8	8	8	8	8	8	8	8	8	8	8	8	8	8

SD = standard deviation, n = number of samples; * particle size distribution in percentage of weight; particle diameter in µm.

Table 1: General properties of surface soils, streambed sediments and tailings materials in the Wallapai Mining District.

The high pH in surface soils and streambed sediments and the low organic matter content are largely in accordance with those of other arid regions (e.g., Vogg 1981, Rösner 1995b). Appreciable carbonate contents are found only southwest of the Emerald Isle Mine and the CMP Mine. If the four samples from these areas were eliminated, the mean for the study area would be reduced to 0.4%, a more representative value for the study area. The content of water-soluble salts is also low compared with other semiarid-arid regions, where EC values of far above 100 µS/cm in soils are normal and values of several thousand µS/cm are no rarity (e.g. Vogg 1981, Rösner 1995b). Characteristic of surface soils and streambed sediments, finally, is the consistently low clay content and high sand content.

The tailings, by contrast, are characterized by extreme acidity and high salinity. The high $C_{org.}$ content cannot be derived from genuine organic matter, however, because the tailings are almost free of vegetation. Instead it is probably due to the analytical process. When the samples are ignited not only organic carbon escapes, but also water of crystallization from clay and sesquioxides. Considering the high proportion of clay and sesquioxides in the tailings, the difference in weight between the initial and final weighings of the sample increases so much that the calculated $C_{org.}$ value is too high (Schlichting et al. 1995).

	Heavy Metals (units are mg/kg)								
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Chloride Mining District									
Streambed Sediments									
Mean	**5.3**	**0.04**	**11.5**	**7.3**	**10967**	**217**	**7.5**	**7.4**	**30**
Maximum	13.0	0.06	18.0	13.0	15000	260	10.0	7.5	41
Minimum	0.6	0.03	3.5	2.8	6900	190	6.0	7.4	20
SD	6.7	0.02	7.4	5.2	4050	38	2.2	0.1	11
n	3	3	3	3	3	3	3	3	3
Surface Soils									
Mean	**7.1**	**0.69**	**14.8**	**4.6**	**14625**	**278**	**8.2**	**10.4**	**40**
Maximum	9.6	1.50	18.0	6.0	18000	330	12.0	12.0	45
Minimum	2.3	0.06	11.0	2.2	9500	200	6.0	9.1	32
SD	3.3	0.60	3.0	1.8	3816	57	2.7	1.3	6
n	4	4	4	4	4	4	4	4	4
Tailings Materials									
Mean	**1155.0**	**10.98**	**13.3**	**220.8**	**46250**	**1433**	**10.8**	**10500.0**	**4390**
Maximum	1700.0	33.00	21.0	420.0	99000	4700	30.0	36000.0	12000
Minimum	680.0	1.50	6.7	53.0	20000	140	1.3	1300.0	860
SD	443.4	14.79	6.8	151.4	36619	2187	13.0	17011.2	5193
n	4	4	4	4	4	4	4	4	4
EF(soil)	162.7	15.9	0.9	48.0	3.2	5.1	1.3	1009.6	110
Mineral Park and Cerbat Mining District									
Streambed Sediments									
Mean	**9.6**	**0.39**	**6.2**	**11.7**	**8600**	**525**	**1.3**	**48.0**	**176**
Maximum	13.0	0.56	7.2	17.0	11000	560	1.3	64.0	270
Minimum	6.2	0.22	5.1	6.3	6200	490	1.3	32.0	82
SD	4.8	0.24	1.5	7.6	3394	49	0.0	22.6	133
n	2	2	2	2	2	2	2	2	2
Surface Soils									
Mean	**5.1**	**0.11**	**13.9**	**12.5**	**13750**	**298**	**7.9**	**25.5**	**59**
Maximum	8.1	0.18	21.0	20.0	16000	330	10.0	37.0	77
Minimum	2.7	0.05	6.6	6.0	12000	250	6.0	14.0	42
SD	2.3	0.06	5.9	5.7	1708	36	1.9	10.8	18
n	4	4	4	4	4	4	4	4	4
Tailings Materials									
Mean	**890.0**	**9.02**	**23.4**	**462.5**	**49500**	**848**	**6.7**	**4340.0**	**3680**
Maximum	3000.0	29.00	49.0	780.0	73000	2600	12.5	16000.0	12000
Minimum	160.0	0.58	1.7	240.0	24000	110	1.3	330.0	440
SD	1407.0	13.44	20.9	260.0	20952	1178	4.6	7774.0	5569
n	4	4	4	4	4	4	4	4	4
EF(soil)	174.5	82.0	1.7	37.0	3.6	2.8	0.8	170.2	62
GWPGL	**5.0**	**0.5**	**10.0**	**130.0**	**n.a.**	**n.a.**	**15.0**	**2.0**	**500**

SD = standard deviation, n = number of samples, EF(soil) = enrichment factor calculated with the mean background concentration from uncontaminated surface soils of the same area, GWPGL = Groundwater Protection Guidance Level (Arizona Department of Health Services 1990). For those heavy metal concentrations below the detection limit the value was set equal to half of the detection limit for the calculation.

Table 2: Mean metal concentrations in surface soils, streambed sediments and tailings material in the Wallapai Mining District.

Table 2 shows the mean metal content of background samples of surface soils and streambed sediments and, for comparison, of tailings. Enrichment factors were additionally calculated for the latter on the basis of the concentrations in the surface soils. The "Groundwater Protection Guidance Levels" (Arizona Department of Health Services 1990) can serve as approximate reference values, although these general pollution criteria are not directly relevant for our study area, because the geogenic As, Cd, Cr and Pb concentrations are higher than these standards. The table also reveals regional differences. The Cu, Pb and Zn contents in the Mineral Park and the Cerbat Mining District are clearly higher than in the Chloride Mining District; the highest Cd concentrations, however, are found in the surface soils of the Chloride Mining District. In the sediments of the tailings As, Cd, Cu, Pb and Zn are highly enriched compared with the background values, while Cr, Ni, Fe and Mn are insignificantly elevated.

4.2 Heavy Metals in Streambed Sediments

Drainage area of the Tennessee Wash (data in Table 3)

Figure 3 shows the enrichment factors for heavy metals in the sediments of the Tennessee Wash. Once the westernmost headwater stream of the Tennessee Wash has passed through the mining area in the Tennessee Canyon, its sediments are measurably contaminated (sample 16). Between the Tennessee Canyon and the Tennessee Mine a "recovery" takes place (sample 25), because the trunk stream merges with an eastern tributary flowing from a less polluted area. Directly below the confluence of the main runoff from the Tennessee Mine tailings, the heavy metal concentrations shoot up (sample 5), but after only a few kilometers they drop off drastically. The highest concentrations are of As, Cd, Pb and Zn. Cu is much lower, with an enrichment factor of 20.9; Fe and Mn reach maximums of 2.9 and 8.7 and Cr is even under 1.

Starting from the most highly contaminated sample, no. 5 (except for Cr, which has its highest concentration in sample no. 28), most heavy metals have already decreased by 80-95% after 5 km (Figure 4). The concentrations of Cr and Fe, which were only moderately enriched anyway, are reduced more slowly downstream.

In smaller tributaries it is also apparent that the metal concentration depends on the distance from the source of contamination. In the Jeep Trail Wash (Table 4) the tailings of the New Jersey Mine extend into the streambed shortly above sample 37 and cause high concentrations mainly of As, Cd, Pb and Zn. The higher concentration in sample 91, 0.4 km downstream, however, cannot be attributed to discharge from another mine at this point. Instead it is probably a local concentration of tailings material, which developed in an area of slower flow velocity (cf. Miller 1997). 1.5 km

Sample	Heavy Metals									Sediment Properties													
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	pH	$C_{org.}$	EC	$CaCO_3$	Clay*	Silt*				Sand*			
	(units are mg/kg)									(H_2O)	($CaCl_2$)	(%)	(µS/cm)	(%)	< 2	2 - 6.3	6.3 - 20	20 - 63	total	63 - 200	200 - 630	630 - 2000	total
Tennessee Wash																							
95	0.6	<0.05	3.5	2.8	6900	200	<13	7.5	20	7.9	7.1	0.6	47	0.0	1.8	0.9	1.4	1.1	3.5	6.7	34.2	53.9	94.7
26	13.0	<0.125	13.0	< 12	11000	190	<12	7.4	41	9.0	7.9	0.7	110	1.0	2.7	1.2	0.9	4.7	6.8	23.9	49.0	17.6	90.5
[16]	160.0	2.10	19.0	50.0	24000	700	16.0	600.0	570	6.8	5.9	0.9	42	0.6	3.7	0.1	1.0	1.2	2.3	31.0	50.9	12.1	94.0
25	62.0	0.25	18.0	< 12	14000	270	<12	120.0	130	8.8	7.9	0.8	168	1.1	2.8	1.5	0.0	2.3	3.8	27.6	60.2	5.6	93.4
[14]	860.0	5.40	3.7	110.0	72000	460	19.0	750.0	2200	3.0	3.1	4.9	1273	0.0	3.6	0.5	0.7	3.2	4.4	57.4	33.5	1.0	92.0
5	1400.0	8.60	4.2	92.0	26000	1700	<12	1500.0	4000	8.0	—	1.2	1845	0.0	—	—	—	—	—	—	—	—	—
[9]	290.0	2.10	13.0	29.0	19000	430	<13	180.0	830	7.6	7.5	1.0	762	1.2	4.7	0.0	1.6	4.7	6.3	41.5	43.5	4.0	89.0
28	100.0	1.90	10.0	18.0	12000	240	<12	170.0	550	8.1	7.5	0.6	114	0.0	1.9	0.6	0.4	0.7	1.7	20.7	63.8	11.9	96.4
32	57.0	1.30	7.6	10.0	8000	180	6.2	89.0	290	8.5	7.8	0.5	80	0.5	1.8	0.9	1.1	0.1	2.1	13.5	52.3	30.3	96.1
1	23.0	<1.2	7.1	7.4	7200	150	5.5	45.0	150	8.5	7.7	0.5	57	0.7	3.5	0.4	1.1	4.1	5.6	39.4	44.7	6.8	90.9
Jeep Trail Wash																							
94	2.4	<0.05	18.0	13.0	15000	260	10.0	7.4	30	6.9	6.2	1.5	42	0.0	3.8	3.5	0.3	5.1	9.0	17.7	41.3	28.2	87.2
37	100.0	<1.2	24.0	7.2	9200	200	15.0	83.0	210	8.8	8.0	1.0	275	3.4	2.9	0.3	1.5	1.8	3.6	17.1	59.6	16.9	93.5
91	230.0	0.89	8.6	15.0	13000	510	9.5	170.0	180	8.4	8.1	1.5	191	3.9	5.8	2.4	2.8	4.0	9.2	16.4	40.2	28.3	84.9
9	290.0	2.10	13.0	29.0	19000	430	<13	180.0	830	7.6	7.5	1.0	762	1.2	4.7	0.0	1.6	4.7	6.3	41.5	43.5	4.0	89.0
Altata Wash																							
101	4.0	0.29	24.0	25.0	23000	690	18.0	42.0	100	6.7	5.9	1.4	25	0.0	4.4	1.4	1.3	3.3	6.0	18.4	46.0	25.3	89.6
[99]	1100.0	12.00	23.0	820.0	28000	9500	13.0	520.0	3500	7.8	7.3	0.8	62	0.0	1.5	1.3	1.9	2.8	6.0	18.2	42.4	31.9	92.5
100	370.0	3.70	25.0	190.0	21000	2400	13.0	150.0	1100	8.5	7.8	0.7	40	0.0	0.9	1.2	2.0	3.1	6.4	17.9	39.2	35.6	92.7
102	20.0	0.56	15.0	36.0	11000	290	8.6	61.0	230	8.2	7.4	0.5	17	0.0	1.3	0.6	2.0	1.6	4.1	8.9	56.1	29.6	94.6
Further channels within the Tennessee Wash drainage area																							
7	620.0	< 12	16.0	130.0	42000	260	< 13	1700.0	1100	—	—	—	—	0.0	—	—	—	—	—	—	—	—	—
30	71.0	3.90	52.0	120.0	32000	220	< 12	370.0	1400	3.4	3.2	1.5	358	0.5	7.5	1.1	2.6	1.1	4.9	16.2	47.3	24.1	87.6

* Particle size distribution in percentage of weight, particle diameter in µm; [ ] = the sample was taken in a tributary not far upstream of the confluence with the main channel; — = not analyzed due to loss of sample material.

Table 3: Metal concentrations and sediment properties in the streambed sediments of the Tennessee Wash drainage area.

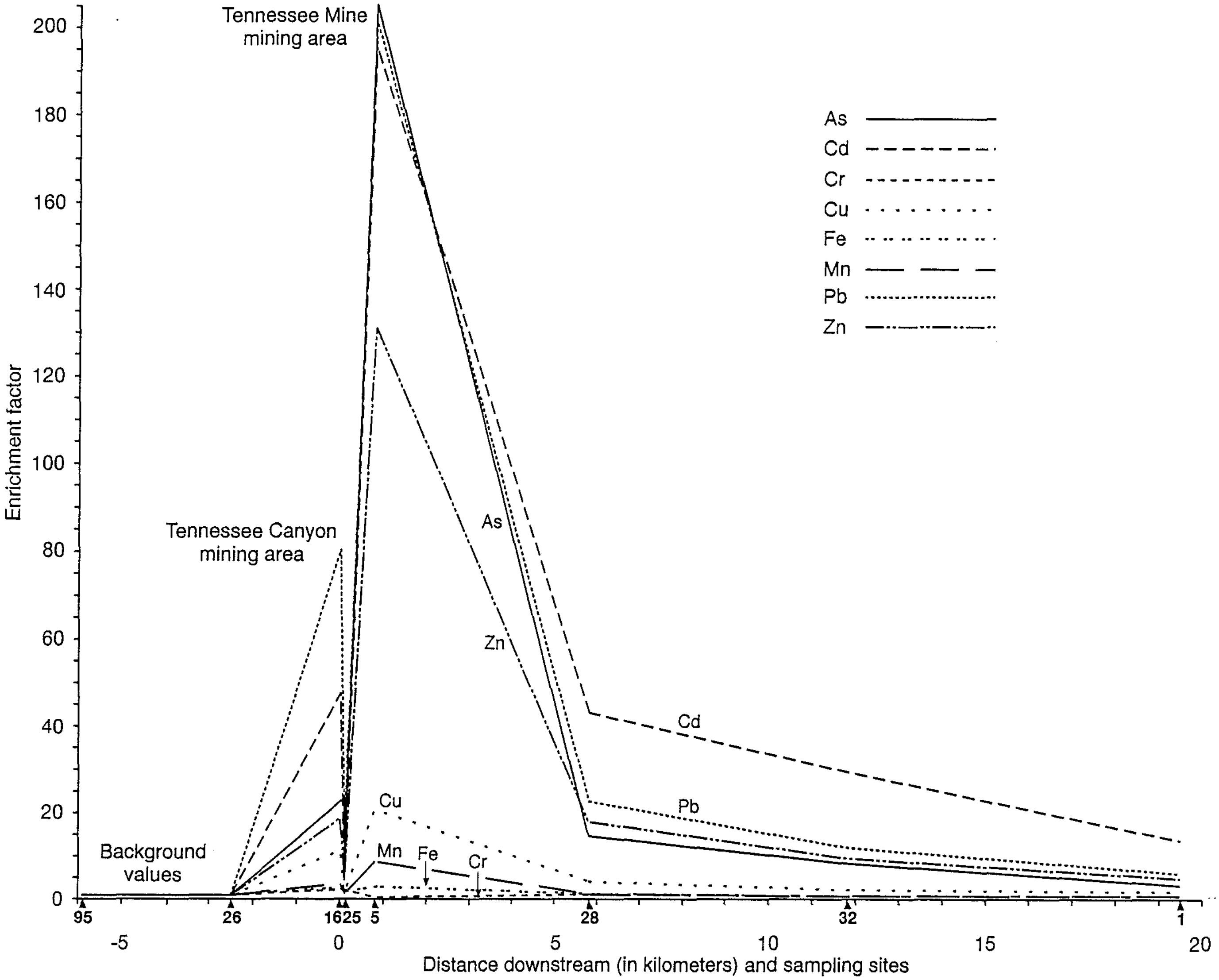


Figure 3: Metal enrichments in the streambed sediments of the Tennessee Wash and its tributaries. Indicated is the downstream distance from the first sample showing mining related contamination. Nickel is not included in the diagram, because > 50% of the values lay below the detection limit.

further downstream (sample 9) the influence of the Tennessee Mine tailings, through which the Jeep Trail Wash passes, is apparent.

For the Altata Wash (Tables 4 and 5), the ephemeral discharge from the Minnesota Connor Mine (sample 99) is the main source of pollution. In addition to As, Cd, Pb and Zn, Cu is now also enriched. This reflects the location of the mine in the "Copper Belt", which extends southward from here (Chloride Chamber of Commerce 1916). Relative to the most highly polluted sample no. 99, reductions of 90-98% within less than 4 km can be calculated for the sediments of the Altata Wash. Cr, Ni and Fe do not show such a drastic reduction, because they were only slightly enriched anyway.

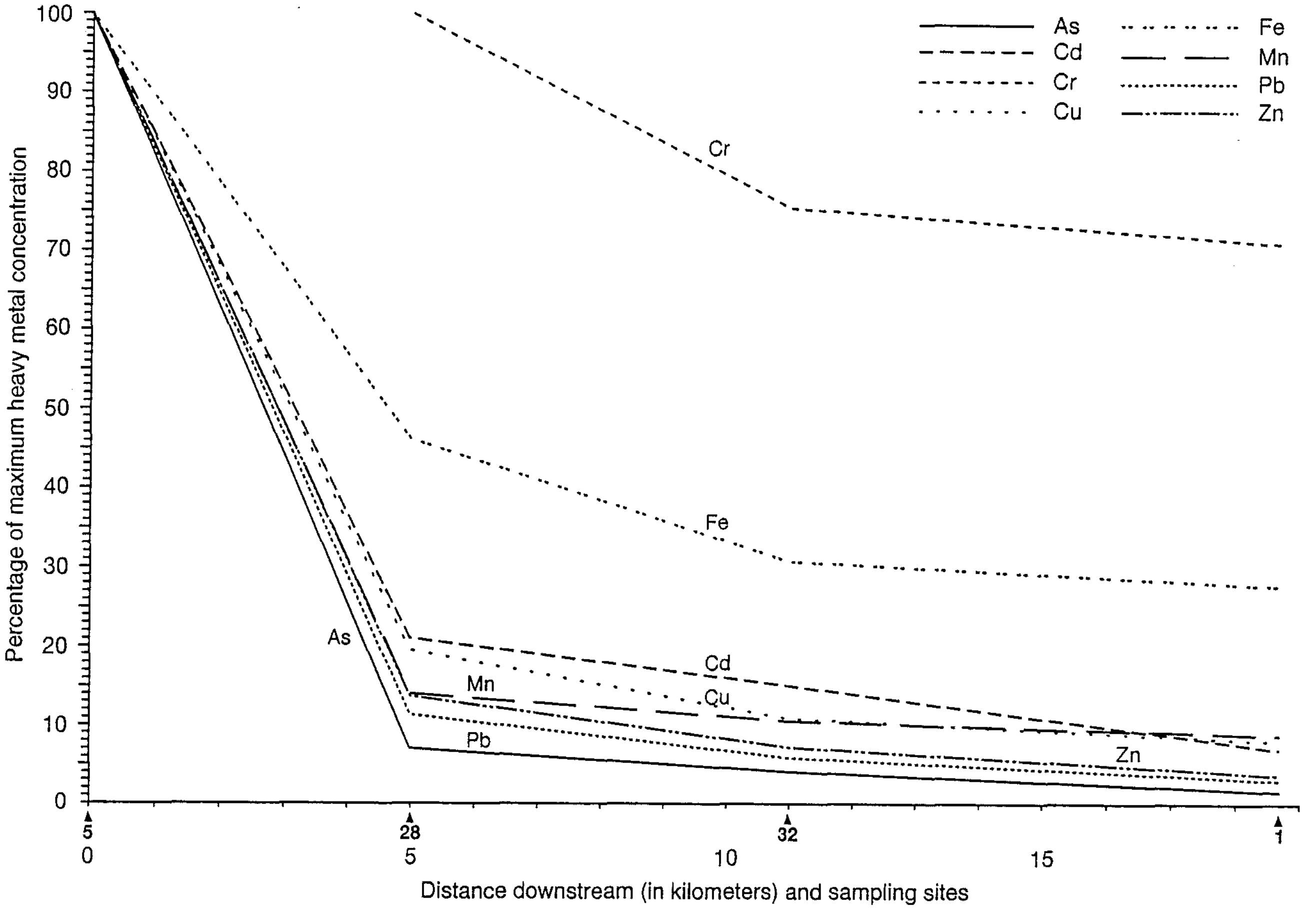


Figure 4: Percentage decrease in the metal concentrations in the sediments of the Tennessee Wash downstream from the mining district. Nickel is not shown because > 50% of the values lay below the detection limit.

Sample	Downstream distance (km)*	Enrichment Factors**								
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Jeep Trail Wash										
37	0.0	41.7	24.0	1.3	0.6	0.6	0.8	1.5	11.2	7.0
91	0.4	95.8	35.4	0.5	1.2	0.9	2.0	1.0	23.0	6.0
9	1.9	120.8	84.0	0.7	2.2	1.3	1.7	0.6	24.3	27.7
Altata Wash										
101	0.0	1.7	11.6	1.3	1.9	1.5	2.7	1.8	5.7	3.3
[99]	0.8	458.3	480.0	1.3	63.1	1.9	36.5	1.3	70.3	116.7
100	1.8	154.2	148.0	1.4	14.6	1.4	9.2	1.3	20.3	36.7
102	4.7	8.3	22.4	0.8	2.8	0.7	1.1	0.9	8.2	7.7

* Distance downstream of the first contaminated sediment sample. ** Enrichment factors are calculated with background sample 94; for those heavy metal concentrations below the detection limit the value was set equal to half of the detection limit for the calculation. [ ] = The sample was taken in a tributary 150 m upstream of the confluence with the Altata Wash.

Table 4: Metal enrichments in streambed sediments of the Jeep Trail Wash and the Altata Wash.

Sample	Downstream	Heavy metal concentration in percent of the maximum concentration								
	distance (km)	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
[99]	0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
100	1.0	33.6	30.8	108.7	23.2	75.0	25.3	100.0	28.8	31.4
102	3.9	1.8	4.7	65.2	4.4	39.3	3.0	66.2	11.7	6.6

[ ] = The sample was taken in a tributary 150 m upstream of the confluence with the Altata Wash.

Table 5: Percent changes in metal concentrations in the sediments of the Altata Wash.

Drainage area of the Tailings Pond Wash (data in Table 6)

The original course of the Tailings Pond Wash (Figure 5) is interrupted by the enormous tailings of the CMP Mine. Its headwater streams extend back into the historic mining area, but they flow into the tailings pond of the still active mine. Immediately below the confluence of acid mine drainage from an adit lying 250 m upstream to the NE, the sediments of the eastern segment - termed here Cashier Wash - reach peak values of 524 for Cu, 127 for Cd and 117 for Zn (sample 73) [Acid mine drainage results from the oxidation of sulfide minerals, such as pyrite. When they are exposed to water, oxygen and microorganisms they produce extremely acidic waters (pH < 3) loaded with high amounts of Fe, Al, Mn, SO_4, and many heavy metals (Singh, Harris and Wilson 1997)]. After only 1100 m (sample 68), however, the metal concentrations have again been reduced by 93.6% for Cu, 83.3% for Zn, 77.1% for Cd and 54.2% for Pb.

1.4 km west of the CMP Mine tailings (sample 3) all enrichment factors lie below 1.6, with the exception of Cu (13.5), Cd (2.7) and Ni (4.6). Evidently the effect of the protective dam thrown up in 1993 is already beginning to show up. A good 2 km downstream an ephemeral stream from the CMP Mine operation site (sample 48) causes a renewed enrichment of As and further downstream of Cu, Ni and Pb in the Tailings Pond Wash (samples 49 and 86). The streambed here is very wide and is crisscrossed by many smaller drainage channels. This uneven discharge could be the explanation for the somewhat irregular downstream decrease in metal concentrations between the sampling sites 49 and 103.

The same explanation probably holds for the renewed Cu and Pb concentrations in the SW Tailings Wash (sample 84) (Table 7). 4.4 km upstream some of the metals had dropped almost to background levels. The dominance of Cu is a reflection of the higher absolute amounts of this metal deriving from the copper mining predominating in the Mineral Park Mining District.

In the streambed sediments of the historic Todd Basin mining area and the Golconda Mine Canyon Zn, Cd and As dominate, by contrast (Table 7), probably due to former Zn mining. The Golconda Mine was the second largest producer of zinc in the Wallapai Mining District in the First World War (Dings 1951).

Sample	Heavy Metals									Sediment Properties													
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	pH	$C_{org.}$	EC	$CaCO_3$	Clay*	Silt*				Sand*			
	(units are mg/kg)									(H_2O)	($CaCl_2$)	(%)	(µS/cm)	(%)	< 2	2 - 6.3	6.3 - 20	20 - 63	total	63 - 200	200 - 630	630 - 2000	total
Tailings Pond Wash (with Cashier Wash)																							
71	13.0	0.22	7.2	6.3	11000	560	< 2.5	32.0	82	7.0	6.2	0.8	19	0.0	3.1	3.9	2.4	6.2	12.5	20.3	37.6	26.6	84.4
72	13.0	0.28	2.5	44.0	23000	860	< 2.5	35.0	150	7.5	7.0	1.2	55	0.0	8.1	2.3	3.5	5.0	10.8	25.7	41.3	14.1	81.1
73	72.0	28.00	8.4	3300.0	17000	710	13.0	240.0	9600	7.1	7.0	1.1	2315	0.0	10.2	1.3	2.3	2.3	6.0	13.3	35.3	35.3	83.8
68	45.0	6.40	7.2	210.0	14000	860	< 13	110.0	1600	8.2	7.6	0.7	63	0.0	1.5	0.1	0.1	0.9	1.1	8.4	58.5	30.5	97.4
3	17.0	< 1.2	10.0	85.0	18000	200	5.8	32.0	120	4.4	3.9	0.6	110	0.0	4.3	0.0	1.1	1.5	2.6	18.0	40.8	34.3	93.1
49	58.0	< 1.2	8.9	75.0	14000	210	3.3	44.0	92	4.3	3.8	1.2	92	0.5	8.7	3.3	7.4	6.8	17.5	12.5	36.1	25.3	73.8
86	67.0	0.28	18.0	120.0	16000	240	6.6	93.0	140	4.6	3.9	0.8	31	0.0	6.1	0.5	3.9	13.0	17.4	44.9	30.2	1.5	76.5
85	7.5	0.10	14.0	34.0	9500	180	< 13	15.0	50	5.2	4.2	0.4	12	0.0	2.3	0.0	1.0	1.7	2.8	15.1	68.9	10.9	94.9
103	15.0	0.15	10.0	45.0	8000	210	4.2	22.0	69	7.1	6.9	0.4	26	0.0	1.2	1.0	2.5	3.9	7.4	15.8	47.3	28.3	91.4
SW Tailings Wash																							
45	52.0	< 1.2	5.7	76.0	18000	< 12	1.7	150.0	24	3.1	3.0	0.5	514	0.0	4.7	1.4	3.7	2.8	7.9	21.7	50.2	15.5	87.4
52	26.0	< 1.2	21.0	49.0	18000	220	15.0	10.0	40	8.3	7.5	0.4	47	0.0	1.6	0.0	0.2	0.7	0.9	15.2	55.8	26.5	97.5
46	7.6	< 1.2	5.2	4.2	7800	310	3.9	54.0	29	8.6	7.7	0.4	33	0.6	1.3	0.5	0.1	1.0	1.6	4.4	56.7	36.0	97.1
84	25.0	0.23	7.3	62.0	9500	270	5.1	36.0	88	8.3	7.6	0.4	25	0.0	1.6	0.2	1.0	1.7	2.9	20.6	65.8	9.2	95.5
Golconda Wash																							
78	160.0	28.00	9.9	350.0	26000	2000	< 13	570.0	10000	6.6	6.2	1.4	79	0.0	6.0	1.5	3.8	17.8	23.1	58.5	11.6	0.8	70.9
79	150.0	19.00	6.3	320.0	22000	1600	< 13	410.0	7800	4.8	4.7	1.0	589	0.0	2.4	0.3	2.3	10.8	13.4	33.3	21.9	29.0	84.3
Todd Basin Wash																							
81	6.2	0.56	5.1	17.0	6200	490	< 2.5	64.0	270	8.3	7.6	0.5	36	1.1	0.8	0.7	0.6	2.1	3.4	23.6	45.9	26.4	95.9
83	820.0	7.30	7.5	250.0	22000	3300	< 13	700.0	5300	5.6	5.4	0.9	191	0.0	3.7	1.0	3.4	10.2	14.6	51.3	25.2	5.2	81.7
Paymaster Wash																							
80	130.0	13.00	6.9	190.0	15000	1300	< 13	290.0	5300	6.3	6.3	0.6	397	0.0	1.7	0.7	1.9	1.4	4.0	18.6	53.1	22.7	94.4
69	220.0	23.00	18.0	370.0	29000	1900	< 13	770.0	9500	6.7	6.3	2.5	120	0.0	19.3	6.0	19.8	36.7	62.5	14.0	1.7	2.6	18.2
Further channels within the Tailings Pond Wash drainage area																							
48	160.0	< 1.2	32.0	310.0	34000	430	11.0	140.0	220	3.9	3.9	5.1	1455	0.0	37.4	8.7	14.7	22.8	46.2	14.6	1.3	0.6	16.4
65a	230.0	1.10	15.0	630.0	83000	200	< 13	420.0	410	3.5	3.4	4.3	494	0.0	8.9	6.7	6.4	4.0	17.1	10.4	27.7	36.0	74.0

* Particle size distribution in percentage of weight, particle diameter in µm.

Table 6: Metal concentrations and sediment properties in the streambed sediments of the Tailings Pond Wash drainage area.

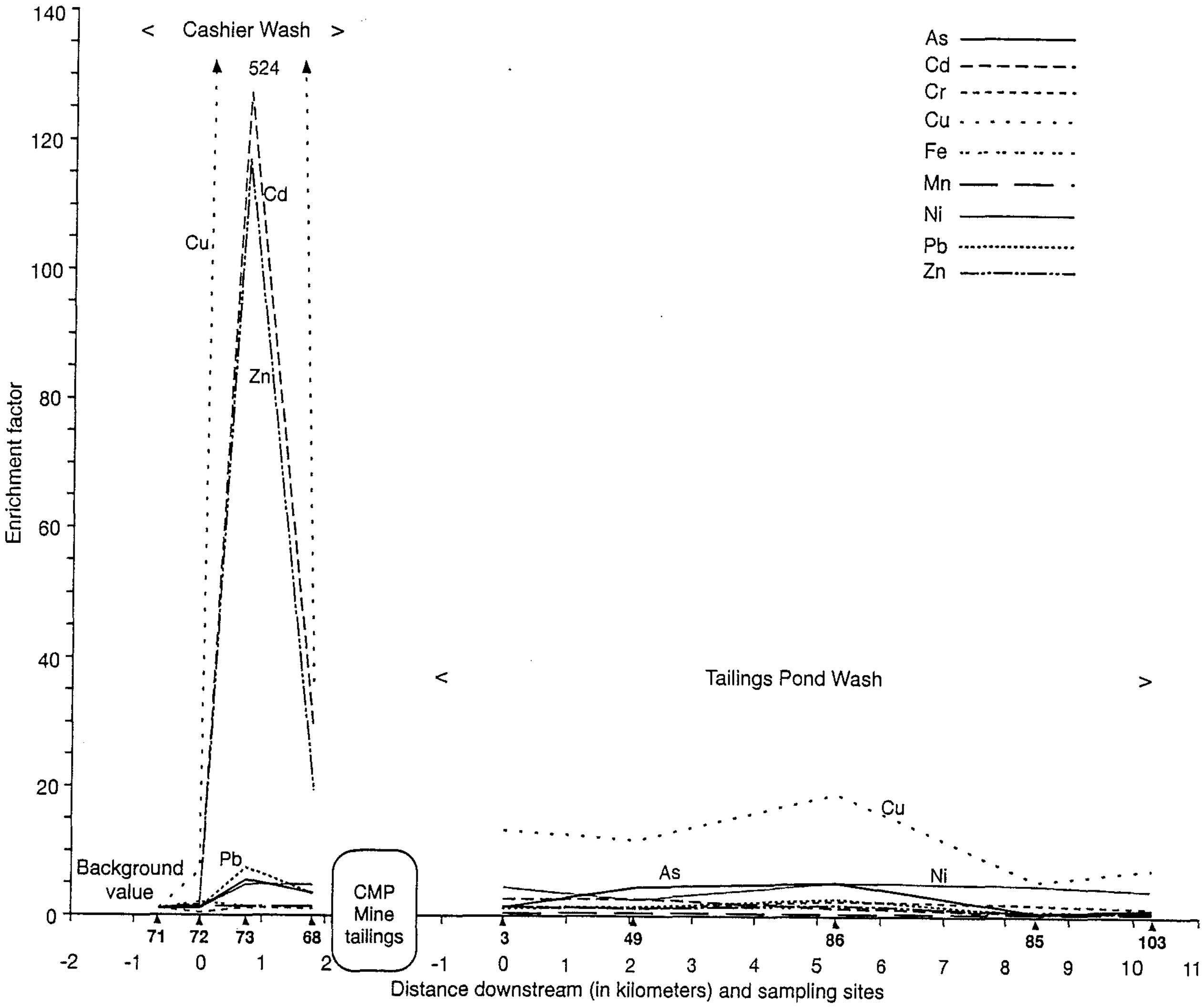


Figure 5: Metal enrichments in streambed sediments of the Tailings Pond Wash.

4.3 Heavy Metals in Surface Soils

Figures 6 and 7 show the enrichment factors for heavy metals in the surface soils both within the mining centers and east and west of them. In the Chloride Mining District (Figure 6, Table 8), the highest heavy metal enrichment factors are found in the immediate vicinity of the Tennessee Mine tailings and in the main mining district east and southeast of Chloride, except for Cr, Cu and Ni. With the exception of Cu the enrichment factors drop significantly within only one kilometer eastward or westward to values that mostly range between 1 and 2, although As, Pb and Zn, for example, are extremely elevated in the tailings. Simultaneously the enrichment factors for the mining districts show great variability, because here highly polluted and less polluted areas alternate within very short distances of each other (e.g., slope between

Sample	Downstream distance (km)*	Enrichment Factors**								
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
SW Tailings Wash										
45	0.0	4.0	2.7	0.8	12.1	1.6	0.0	1.4	4.7	0.3
52	1.6	2.0	2.7	2.9	7.8	1.6	0.4	12.0	0.3	0.5
46	4.6	0.6	2.7	0.7	0.7	0.7	0.6	3.1	1.7	0.4
84	9.0	1.9	1.0	1.0	9.8	0.9	0.5	4.1	1.1	1.1
Golconda Wash										
78	0.0	25.8	50.0	1.9	20.6	4.2	4.1	4.8	8.9	37.0
79	0.6	24.2	33.9	1.2	18.8	3.5	3.3	4.8	6.4	28.9
Todd Basin Wash										
83	—	132.3	13.0	1.5	14.7	3.5	6.7	4.8	10.9	19.6
Paymaster Wash										
[79]	—	24.2	33.9	1.2	18.8	3.5	3.3	4.8	6.4	28.9
[83]	—	132.3	13.0	1.5	14.7	3.5	6.7	4.8	10.9	19.6
80	0.0	21.0	23.2	1.4	11.2	2.4	2.7	4.8	4.5	19.6
69	1.1	35.5	41.1	3.5	21.8	4.7	3.9	4.8	12.0	35.2

* Distance downstream of the first contaminated sediment sample. ** Enrichment factors are calculated with background sample 71 for the SW Tailings Wash and sample 81 for the Golconda, Todd Basin and Paymaster Wash; for those heavy metal concentrations below the detection limit the value was set equal to half of the detection limit for the calculation. [ ] = The sample was taken in a tributary 50 m upstream of the confluence with the Paymaster Wash.

Table 7: Metal enrichments in streambed sediments of the SW Tailings Wash and in the drainage area of the Paymaster Wash.

waste rock dumps, areas above and below the tailings, aeolian sands in front of the tailings, etc.). In the tailings Cr and Ni are only slightly elevated, at most, compared with the background values. The few enrichment factors > 1 for Cr and Ni occurring outside of the central mining district are therefore probably still within the range of geogenic variation. We shall go into the relatively high Cu contents east of the mining district in more detail in the Discussion.

Figure 7 and Table 9 show data from the area influenced by the CMP Mine in the Mineral Park Mining District and from the historic mining district in the inner Cerbat Mountains (Cerbat Mining District). The As, Cd, Cu, Mn, Pb and Zn concentrations in the tailings of the historic mining districts (Todd Basin, Golconda Mine Canyon; cf. data from the Chloride Mining District) are in some cases conspicuously higher than in those of the CMP Mine. The reasons are probably related to the processing techniques used in earlier times, which extracted the metals incompletely from the ores (Bureau of Land Management 1990). Consequently the same metals are more highly concentrated in the soils of Todd Basin and the Golconda Mine Canyon than around the CMP Mine. Because the metal concentrations in the surface soils of the central CMP Mine area are relatively low, the reduction toward outward lying areas is not as obvious as in the Chloride Mining District. Moreover, As, Cd and Cu vary more greatly than was the case in the Chloride Mining District.

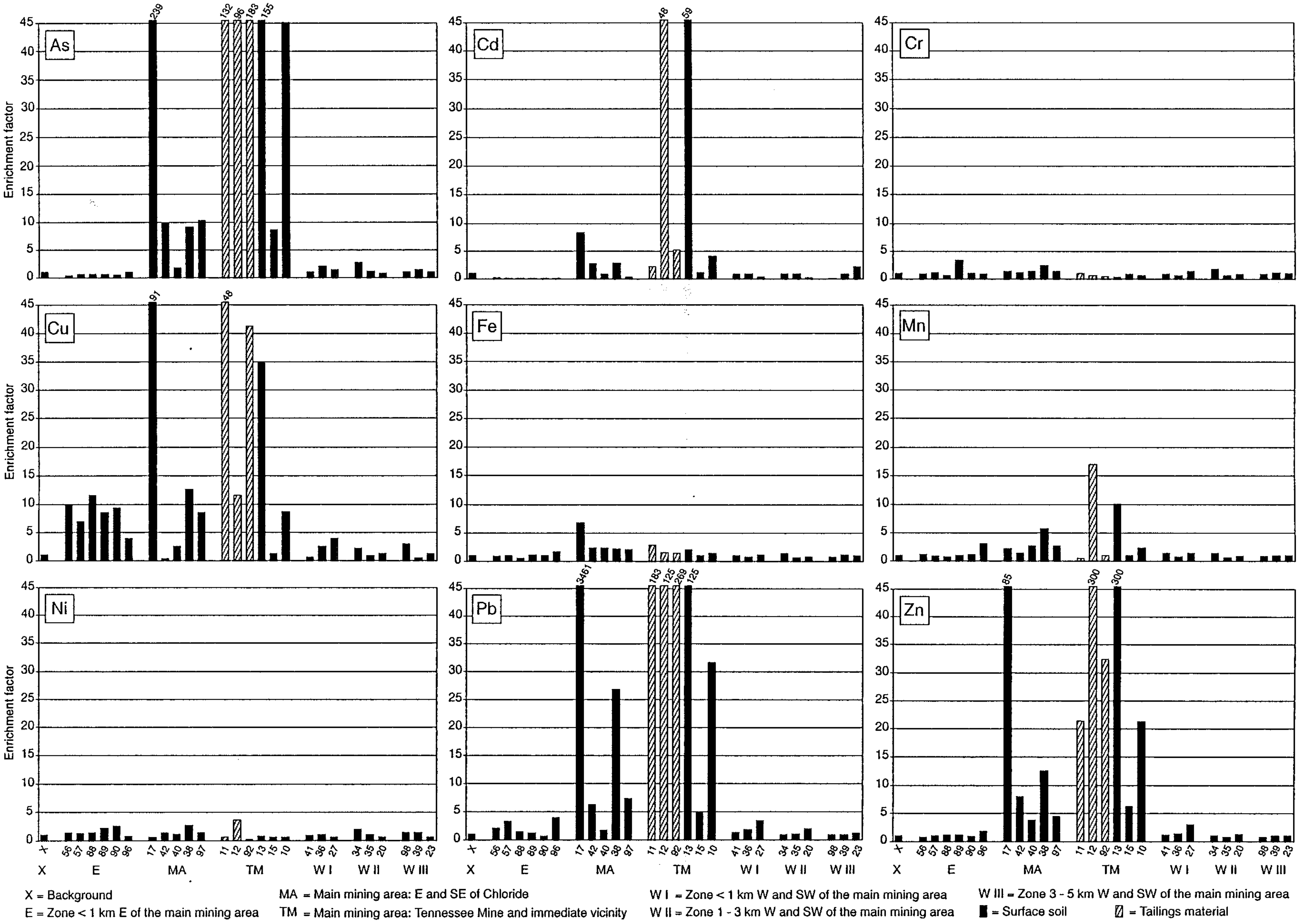
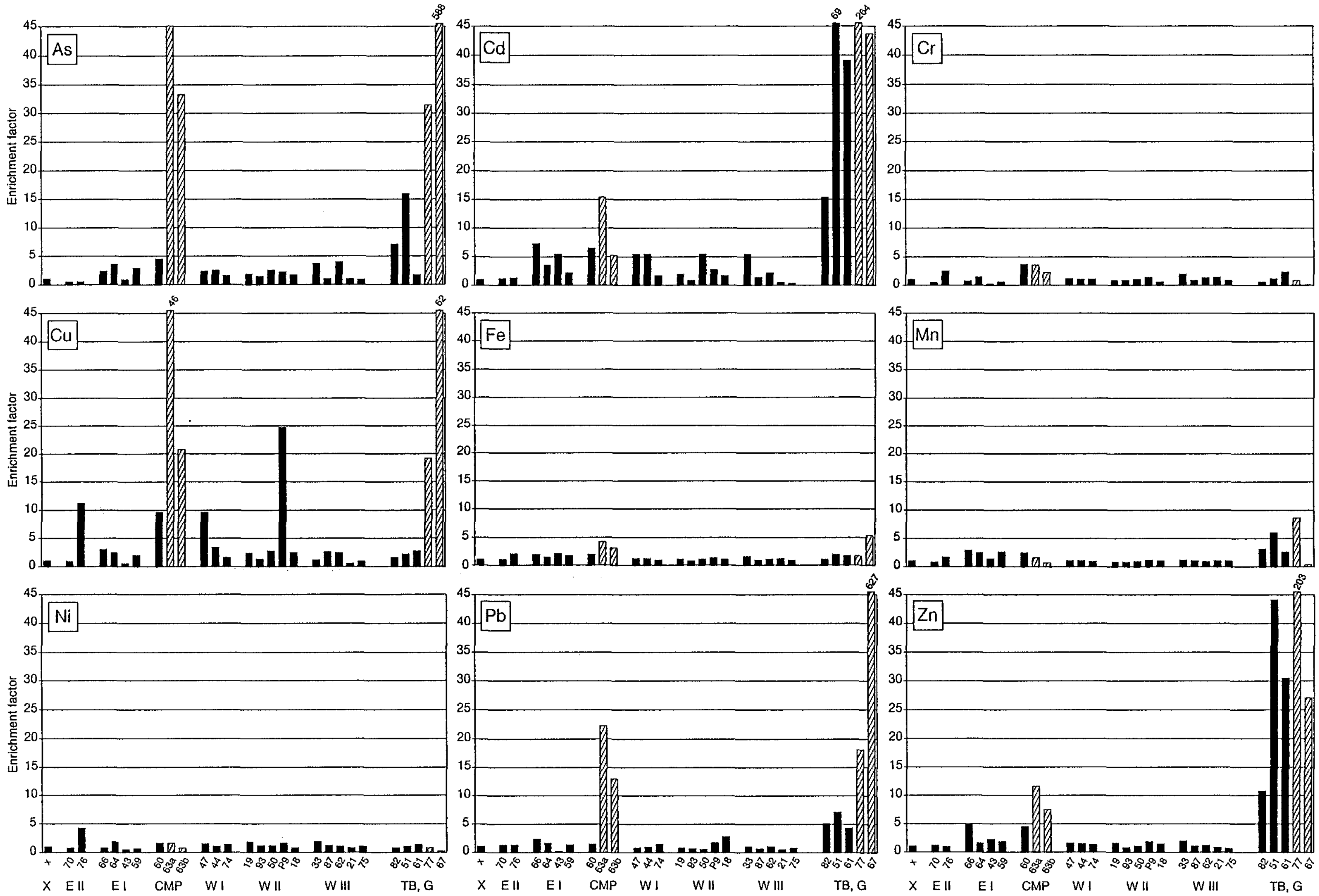


Figure 6: Metal enrichments in surface soils and tailings material in the Chloride Mining District.

Sample	Heavy Metals									Soil Properties													
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	pH	$C_{org.}$	EC	$CaCO_3$	Clay*	Silt*				Sand*			
	(units are mg/kg)									(H_2O)	($CaCl_2$)	(%)	(µS/cm)	(%)	< 2	2 - 6.3	6.3 - 20	20 - 63	total	63 - 200	200-630	630-2000	total
Background																							
x	7.1	0.69	14.8	4.6	14625	278	8.2	10.4	40	7.7	6.8	2.2	79	0.9	10.9	3.9	6.4	14.8	25.1	17.8	20.9	25.2	63.9
Zone < 1 km E of the main mining area																							
56	2.8	0.14	14.0	45.0	13000	320	12.0	22.0	30	7.3	6.0	2.0	47	0.3	7.8	3.0	4.0	8.2	15.2	34.4	29.5	13.1	77.0
57	4.8	< 0.125	18.0	32.0	16000	260	11.0	34.0	44	7.1	6.0	3.1	55	0.3	9.0	3.3	4.6	10.0	17.8	30.6	21.0	21.6	73.2
88	4.7	0.08	10.0	53.0	7800	220	12.0	15.0	49	6.2	5.7	1.5	104	0.0	8.1	1.3	4.7	7.9	13.9	49.6	21.6	6.7	77.9
89	4.0	0.05	50.0	39.0	18000	310	18.0	12.0	49	5.9	5.3	1.5	98	0.0	9.1	3.1	4.9	10.8	18.8	35.4	25.8	10.9	72.0
90	3.2	< 0.10	17.0	43.0	15000	320	21.0	7.6	36	5.7	5.3	2.2	175	0.0	12.0	1.7	4.4	11.4	17.5	41.5	23.3	5.6	70.5
96	7.4	0.13	13.0	18.0	25000	870	< 13.0	42.0	73	6.4	5.5	2.2	35	0.0	11.8	1.7	3.4	19.2	24.3	16.2	23.9	23.8	63.9
Main mining area: E and SE of Chloride																							
17	1700.0	5.80	21.0	420.0	99000	600	< 12.0	36000.0	3400	2.4	2.4	5.2	1910	0.0	28.3	10.9	9.1	9.4	29.4	14.1	14.4	13.9	42.3
42	71.0	1.90	18.0	1.8	33000	400	12.0	65.0	320	7.4	6.5	2.1	26	0.0	10.4	4.3	5.9	10.5	20.7	21.0	22.9	25.1	68.9
40	13.0	< 1.20	21.0	12.0	33000	760	10.0	18.0	150	7.8	7.2	1.8	67	0.0	7.5	3.7	4.2	8.4	16.3	16.6	30.2	29.4	76.2
38	65.0	2.00	37.0	58.0	32000	1600	22.0	280.0	500	7.9	7.2	2.1	49	0.0	8.5	4.4	3.8	9.5	17.7	27.5	26.0	20.3	73.8
97	74.0	0.40	21.0	39.0	31000	760	< 25.0	77.0	180	7.0	6.1	2.2	26	0.0	9.3	10.4	2.6	6.9	19.8	22.5	28.7	19.6	70.9
Main mining area: Tennessee Mine and immediate vicinity																							
11	940.0	1.50	17.0	220.0	43000	140	< 12.0	1900.0	860	3.2	3.3	1.8	2340	0.0	7.5	2.8	8.7	21.3	32.8	44.2	13.0	2.5	59.7
12	680.0	33.00	8.6	53.0	23000	4700	30.0	1300.0	12000	6.9	6.9	1.6	2030	0.0	3.6	1.6	5.0	20.3	26.9	52.2	13.9	3.4	69.5
92	1300.0	3.60	6.7	190.0	20000	290	< 2.5	2800.0	1300	6.5	6.5	1.3	1370	0.0	20.1	11.2	18.2	19.4	48.8	19.6	1.7	9.8	31.1
13	1100.0	41.00	5.9	160.0	31000	2800	< 12.0	1300.0	12000	7.9	7.5	0.4	88	0.0	2.0	0.2	0.7	0.6	1.5	27.6	68.6	0.3	96.5
15	62.0	0.85	13.0	< 12.0	15000	310	< 12.0	50.0	250	7.2	6.2	1.6	30	0.0	6.9	3.1	3.2	9.1	15.4	24.7	33.1	20.0	77.7
10	320.0	2.80	10.0	40.0	21000	630	< 12.0	330.0	850	4.6	4.1	1.3	88	0.0	4.8	0.0	4.3	17.2	21.5	39.6	16.9	17.2	73.8
Zone < 1 km W and SW of the main mining area																							
41	7.8	< 1.20	13.0	2.8	14000	430	7.1	14.0	46	7.4	6.2	1.4	17	0.0	5.2	2.4	3.2	12.4	18.0	14.9	19.1	42.9	76.8
36	15.0	< 1.20	10.0	12.0	11000	220	7.8	19.0	61	7.6	6.8	1.7	28	0.0	11.4	2.8	3.8	14.9	21.5	28.6	25.0	13.6	67.2
27	11.0	0.26	21.0	18.0	17000	390	< 12.0	35.0	120	7.2	5.9	1.4	25	0.0	6.4	4.2	7.7	17.5	29.4	23.4	24.5	16.4	64.2
Zone 1 - 3 km W and SW of the main mining area																							
34	19.0	< 1.20	27.0	10.0	22000	390	16.0	8.9	45	7.5	6.8	1.4	73	0.0	6.1	2.3	4.0	10.4	16.7	27.7	26.4	23.1	77.2
35	8.7	< 1.20	11.0	4.3	9500	200	8.3	11.0	32	7.4	6.3	1.2	21	0.0	7.2	2.5	5.7	17.4	25.6	16.9	22.6	27.7	67.2
20	6.0	0.14	13.0	< 12.0	12000	250	< 12.0	21.0	51	7.4	6.7	1.4	60	0.0	9.3	2.5	3.2	14.1	19.8	21.1	23.7	26.2	71.0
Zone 3 - 5 km W and SW of the main mining area																							
98	7.2	< 0.10	14.0	14.0	12000	250	< 25.0	9.7	32	8.1	7.5	1.4	61	0.0	10.7	2.9	3.7	12.7	19.3	22.7	25.4	21.9	70.0
39	9.6	< 1.20	18.0	2.2	18000	310	12.0	9.1	40	7.9	7.1	1.8	40	0.0	11.9	3.0	4.6	12.9	20.5	18.0	22.8	26.9	67.6
23	7.6	1.50	16.0	< 12.0	14000	270	< 12.0	12.0	43	8.1	7.5	2.8	151	2.9	11.4	5.3	9.1	18.0	32.4	17.0	16.4	22.8	56.2

* Particle size distribution in percentage of weight, particle diameter in µm. x = mean of samples P1, 23, 35, 39. 17 = sample of tailings material.

Table 8: Metal concentrations and soil properties in the surface soils of the Chloride Mining District.



X = Background
E II = Zone 1 - 3 km E and SE of CMP Mine mining area
E I = Zone < 1 km E and SE of CMP Mine mining area
CMP = Immediate vicinity of CMP Mine operation place, CMP Mine tailings
W I = Zone < 1 km W of CMP Mine mining area
W II = Zone 1 - 4 km W of CMP Mine mining area
W III = Zone 4 - 7 km W of CMP Mine mining area
TB, G = Area of Todd Basin and Golconda Mine Canyon
▮ = Surface soil
▨ = Tailings material

Figure 7: Metal enrichments in surface soils and tailings material in the Mineral Park and Cerbat Mining District.

Sample	Heavy Metals									Soil Properties													
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	pH	$C_{org.}$	EC	$CaCO_3$	Clay*	Silt*				Sand*			
	(units are mg/kg)									(H_2O)	($CaCl_2$)	(%)	(µS/cm)	(%)	< 2	2 - 6.3	6.3 - 20	20 - 63	total	63 - 200	200-630	630-2000	total
Background																							
x	5.1	0.11	13.9	12.5	13750	298	7.9	25.5	59	7.3	6.5	1.3	54	1.1	7.5	2.1	3.3	10.0	15.3	23.1	29.3	24.8	77.2
Zone 1-3 km E and SE of CMP Mine mining area																							
70	2.7	0.13	6.6	12.0	14000	250	< 13	32.0	72	6.3	5.5	1.8	36	2.4	5.8	2.1	4.8	12.0	18.8	19.8	24.9	30.7	75.3
76	2.3	0.15	35.0	140.0	28000	520	33.0	34.0	57	7.0	6.3	2.1	39	0.0	6.4	3.7	5.7	11.7	21.2	32.9	25.0	14.4	72.4
Zone < 1 km E and SE of CMP Mine mining area																							
66	12.0	0.81	11.0	38.0	26000	880	< 13.0	61.0	280	7.5	7.0	3.1	75	0.0	10.9	5.2	6.3	9.4	20.9	22.6	26.1	19.7	68.3
64	18.0	0.39	20.0	31.0	20000	740	14.0	39.0	95	6.7	6.0	1.8	40	0.0	13.8	6.5	7.1	18.1	31.6	17.9	14.5	22.2	54.6
43	4.5	< 1.20	4.4	6.6	28000	430	4.1	8.0	130	7.5	6.5	1.8	23	0.0	9.1	3.0	5.0	11.5	19.5	26.9	26.9	17.7	71.4
59	15.0	0.25	8.9	24.0	23000	800	5.9	35.0	110	7.2	6.0	2.3	44	0.3	9.2	3.9	6.1	9.0	19.0	24.8	27.2	19.8	71.8
Immediate vicinity of CMP Mine operation place, CMP Mine tailings																							
60	23.0	0.72	52.0	120.0	26000	750	13.0	38.0	260	8.5	7.7	2.8	168	5.5	12.2	5.9	5.2	10.7	21.8	19.4	23.8	22.7	65.9
63a	230.0	1.70	49.0	570.0	58000	470	< 25.0	570.0	680	3.1	3.1	5.0	3150	0.0	23.3	14.9	26.1	19.0	60.0	11.2	5.5	0.0	16.8
63b	170.0	0.58	31.0	260.0	43000	210	< 13.0	330.0	440	3.2	3.1	2.8	1595	0.0	15.9	2.1	8.6	20.3	30.9	51.3	1.8	0.1	53.2
Zone < 1 km W of CMP Mine mining area																							
47	12.0	< 1.20	16.0	120.0	16000	310	11.0	19.0	97	8.5	7.8	2.1	96	3.5	11.8	2.9	5.1	20.7	28.7	20.0	16.9	22.6	59.5
44	13.0	< 1.20	14.0	42.0	16000	310	8.3	24.0	89	8.3	7.5	1.8	73	0.0	7.1	2.9	4.9	20.6	28.5	24.6	21.6	18.3	64.5
74	8.1	0.18	15.0	20.0	13000	290	10.0	37.0	77	7.3	6.6	1.3	42	1.0	8.0	2.1	3.7	11.7	17.5	22.7	29.2	22.5	74.5
Zone 1 - 4 km W of CMP Mine mining area																							
19	9.2	0.22	13.0	30.0	14000	250	14.0	20.0	95	8.7	7.6	1.9	132	13.9	10.0	5.2	3.5	9.1	17.8	16.4	24.8	31.0	72.2
93	7.4	< 0.20	12.0	16.0	10000	230	9.3	16.0	46	8.7	8.0	1.6	85	18.9	15.8	7.2	4.4	14.7	26.3	16.8	20.2	20.9	57.9
50	13.0	< 1.20	15.0	35.0	14000	280	9.6	13.0	64	8.5	7.7	1.9	152	13.3	8.6	4.7	7.0	22.0	33.7	19.4	16.7	21.5	57.7
P9	11.0	0.30	21.0	310.0	17000	350	13.0	45.0	110	8.4	7.9	1.7	85	5.5	16.5	3.6	5.2	14.4	23.2	21.2	20.7	18.4	60.4
18	8.7	0.19	10.0	31.0	14000	300	< 12.0	70.0	88	8.1	7.2	1.4	66	0.7	5.7	2.6	2.0	8.5	13.1	19.7	32.6	29.0	81.3
Zone 4 - 7 km W of CMP Mine mining area																							
33	19.0	< 1.20	26.0	14.0	22000	350	15.0	28.0	120	7.7	7.0	1.5	74	0.4	5.9	1.3	4.6	11.6	17.4	31.1	27.7	17.8	76.7
87	5.6	0.16	13.0	33.0	12000	310	9.1	16.0	60	7.4	6.6	1.6	39	0.0	8.5	3.1	5.1	13.6	21.7	16.9	26.2	26.7	69.8
62	20.0	0.25	18.0	31.0	14000	260	8.0	28.0	73	7.8	6.9	1.5	74	0.2	6.6	2.6	3.1	14.7	20.4	20.4	28.8	24.0	73.2
21	5.2	< 0.125	21.0	< 12.0	16000	320	< 12.0	14.0	44	8.4	7.6	1.3	111	0.9	7.9	2.4	1.6	6.4	10.4	18.3	31.5	31.9	81.7
75	4.4	0.05	13.0	12.0	12000	330	9.0	19.0	42	7.3	6.4	1.0	26	0.0	8.2	1.8	2.9	10.0	14.6	31.4	31.6	14.2	77.2
Area of Todd Basin and Golconda Mine Canyon																							
82	36.0	1.70	8.7	19.0	15000	940	< 13.0	130.0	640	6.7	6.1	2.4	48	0.0	4.9	2.3	5.7	15.3	23.4	28.2	23.2	20.4	71.7
51	81.0	7.60	17.0	28.0	27000	1800	7.7	180.0	2600	7.9	7.0	2.2	56	0.6	27.7	6.4	7.5	10.5	24.5	17.5	18.1	12.3	47.8
61	8.6	4.30	32.0	35.0	23000	780	10.0	110.0	1800	7.4	6.5	3.1	85	0.3	13.4	4.3	4.6	9.2	18.1	11.7	21.4	35.5	68.5
77	160.0	29.00	12.0	240.0	24000	2600	< 13.0	460.0	12000	6.5	6.4	1.1	1840	0.0	10.9	7.0	11.3	17.2	35.5	25.7	14.5	13.5	53.6
67	3000.0	4.80	1.7	780.0	73000	110	< 2.5	16000.0	1600	2.3	2.2	4.9	2405	0.0	46.1	17.6	11.7	5.1	34.4	4.8	6.7	8.0	19.5

* Particle size distribution in percentage of weight, particle diameter in µm. x = mean of samples 70, 74b, 21, 75b. 63 = sample of tailings material.

Table 9: Metal concentrations and soil properties in the surface soils of the Mineral Park and Cerbat Mining Districts

4.4 Vertical Distribution of Heavy Metals

Soil profiles

Profile 8 from the Chloride Mining District and profile 9 from the Mineral Park Mining District are examples of the vertical distribution of the heavy metals (Figure 8).

Profile 8 lies only 100 m west of the Tennessee Mine tailings. It is a weakly developed Cambic Arenosol (soil classification according to FAO-UNESCO 1988) on poorly sorted cobble-rich fan deposits. All metals are most highly concentrated in the uppermost 5 cm and decrease noticeably below that; the reduction is most pronounced for Zn, Pb and Cd. Between 20 and 25 cm the values again resemble the mean background values for surface soils, except for As and Cu (cf. Table 2). Hence in this profile there is no evidence of a downward displacement of heavy metals with a corresponding horizon of redeposition. On the contrary, the slightly alkaline pH and the low salinity indicate that the metals are immobilized (Herms 1989). The heavy metal concentration in the surface layer is due to local aeolian deposition from the immediately adjacent aeolian sands in front of the tailings.

Profile 9 lies 6 km southwest of the CMP Mine operation site on the distal part of an alluvial fan that originated in the same canyon in which the CMP Mine operation

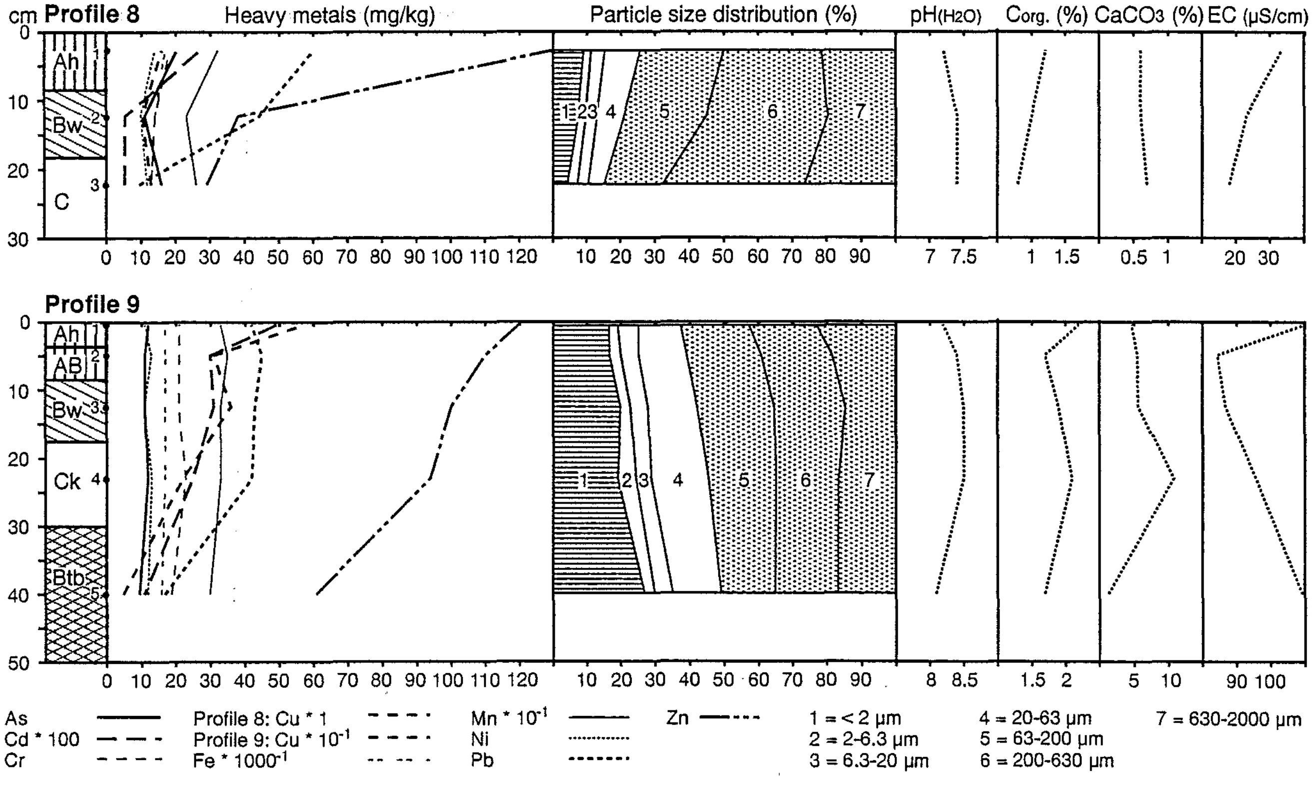


Figure 8: Vertical distribution of the metal concentrations and soil properties in profile 8 and profile 9.

site is located. All wastewater from the processing plants flows from there into the feeder channel. At the mouth of the canyon the feeder channel branches radially into many small channels, which formerly used to distribute the water over the fan (today the wastewater is discharged southward onto the tailings). The soil in this profile is a Calcaric Cambisol (soil classification according to FAO-UNESCO 1988) on sandy loamy alluvial fan deposits containing many pebbles, overlying a buried argic B horizon. Here too, except for Cu, there is no increase in heavy metals in lower horizons, and the moderately alkaline pH value, the somewhat higher proportion of organic matter and the 5-10% carbonate content indicate that the metals are fixed (Herms 1989, Schachtschabel et al. 1992). The only explanation for the extremely high Cu content (220-570 mg/kg in the uppermost 30 cm of the profile) is that this layer was not deposited until after the Duval Mine (today the CMP Mine) began operating, when the discharge from there onto the alluvial fan was still in full swing. Further evidence supporting this explanation is the drastically decreased heavy metal content in the buried argic B horizon and the fact that the Cu concentrations in the surface soils of this alluvial fan (samples 44, 47, 50) are higher than in other surface soils west of the mining district.

Dual samples of surface soils

According to investigations by Blume and Hellriegel (1981, cited in Brümmer et al. 1986), higher heavy metal concentrations in the uppermost centimeters of the surface soil are an indication of atmospheric deposition. 11 dual samples were taken to investigate the distribution of heavy metals within the surface soils from this point of view (Table 10). Of a total of 99 pairs of values, 46 showed higher metal contents in the lower sample and only 33 in the upper sample. 10 pairs had the same concentrations, and 10 could not be evaluated because one or both values lay below the detection limit. Where there were differences, however, in 67% of the cases they were so slight as to lie within a possible analytical or geogenic range of variation of 10%. Statistically there is also no correlation between depth and heavy metal concentration.

5 DISCUSSION

5.1 Distribution of Metals in Streambed Sediments

Distribution in humid and in arid regions

It is well known that heavy metal concentrations normally decrease downstream (Wolfenden and Lewin 1978, Marcus 1987, Bradley 1989, Rampe and Runnels 1989, Moore and Luoma 1990, Miller 1997). This was also demonstrated for our study area. Where it was not the case, the explanation was easily found in local conditions. The decrease seems to occur less rapidly in humid climates, however, than under semiarid

Sample	Heavy Metals (units are mg/kg)								
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
43a	2.4	0.23	**9.2**	**16.0**	26000	**550**	< 13.0	**40.0**	**150**
43b	**4.5**	< 1.20	4.4	6.6	**28000**	430	4.1	8.0	130
64a	18.0	**0.46**	18.0	**53.0**	17000	520	< 13.0	**40.0**	**130**
64b	18.0	0.39	**20.0**	31.0	**20000**	**740**	**14.0**	39.0	95
66a	9.8	0.73	**12.0**	37.0	25000	810	< 13.0	59.0	260
66b	**12.0**	**0.81**	11.0	**38.0**	**26000**	**880**	< 13.0	**61.0**	**280**
74a	7.2	0.18	10.0	**25.0**	11000	230	7.9	28.0	77
74b	**8.1**	0.18	**15.0**	20.0	**13000**	**290**	**10.0**	**37.0**	77
75a	4.0	0.09	11.0	12.0	9900	270	< 13.0	**24.0**	40
75b	**4.4**	< 0.10	**13.0**	12.0	**12000**	**330**	9.0	19.0	**42**
87a	**13.0**	0.16	13.0	31.0	12000	270	8.0	**17.0**	**65**
87b	5.6	0.16	13.0	**33.0**	12000	**310**	**9.1**	16.0	60
93a	6.6	< 0.20	12.0	**17.0**	9600	220	8.2	16.0	**50**
93b	**7.4**	< 0.20	12.0	16.0	**10000**	**230**	**9.3**	16.0	46
96a	**9.3**	**0.16**	**15.0**	**24.0**	**27000**	**960**	< 25.0	**47.0**	**100**
96b	7.4	0.13	13.0	18.0	25000	870	< 13.0	42.0	73
97a	36.0	0.39	17.0	**49.0**	29000	690	12.0	**85.0**	**200**
97b	**74.0**	**0.40**	**21.0**	39.0	**31000**	**760**	< 25.0	77.0	180
98a	6.6	< 0.10	13.0	11.0	11000	220	< 13.0	7.8	29
98b	**7.2**	< 0.10	**14.0**	**14.0**	**12000**	**250**	< 25.0	**9.7**	**32**
P9a	**12.0**	**0.49**	21.0	**570.0**	**18000**	330	11.0	42.0	**120**
P9b	11.0	0.30	21.0	310.0	17000	**350**	**13.0**	**45.0**	110
r	0.11	0.03	0.07	-0.11	0.07	0.07	0.24	-0.08	-0.06

a = 0 - 1 cm sampling depth, b = 2.5 - 7.5 cm sampling depth. **4.5** = the higher metal concentration of a pair of values is set in bold types. r = correlation coefficient for depth and metal concentration; for those heavy metal concentrations below the detection limit the value was set equal to half of the detection limit for the calculation; significance levels: 0.40 (5 %), 0.52 (1 %), 0.63 (0.1 %).

Table 10: Metal distribution in dual samples of some surface soils.

and arid conditions. For the Clark Fork River in the temperate mountain region of western Wyoming, in whose drainage area large scale copper and silver mining was done, Moore and Luoma calculated enrichment factors of 20 (25) for Cu (Zn) after more than 190 km. After more than 500 km an enrichment factor of almost 5 was still calculated (Moore and Luoma 1990: 1281, Figure 2). Moran and Wentz (1974, cited in Rampe and Runnels 1989) showed that the impact of acid mine drainage may still be felt tens of kilometers downstream in Colorado's mountain streams. In the River Tyne in northern England the concentration of Zn decreases by around 53% and of Pb by 65% in the first 5 km; only after 75 km has Zn decreased by 82% and Pb by 95% (calculated according to data from Macklin 1996 in Miller 1997: 105). In the Upper Towy River in Wales, reductions of 60% for Pb, 62% for Cd and 75% for Zn can be observed in the first 5 km; after 11 km the concentrations have only been reduced to 68% to 82% of the initial value (calculated from samples 540, 536, 530 in Wolfenden and Lewin 1978: 72).

In contrast to this, in our study area the reduction in heavy metal concentrations amounted to 80-95% after 5 km, in some cases already after 3 km, and to 92-98% after 18 km (exceptions: Cr and Fe). In Queen Creek, southern Arizona, the Cu concentration had already decreased by 74% to 81% after 5 km (calculated from samples 49 and 44 in Marcus 1987: Table 1). Rampe and Runnels (1989) also noted a very rapid "recovery" in Boulder Creek.

Heavy metal transport

How rapidly the heavy metal concentrations decrease in streambed sediments depends on how they are transported. Analyses of the surface water discharge in the washes in the spring of 1995 (cf. Rösner 1995a, 1996) showed that the concentration in the main stream increased to way above the background values as soon as tailings discharge or acid mine drainage from old adits flowed into it. Immediately below the contamination, however, most of the dissolved heavy metal load had precipitated (Rösner 1995a: 16, Rösner 1996: 84). For purposes of illustration, Table 11 shows the Eureka Wash. Mixing of acid mine drainage with the alkaline water of the Eureka Wash causes rapid precipitation of the metals (cf. Rampe and Runnels 1989). The high pH values, between 7.5 and 8.5, that are the rule in unpolluted surface water in the Cerbat Mountains (Rösner 1995a: Figures 7 and 8) make it impossible to transport metals in dissolved phase over long distances.

Sampling site		Heavy Metals (units are mg/l)								
	pH	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Right above the confluence with acid mine drainage	7.0	< 0.005	0.019	< 0.05	1.2	0.3	0.6	0.10	< 0.005	8.4
Acid mine drainage from a collapsed adit	3.0	0.009	0.160	0.07	41.0	81.0	8.6	0.73	0.005	23.0
Right below the confluence with acid mine drainage	6.5	< 0.005	0.022	< 0.05	2.2	2.5	0.8	0.10	< 0.005	8.6
DWS standards	n.a.	0.050	0.005	0.10	1.00	n.a.	n.a.	0.14	0.050	5.00

Domestic water source (DWS) standards are numeric water quality criteria after Arizona Administrative Code (Arizona Department of Environmental Quality 1995). n.a. = no standard available.

Table 11: Metal concentrations (in mg/l) in the Eureka Wash immediately before and after the influx of acid mine drainage (Rösner 1995a, 1996).

Additionally, the loss of water by infiltration into the channel bed and the high evaporation often reduce the rate of discharge within the Cerbat Mountains so highly that the solution becomes supersaturated. The metals then precipitate and form thin, highly polluted deposits in the dry streambeds. [A sample of such a deposit taken at the same site as sample 65 (cf. Figure 2) shows the following concentrations (units are mg/kg): As: 1.2, Cd: 200, Cr: 3.7, Cu: 3100, Ni: 97, Pb: 87, Zn: 46,000.] Because of the alkaline water it is unlikely that they will go into solution again during subsequent discharge events.

Transport of the metals over greater distances must therefore occur in solid phase. Normally heavy metals correlate highly with particle sizes < 63 µm, especially with clay minerals (Marcus 1987, Bradley 1989, Horowitz 1991, Miller 1997). The correlation matrix in Table 12 reveals hardly any, or only slight, relationships to the finer particle sizes (< 20 µm) - except for Fe - but significant positive correlations between As, Cd, Mn, Pb and Zn and the fractions 20-63 µm and 63-200 µm and consistently negative correlations with the fraction 200-630 µm. This indicates that the metals are mainly present in the particle size classes 20-200 µm. Since Mn simultaneously correlates significantly with As, Cd, Pb and Zn, and Fe with As and Pb, these metals are evidently bound to finely dispersed manganese particles or iron

		Correlation matrix*									Statistical characteritics				
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Mean	Max.	Min.	SD	n
pH(H_2O)		—	—	—	—	**-0.59**	—	—	—	—	6.8	9.0	3.0	1.8	40
pH($CaCl_2$)		—	—	—	—	**-0.57**	—	—	-0.32	—	6.2	8.1	3.0	1.7	38
Corg. (%)		—	—	—	—	**0.83**	—	0.34	0.34	—	1.2	5.1	0.4	1.1	40
EC (µS/cm)		0.44	0.41	—	**0.63**	0.37	—	—	**0.49**	0.40	307.6	2315.0	11.9	524.4	40
$CaCO_3$ (%)		—	—	—	—	—	—	—	—	—	0.4	3.9	0.0	0.8	40
Clay**	< 2	—	—	0.35	—	0.33	—	—	—	—	4.9	37.4	0.8	6.4	39
Silt**	2 - 6.3	—	—	—	—	0.44	—	—	—	—	1.5	8.7	0.0	1.9	39
	6.3 - 20	—	0.32	—	—	0.31	—	—	0.37	0.36	2.7	19.8	0.0	3.8	39
	20 - 63	—	0.48	—	—	—	—	—	0.45	**0.53**	5.1	36.7	0.1	7.0	39
Sand**	63 - 200	0.42	—	—	—	—	—	—	**0.49**	0.31	22.4	58.5	4.4	13.2	39
	200 - 630	—	**-0.50**	—	—	-0.44	—	—	**-0.52**	**-0.55**	42.9	68.9	1.3	15.8	39
	630 - 2000	—	—	—	—	—	—	—	-0.34	—	20.5	53.9	0.6	12.9	39
As			—	—	—	0.42	**0.65**	—	**0.83**	0.31	180.7	1400.0	0.6	313.2	40
Cd				—	**0.64**	—	0.41	—	**0.51**	**0.98**	4.4	28.0	0.0	7.6	40
Cr					—	—	—	0.39	—	—	13.1	52.0	2.5	9.5	40
Cu						—	—	—	—	**0.58**	202.8	3300.0	2.8	532.0	40
Fe							—	0.34	**0.50**	—	19632.5	83000.0	6200.0	15345.1	40
Mn								—	0.40	0.40	877.7	9500.0	6.0	1572.0	40
Ni									—	—	7.7	19.0	1.3	4.5	40
Pb										**0.57**	229.2	1500.0	7.4	303.9	40
Zn											1664.6	10000.0	20.0	2906.2	40

* All streambed sediment samples are included in the calculations of the correlation coefficients. Significance levels: 0.30 (5 %), 0.39 (1 %), **0.49 (0.1 %)**. Only correlation coefficients at a significance level of 5 % or better are presented; therefore, a dash (—) indicates that there was no significant correlation. ** Particle size distribution in percentage of weight, particle diameter in µm. SD = standard deviation; n = number of samples.

Table 12: Correlation between metals and sediment properties (on the left side of the table), and statistical characteristics (on the right side of the table) of the streambed sediments.

oxide or manganese oxide coatings when they are transported (Horowitz 1991). The high intercorrelation of some of the metals demonstrates that the various ore minerals occur in association, as described by Schrader (1909) and Dings (1951), and are therefore washed out of the waste rock dumps and tailings together. The good positive correlation between the metals and the EC values are also an indication that tailings material with its high salt content is being washed out. Were we, as a test, to take the streambed sediment samples that lie in the close vicinity of tailings out of the calculations, the correlation with the EC values would tend toward zero.

If the metals are transported mainly when they are bound to sediments, their distribution pattern depends on the climatic and morphologic factors controlling sediment transport. Since most of the washes in the study area are ephemeral, the contaminated sediments can only be disseminated during a limited period of the year. The low amounts of discharge due to precipitation (cf. section "study area") are reduced still further - quite visibly - by infiltration into the sandy and gravelly sediments of the channel beds. Therefore normally the discharge from the Cerbat Mountains does not extend much more than a couple of hundred meters into the foreland. Even during the rare heavy rainfalls, like the one occurring in the spring of 1995 during one of the research campaigns, only the water of the larger washes (e.g., Tennessee Wash, Tailings Pond Wash) reaches the main stream, the Sacramento Wash, for a few hours. As a result of these discharge conditions, sediment transport is sporadic and uneven and normally over short distances. Additionally, it must be expected that contaminated sediments will be diluted by uncontaminated sediments, such as Marcus (1987) demonstrated for Queen Creek, Arizona.

Thus the conditions under which heavy metal transport takes place in dryland rivers differ from those in perennial watercourses, in which remobilization and further transport of sediments bearing heavy metals can occur more frequently and regularly (cf. Symander 1978, Symander and Herrman 1979).

A further difference is the accumulation of extensive fine-grained floodplain sediments in humid regions, which according to Bradley (1989) and Miller (1997) implies the danger of constant remobilization and thus the further spread of the metals stored in them. Extensive floodplains cannot form in the narrow, steep canyons of the Cerbat Mountains or outside of the Cerbat Mountains, because the streambed channels are cut as much as 5-6 m deep into the pediments or the upper bajadas. Lateral accretion deposits could only occur theoretically where the terrain is more level and the channel is not so deeply incised, i.e., around 8-10 km away from the edge of the Cerbat Mountains, but only small amounts of heavy metals are transported that far (cf. above).

5.2 Distribution of Metals in Surface Soils

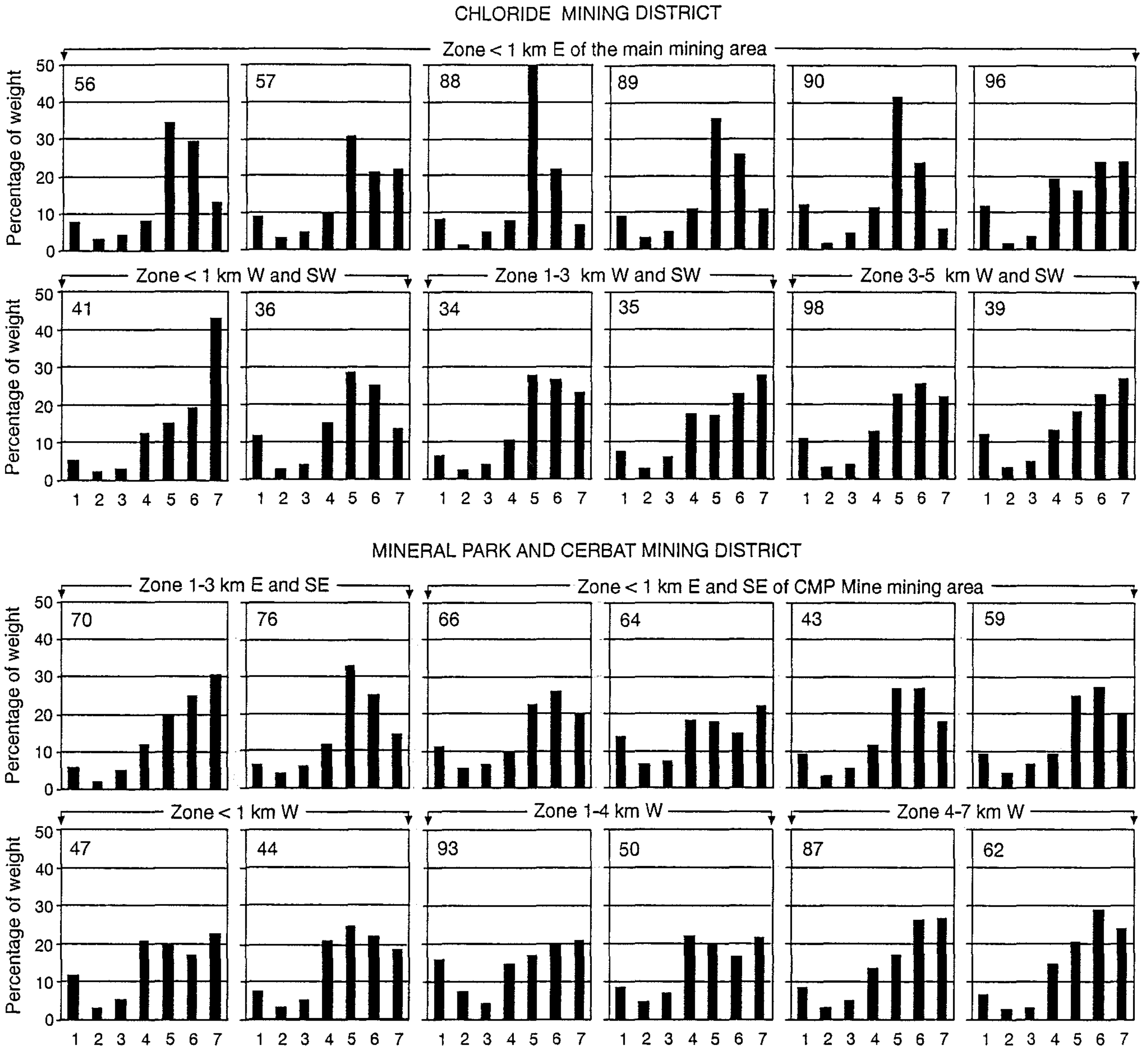
In the Wallapai Mining District there was no smelter that might have emitted smoke particles containing heavy metals. Consequently the metals in the surface soils can only have gotten there via wind erosion and wind transport of contaminated sediments, provided we can exclude the possibility that runoff processes from mines at higher elevations played a role. Since the metal concentrations decrease at relatively short distances from the mining center, sediment transport by wind cannot be very effective. Three factors point to this:

First, considering the prevailing westerly winds, it could be expected that a lot of dust from the tailings and waste rock dumps would be deposited on the slopes lying less than 1 km to the east of the main mining district in the Chloride Mining District. Nevertheless, only a few individual samples show slight enrichments of Cr, Mn, Ni or Pb (cf. Figure 6, Table 8); the only exception is Cu. This suggests that there is no appreciable aeolian deposition. The higher Cu enrichments are probably of local petrographic origin. According to Dings (1951: 144), in rare cases chalcopyrite occurs disseminated in small grains in the granite. This is supported by the fact that in these samples the correlation between Cu and fine-grained sand (63-200 μm) is highly significant at the 0.1% level, a correlation that occurs exclusively in these samples ($r = 0.96$).

Second, the vertical distribution of heavy metal concentrations within the surface soils is unspecific and does not provide any indication of an aeolian source of sediments (cf. Table 10).

Third, the dominant size fraction in the surface soils is sand, which is not consistent with deposition of a large amount of dust from the tailings and waste rock dumps (Figure 9). The sand itself, especially the medium and coarse-grained sand, can scarcely have come from there. Grains of sand > 100 μm are transported only by saltation or reptation, and 90% do not move higher than 60 cm; the majority even move less than 13 cm (Sharp 1964, Livingstone and Warren 1996). In the Cerbat Mountains the sand would have had to overcome 20°-25° slopes covered with low shrubs and bushes and differences of elevation of 70-160 m from the place of origin.

It cannot be the plant cover that is responsible for the slight degree of wind erosion, because for the most part there is no vegetation on the tailings and waste rock dumps. On the pediments and bajadas west of the Cerbat Mountains the average coverage is only 20%, and in the mountains it varies between 30% and 40%, or 20% around the mines (Rösner 1998). Evidently the most important factor is the structure of the soil surface. The top few millimeters are always more or less consolidated in relation to the looser material underneath (Figure 10). This corresponds to the data from the dual samples, which show that salts are concentrated in the uppermost



1 = Clay (< 2 µm); 2 = Silt (2 - 6.3 µm); 3 = Silt (6.3 - 20 µm); 4 = Silt (20 - 63 µm); 5 = Sand (63 - 200 µm); 6 = Sand (200 - 630 µm); 7 = Sand (630 - 2000 µm)

Figure 9: Particle size distribution in some surface soils in the Wallapai Mining District.

centimeters. On the CMP Mine tailings the difference in the EC values even lay between 3150 μS/cm in the upper sample and 1595 μS/cm in the lower one.

Such "structural crusts" have been described frequently (e.g., McIntyre 1958, Gillette et al. 1982, Mualem et al. 1990). Usually impacting raindrops are responsible. They break down aggregates, dislodge soil particles, and compress the upper few millimeters of soil (McIntyre 1958, Mualem et al. 1990). The cohesive forces among

Figure 10: Example of a "structural surface crust".

the primary soil particles increase as the soil dries, and higher clay contents encourage the formation of crusts (Mualem et al. 1990). Even slight salt concentrations can contribute to surface crusting (Nickling and Ecclestone 1981, Nickling 1984). All of this has the effect of inhibiting deflation, not only in the surface soils, but especially in the material of the tailings with its high clay and silt content. To what extent bacteria, fungi or algae are involved cannot be determined from the available data.

According to studies by Gillette et al. (1982), even weak crusts will protect the soil from wind erosion, whereas disturbed soils are easily eroded. In the spring of 1995, for instance, the large tailings of the CMP Mine were being leveled with a caterpillar when a very strong wind was blowing. Enormous clouds of dust were blown up and driven into the mountains by the wind. At the same time nothing was happening on the large old Tennessee Mine tailings. A desert pavement, like that common on pediments and bajadas in our study area, also helps greatly to protect against erosion, according to Gillette et al. (1982).

5.3 Potential Environmental Hazard due to Mining-Related Metals

The magnitude of the environmental risk related to metals is determined primarily by their mobility. With a few exceptions, the higher the content of small particle sizes (especially clay), organic matter and oxides (especially iron and manganese oxide) is and the higher the pH is, the better the metals are adsorbed in the soil (Herms and Brümmer 1984, Brümmer et al. 1986, Herms 1989, Sauerbeck 1989, Horowitz 1991, Schachtschabel et al. 1992). However, with increasing salt concentrations (particularly of sodium salts) especially metals with weak bonds such as Cd and Zn go into solution (Herms and Brümmer 1984, Herms 1989). Due to their varying adsorption capacity the mobility of the individual trace elements in the soil varies: Cd and Zn > Cu and Ni > Pb, Cr, Hg and As (listed from high to low mobility) (Sauerbeck 1989, Bergmann 1989).

If we look at the correlations between the factors investigated in the streambed sediments (Table 12) and the surface soils (Table 13) from the point of view of mobility, we can derive the following interpretations:

The highly significant intercorrelations between most of the metals (e.g., Cd and Zn in soils: $r = 1$!) reflect the natural associations of the ore minerals, which were described in detail by Schrader (1909) and Dings (1951). This is attributable to the fact that the processes of mining and processing released a very similar spectrum of heavy metals into the environment. The correlations with Fe and Mn will be discussed further on.

Except for Fe in the streambed sediments the metal contents do not correlate with the relatively high pH values. This could mean that in our study area the pH does not play a crucial role in fixing the metals in soils and sediments, but that the effects of other factors predominate. Independent of this, in neutral to alkaline soils the metals remain immobilized as long as the pH does not drop below the limit for a given metal (e.g., Herms and Brümmer 1984, Brümmer et al. 1986, Gäbler 1997). According to a compilation by Schachtschabel et al. (1992) this limit is 6.5 for Cd, between 5.5-6.5 for Zn and Ni and between 4-4.5 for Cu, As, Cr, and Pb.

For organic matter there is a significant positive correlation only with Fe. Because of the low humus content the organic sorption complexes evidently do not play an important role in the immobilization of heavy metals.

The high positive correlations with the total salt concentration in the streambed sediments reveal nothing about the binding of the heavy metals. They indicate that tailings material is entering the washes directly, as discussed above.

Despite their known sorption properties, the only correlation with the finest particles (clay < 2μm, fine silt 2-6.3 μm) is a weak one with Cr, Cu and Fe. This is

		Correlation matrix*									Statistical characteritics				
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Mean	Max.	Min.	SD	n
pH(H_2O)		—	—	—	—	—	—	—	—	—	7.4	8.7	4.6	0.8	60
pH($CaCl_2$)		—	—	—	—	—	—	—	—	—	6.7	8.0	4.1	0.8	60
Corg. (%)		-0.32	—	—	—	0.39	—	—	—	—	1.8	3.1	0.4	0.6	60
EC (µS/cm)		—	—	0.25	0.25	—	—	—	—	—	68.6	175.0	16.6	36.8	60
$CaCO_3$ (%)		—	—	—	—	-0.25	—	—	—	—	1.5	18.9	0.0	3.7	60
Clay**	< 2	—	—	—	0.29	—	—	—	—	—	8.9	27.7	1.6	4.2	60
Silt**	2 - 6.3	—	—	—	—	0.35	—	—	—	—	3.4	10.4	0.0	2.0	60
	6.3 - 20	-0.30	—	—	—	—	—	—	-0.26	—	4.7	9.1	0.4	1.8	60
	20 - 63	-0.32	-0.33	—	—	—	-0.28	—	-0.33	-0.35	12.4	24.3	0.6	4.6	60
Sand**	63 - 200	—	—	—	—	—	—	0.31	—	—	23.4	49.6	9.0	7.3	60
	200 - 630	**0.62**	**0.60**	—	—	—	0.38	—	**0.59**	**0.60**	25.7	68.6	14.5	8.5	60
	630 - 2000	-0.39	-0.38	—	—	—	-0.36	—	-0.39	-0.38	21.4	42.9	0.3	7.3	60
As			**0.96**	—	—	0.30	**0.72**	—	**0.98**	**0.95**	40.3	1100.0	2.3	145.8	60
Cd				—	—	0.31	**0.78**	—	**0.96**	**1.00**	1.3	41.0	0.1	5.3	60
Cr					—	0.33	—	**0.63**	—	—	16.7	52.0	4.4	9.0	60
Cu						—	—	—	—	—	44.2	570.0	1.8	84.2	60
Fe							**0.66**	0.26	0.36	0.32	18246.7	33000.0	7800.0	6917.0	60
Mn								—	**0.81**	**0.79**	508.2	2800.0	200.0	436.4	60
Ni									—	—	10.0	33.0	4.1	4.8	60
Pb										**0.96**	65.8	1300.0	5.6	172.1	60
Zn											394.2	12000.0	29.0	1577.6	60

* All surface soil samples are included in the calculations of the correlation coefficients with the exception of samples from tailings and from soil profiles at a depth greater than 7.5 cm. Significance levels: 0.25 (5 %), 0.32 (1 %), **0.41 (0.1 %)**. Only correlation coefficients at a significance level of 5 % or better are presented; therefore, a dash (—) indicates that there was no significant correlation. ** Particle size distribution in percentage of weight, particle diameter in µm. SD = standard deviation; n = number of samples.

Table 13: Correlation between metals and soil properties (on the left side of the table), and statistical characteristics (on the right side of the table) of the surface soils (not included are the samples from the soil profiles from a depth > 7.5 cm and samples from the tailings).

partially attributable to their low proportion. On the other hand, it can mean that no direct binding of the heavy metals to clay minerals occurs (cf. below). In contrast, in the surface soils (Table 13) there is a highly significant positive correlation between As, Cd, Mn, Pb and Zn and the fraction of medium-grained sand (200-630 µm) and simultaneously a negative correlation with coarse-grained silt (20-63 µm) and with coarse-grained sand (630-2000 µm). These metals therefore occur predominantly in the fraction of medium-grained sand.

Since As, Cd, Pb and Zn simultaneously show a significant positive correlation with Mn and Fe, we can assume that they are adsorbed to iron and manganese oxides, although the type cannot be determined with the available data. Cr and Ni, in contrast, are more probably coupled to iron oxides.

Iron and manganese oxides are excellent trace element collectors because of their amorphous or poorly crystallized structure, their large surface area and their high cation exchange capacity (Forstner and Wittmann 1981, Horowitz 1991, Horowitz and Elrick 1987). They occur either as finely dispersed particles or as coatings on mineral grains (Horowitz 1991). This explains why in the investigated samples there is a poor correlation with clay minerals, whose surfaces will first be occupied by iron and manganese oxides. It also explains the dominance of the metals in the fraction of medium-grained sand (Table 13), because the coatings can cause aggregation of the finer particle sizes and thus an increase in size. Conversely, this makes the positive correlation with the finer particle size fractions in the streambed sediments understandable (Table 12), because during transport in flowing water such aggregates can easily be broken apart by mechanical processes.

According to Horowitz (1991) trace elements associated with ferromanganese coatings are probably stable or not available to the environment, as long as there are no significant changes in the soil milieu. We probably do not need to fear significant changes in the solution conditions in the soil in our study area, considering the soil moisture deficit from March to mid-November (cf. Hendricks 1985: 42, Figure 32) and the presumably highly decreased infiltration capacity due to the surface crusts (cf. Mualem et al. 1990). Accordingly there is no demonstrable degree of vertical metal transport into deeper horizons, as the two profiles 8 and 9 showed.

Groundwater analyses (Rösner 1995a, 1996) showed that the underground water is only contaminated in the immediate vicinity of the mines, if at all. For instance, there are no elevated concentrations of metals in the groundwater of Chloride, which lies at the foot of the Cerbat Mountains only 800-1300 m west of the Tennessee Mine with its highly contaminated groundwater. The most plausible explanation for this still appears to lie in the special tectonic conditions at the foot of the Cerbat Mountains, which may impede groundwater flow from the mining area to the Chloride aquifer (Rösner 1995a: 20, 1996: 85). Nevertheless, from the new findings presented in this study it can be inferred that fixation of the metals in soils and sediments and the aridic to xeric soil moisture regime play an important auxiliary role.

Furthermore, vegetation analyses confirmed that a considerable proportion of the total heavy metal content is evidently not available to plants, because on contaminated sites the metal concentrations in plants did not increase proportionally to the heavy metal concentrations in the soil (Rösner 1998). Apart from specific protective mechanisms possessed by the plants, this can only be due to the binding of the metals in the soil to Fe and Mn oxides and the shortage of soil water as solution medium (Rösner 1998).

6 SUMMARY AND CONCLUSIONS

The remnants of historic mining in the Wallapai Mining District continue to represent sources of heavy metal contamination for streambed sediments and surface soils. On the whole, however, metal concentrations decrease strongly within short distances of the mining districts, with the exception of some modifications due to a few point sources of pollution.

For the streambed sediments three reasons were identified for the quick recovery from the effects of pollution. First, the contaminated, acidic water from collapsed mine adits or from tailings becomes mixed with clean unpolluted, alkaline stream water, causing rapid precipitation and sedimentation of the dissolved metals. Second, transmission losses and evaporation often reduce the amount of water so much within the Cerbat Mountains that supersaturation and precipitation of the metals occur. Third, to what extent the metals are transported further downstream with contaminated sediments depends on the nature of flow in the ephemeral stream channels, which is controlled by local climatic conditions (amount, type and distribution of rainfall) and the permeability of the channel bed material.

For the surface soils we can hazard the following interpretation, based on the horizontal distribution of metal concentrations and the particle size distributions: contaminated sediments are spread by the wind, but the amounts transported are not very large and they are not transported over any great distances; thin surface crusts play an important role in protecting against wind erosion. They protect particularly the finer grained and salt enriched surfaces of the tailings from deflation. We do not mean to dispute that dust storms and sandstorms can occur in this part of northwestern Arizona, but they evidently do not have any great impact as far as the spread of sediments is concerned. When they occur, how frequently they occur and what impact they have on sediment transport will have to be left to further investigations, like those done by Brazel et al. (1986) and Brazel and Nickling (1986) especially for southern Arizona.

The data from the Wallapai Mining District additionally show that the mobility of heavy metals in soils and sediments is evidently highly restricted. Although this cannot be proven without any trace of doubt, we can plausibly narrow the reasons down to the following: the stable binding to Fe and Mn oxides, which have the reputation of being good heavy metal collectors (Brümmer et al. 1986, Horowitz 1991, Schachtschabel et al. 1992), the soil moisture deficit prevailing here for most of the year, and the high pH values (around 7 and above), which would prevent the metals investigated here from going into solution even if enough water were available.

Judging from the distribution and potential mobility of the heavy metals and the results of recent groundwater and vegetation studies, the environmental hazard in this region remains at a tolerable level.

Compared with humid regions there are differences, which though they cannot be formulated quantitatively, can at least be described qualitatively. For instance, solution and suspension naturally play a much more important role in heavy metal transport in perennial streams than in ephemeral streams and contribute significantly to a more extensive downstream distribution (Horowitz 1991, Symander 1978, Symander and Herrman 1979). Another reason is that rivers in temperate latitudes have a much greater tendency to form fine-grained floodplains, from which heavy metals can later be remobilized time and again (Bradley 1989, Miller 1997).

In principle thin surface crusts do occur in humid regions as well (Norton et al. 1993, Chiang et al. 1993), but they form more easily in arid regions (Mualem et al. 1990). For one thing, the sparse plant cover is unable to absorb the impact of the raindrops, and soil openings become sealed by particles shifted by raindrop splash. Moreover, high evaporation and frequent and strong winds cause the soil surface to dry rapidly, which again encourages the cohesion of the particles and salt enrichment. On the other hand, when the surface is disturbed stronger wind erosion can be expected, because the soil is dried out for months and the winds are usually strong. This contrasts with humid regions, where the greater remaining soil moisture retards deflation (Livingstone & Warren 1996).

The greatest difference is probably the more favorable soil moisture budget in regions that are moist all year round. The low pH values, particularly under forest cover, resulting from the more intensive soil formation lead to a milieu that encourages the mobilization of metals, theoretically leading to a greater hazard to groundwater and vegetation (Gäbler 1997, Brümmer et al. 1986, Schachtschabel et al. 1992).

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