Applied Geochemistry, Vol. 6, pp. 75–88, 1991
Printed in Great Britain

Pergamon Press plc

Large-scale distribution of metal contamination in the fine-grained sediments of the Clark Fork River, Montana, U.S.A.

ELLEN V. AXTMANN and SAMUEL N. LUOMA
U.S. Geological Survey, Mail Stop 465, 345 Middlefield Road, Menlo Park, CA 94025, U.S.A.

(*Received* 16 *June* 1989; *accepted in revised form* 19 *April* 1990)

Abstract—Historic discharges from the mining and smelting complex at the head-waters of the Clark Fork River have resulted in elevated Ag, Cd, Cu, Pb and Zn concentrations in the <60 μm fraction of both bed and flood-plain sediments of the river. Processes affecting the trends in longitudinal distributions of these metals were investigated by repeated sampling over a 380 km river reach between August 1986 and July 1989. At the most upstream site, bed-sediment metal concentrations were enriched 18–115 times above least enriched tributaries, depending on the metal. All metals decreased exponentially with distance downstream away from mining. The exponential model predicts that elevated metal concentrations should occur over 550 km downstream, in Lake Pend Oreille. Longitudinal trends, obvious on a scale of hundreds of kilometers, were obscured by small-scale spatial variability when shorter stretches of the river were considered. Longitudinal dispersion appeared to be controlled largely by physical dilution with less-contaminated sediments.

Evidence suggests that erosion of contaminated flood-plains contributes to metal contamination in the bed sediments. Tributary input appeared to have little influence on the large-scale, downstream distribution of metals; however, it did contribute to local variability in bed-sediment metal concentrations. Association of metals with specific mineral grains, as well as variability in total organic C and Fe concentration, appeared also to contribute to variability.

Some year-to-year variability in bed-sediment metal concentrations was observed, however, trends in longitudinal dispersion were not significantly different between at least two of the years sampled.

INTRODUCTION

AN INCREASED awareness of long-term adverse effects has prompted numerous studies of the fate of metals in rivers. These studies show that metals of anthropogenic and natural origin are concentrated in the particulate load, and that this material is largely responsible for the transport and storage of metals in non-acidic river systems (GIBBS, 1973; REECE *et al.*, 1978; JENNETT and FOIL, 1979; JENNE *et al.*, 1980; TESSIER *et al.*, 1980; BRADLEY and LEWIN, 1982; SALOMONS and FORSTNER, 1984; MARRON, 1987; LEENAERS *et al.*, 1988). Such studies indicate that the distribution of sediment-bound metals in a river can be affected by the source and form of primary inputs (BRADLEY and COX, 1986), the physical and chemical characteristics of the river (GEESEY *et al.*, 1984), the nature of the sediment itself (TESSIER *et al.*, 1980, 1982), and inputs of sediment from flood-plain erosion, bed scour and tributaries (WOLFENDEN and LEWIN, 1977; BRADLEY and COX, 1986; PARKS *et al.*, 1986; LEENAERS *et al.*, 1988). Although most studies emphasize physical or chemical processes occurring on spatial scales of 1–100 km (LEWIS, 1977; TESSIER *et al.*, 1982; CHAPMAN *et al.*, 1983; NORDSTROM and BALL, 1985; JONES, 1986; PAGENKOPF and CAMERON, 1979; MORIARTY *et al.*, 1982; HOUBA *et al.*, 1983; PARKS *et al.*, 1986; BRADLEY and COX, 1987), larger scale distribution of contamination is indicated in a few instances (JACKSON 1978; HOROWITZ *et al.*, 1988).

High-gradient rivers with coarse-grained sediments create special difficulties for studying metal contamination because of the heterogeneity of bed material. In western North America many such rivers are associated with areas of mineral extraction activities. One example is the Clark Fork River, Montana, where large-scale copper mining and smelting occurred for more than a century in the head-waters. Small-scale mining activities in the tributaries, agriculture, one small city (Missoula, population 40,000) and one paper-pulp mill are the other major human activities in the upper 550 km of the river. Thus the Clark Fork River provides an opportunity to study metal contamination from a single large source over long distances in the absence of confounding variables common in many other systems.

Earlier studies demonstrated that As, Cd, Cu, Pb and Zn were significantly enriched in flood-plain and bed sediments of the Clark Fork River (ANDREWS, 1987; BROOK and MOORE, 1988; MOORE *et al.*, 1989). A downstream decline in metal concentrations in fine-grained bed sediments was reported by ANDREWS (1987), but was not as obvious over the shorter reach studied by BROOK and MOORE (1988). Both ANDREWS (1987) and MOORE *et al.* (1989) reported finding the highest metal concentrations in fine-grained fractions of the sediment, although MOORE *et al.* (1989) point out that in a river with coarse-grained sediment such as the Clark Fork River, this fine-grained material may not be the most important fraction of the metal load in the river.

The purpose of this paper is to characterize better,

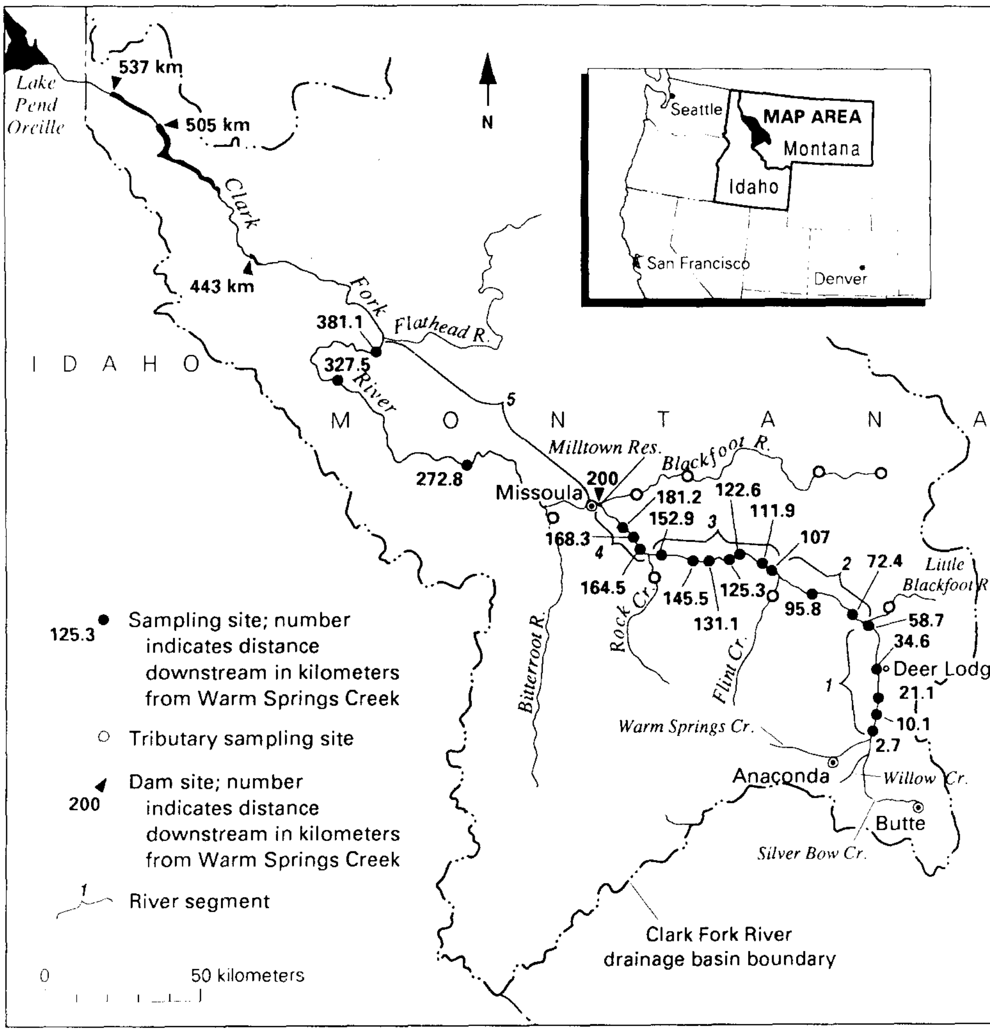

FIG. 1. Map of Clark Fork River Basin, Montana. Sampling sites are marked by kilometers downstream from Warm Springs Creek.

the distributions of Ag, Cd, Cu, Pb, Zn, Fe and Mn contamination in bed and flood-plain sediments through the upper 381 km of the Clark Fork River, with the goal of improving understanding of the fate of metals in rivers of this type. The study investigates several questions important in metal contaminated rivers, including the downstream extent of contamination, the effects on trend characterization of sampling on different spatial scales, differences in concentrations between years, and the influences of flood-plain and tributary inputs on metal concentrations. Analysis of fine-grained sediment fractions has been recommended in surveillance of metal contamination in sediments. Eliminating coarse particles reduces biases resulting from differences in particle size distributions among samples (SALOMONS and FORSTNER, 1984; BRADLEY and COX, 1987). Fine-grained sediments (<60 μm) were chosen for this study to aid definition of trends, and also because benthic organisms (which are being studied simultaneously; LUOMA *et al.*, 1989) may be directly exposed to fine-grained sediments.

STUDY AREA

The Clark Fork River drains an area of ~57,400 km^2 in west–central Montana, and is the largest tributary of the Columbia River. The river is formed by the confluence of Silver Bow, Willow, and Warm Springs Creeks (henceforth, all sites are referred to by their location in kilometers as measured downstream from the confluence of Warm Srings Creek (Fig. 1); RIVER MILE INDEX, 1976). At its head-waters the Clark Fork River has a mean daily flow of 4.5 m^3 s^{-1} (Fig. 1). By the time it reaches Lake Pend Oreille, 554 km from this confluence, the mean daily flow is 634 m^3 s^{-1}.

In 1864, placer gold deposits were discovered at the head-waters of Silver Bow Creek. Since that time, Cu, Ag, Pb, Zn and Mn have been mined from mineralized zones associated with the Boulder Batholith (PERRY, 1932). Copper in the Butte district is predominantly in the form of sulfide minerals, the most common being chalcocite, bornite, enargite and chalcopyrite. Other associated sulfides include pyrite, sphalerite, galena and acanthite (MILLER, 1973). Between 1880 and 1972, >400 million metric tons of ore were mined in the Butte district (MILLER, 1973). Until the completion of settling ponds on Silver Bow Creek in the mid-1950s, >100 million metric tons of mine and smelter tailings were released via Silver Bow and Warm Springs Creeks into the Clark Fork River (ANDREWS, 1987). Below the tailings ponds, water in the Clark Fork River is approximately neutral (pH 6.4–8.8) although pH values from 2.4–7 have been recorded in Silver Bow Creek (BOETTCHER and GOSLING, 1977; BROSTEN and JACOBSON, 1985).

It is estimated that >2 M m^3 of contaminated sediments were deposited in the flood-plains of the Clark Fork River during the last 125 a (J. N. MOORE, University of Montana, pers. commun.). The present river channel meanders through this contaminated flood-plain. The meanders are mostly unrestricted in areas of open flood-plain, especially in the upper 100 km. However, aerial photographs (USEPA, 1983) show considerable channel straightening from ~110 to 160 km. Meanders in this region are constrained in several places as a result of construction of two railroads (around the turn of the century) and a large highway (between the mid-1960s and late 1970s). Four hydroelectric dams also were constructed along the river between 1906 and 1907 (the most upstream dam) and the 1950s (Fig. 1).

The extent of historical mining activity differed among the major tributaries. Flint Creek (Fig. 1) drains a silver and gold mining district at Philipsburg, and the head-waters of the Blackfoot River are affected by acid mine drainage from several small silver and lead mines (JOHNSON and SCHMIDT, 1988). Some acid mine drainage is also reported in the watershed of the Little Blackfoot River (JOHNSON and SCHMIDT, 1988). Although small-scale placer mining was reported on the Bitterroot River and Rock Creek (DINGMAN, 1932), mining activity on these streams is much less than on other tributaries.

METHODS

Bed sediments

Field sampling of bed sediment, conducted between August 1986 and July 1989, was designed to test six questions.

1. Do trace metal concentrations in Clark Fork River sediments exceed "reference" concentrations defined by tributaries with the least history of mining activity? To test this question bed sediments were collected from five of the largest tributary streams within 25 km of their mouths for comparison with the Clark Fork River samples (Fig. 1); and a four-sample downstream transect of bed sediment was collected from the Blackfoot River, a tributary of similar size to the Clark Fork River.

2. Do metal concentrations in fine-grained sediments of the Clark Fork River display a discernable downstream trend over hundreds of kilometers? To test this question bed sediments were collected from 17 sites, in 1986 and 1987, at an average interval of 11 km throughout the upper 181 km of the Clark Fork River and at three more sites in the next 200 km of the river (Fig. 1). Downstream trends were compared between 1986 and 1987 by regressing ln-transformed metal data from individual years against kilometers, then analysis of covariance was performed to check for equality of slopes and intercepts between years. The slopes for Ag, Cd, Cu, Pb and Zn were not significantly different ($p < 0.05$) between years, and therefore 1986 and 1987 data were combined in the overall trend analysis.

3. Are trends in metal concentrations discernable on spatial scales of tens of kilometers in the Clark Fork River? The river was divided into segments, defined as reaches between major tributaries (Fig. 1), and data from within segments were aggregated to statistically test differences on such spatial scales (Mann–Whitney; $p < 0.05$).

4. Are metal concentrations in the Clark Fork River affected by a tributary near its confluence with the Clark Fork River? In 1989, triplicate samples were collected from each of seven sites located within 10 km upstream and downstream of the confluence of Flint Creek to assess this question.

5. What is the typical variability in metal concentration among deposits of fine-grained sediment at a site in a rocky bottom river? Five to seven replicate samples were collected at each of six sites on the Clark Fork River and one site in the upper Blackfoot River during 1987 and 1988. Samples were collected from individual fine-grained sediment deposits within a 30-m section and when possible from both sides of the river.

6. Do metal concentrations in sediments collected at low flow differ among years? Two statistical tests were employed to answer this question. The slopes of downstream trends observed in 1986, 1987 and 1988 were compared by analysis of covariance for significant differences. In the second test, differences between years were determined by comparing within-site variability with year-to-year variability at five sites where both sets of data were available. Replicate samples from each of these sites were compared with single samples collected in other years, employing one-way ANOVA or a t-test (SOKAL and ROHLF, 1969) (i.e. the hypothesis (H_0) was tested that a single sample collected from a site one year is from the same population as the replicate samples collected at the same site in a different year).

At each site, fine-grained bed sediments were scraped from the surface of several deposits in slack waters at the edge of the river using a polypropylene scoop and immediately wet-sieved in ambient river water through a 60 μm nylon mesh sieve (U.S. Standard Sieve Mesh #230). Slurries were transported on ice, then dried at 80°C, and ground to a fine powder for analysis. Dried subsamples were subjected to a hot, concentrated HNO_3 reflux (LUOMA and BRYAN, 1981). Samples collected in 1989 were subjected to a concentrated HF–HNO_3–HCl microwave digestion (BROOK and MOORE, 1988). Reagent blanks were taken through the same digestion procedures. Silver, Cd, Cu, Pb, Zn, Fe and Mn were determined on the 1986–1988 samples using flame atomic absorption spectrometry. Samples collected in 1989 were analyzed for Cu, Pb and Zn by inductively coupled argon plasma spectrometry.

Although the HNO_3 reflux may not liberate trace metals in silicate lattices, recoveries for routinely conducted analyses of the NBS reference material 1645 (River Sediment) were consistent, and ranged between 79 and 97%, depending on the metal (Table 1). Values for Cu, Pb, Mn and Zn were all within the acceptable range reported by NBS. The

Table 1. Results of analysis of NBS Standard Reference Material 1645 (River sediment) using hot HNO_3 digestion (1986–1989) and HF–HNO_3–HCl microwave digestion (1989)

Element	NBS value	1986–1988 $n = 11$	% recovery	1989 $n = 7$	% recovery
Ag	Not reported	2.1 ± 0.5	—	—	—
Cd	10.2 ± 1.5	8.2 ± 0.4	79	—	—
Cu	109 ± 19	107 ± 4	97	105 ± 5	96
Fe	11.3 ± 1.2	9.9 ± 0.3	86	—	—
Mn	785 ± 97	702 ± 44	87	—	—
Pb	714 ± 28	687 ± 15	96	651 ± 37	91
Zn	1720 ± 170	1581 ± 115	95	1642 ± 68	95

Metal concentrations (with the exception of Fe) are reported in $\mu g/g$ ± 95% confidence interval. Iron concentrations are reported in weight per cent.

HF–HNO_3–HCl microwave digestions of NBS reference material 1645 agreed closely with the HNO_3 digests; all metals except Pb fell within the acceptable range reported by NBS.

Total C and inorganic C were analyzed on some subsamples of bed sediment. Total C was determined by total combustion of the sediment and CO_2 detection by an infrared analyzer. Inorganic C was measured as the acid-soluble fraction of the sediment. A hot phosphoric acid digest was used to convert carbonate to CO_2, which was measured on the carbon analyzer. Total organic C was determined by difference.

Flood-plain sediments

Flood-plain sediments were collected from 16 sites in the upper 181 km of Clark Fork River in 1986 and 1987 in order to compare contamination in banks that might slump into the river with contamination in the river bed. To satisfy this objective the flood-plain sediments were collected from a vertical trench on the face of eroding cutbanks, thus obtaining an estimate of the input to the river from all soil horizons in the cutbank. The face of the cutbank was scraped off to expose a fresh surface, then a narrow trench sample of 1–2 kg was taken using a polypropylene scoop, sampling from just below the root zone to the bottom of the cutbank. Layers of large cobbles were not sampled. Replicate trench samples were transported back to the laboratory where they were air-dried, and wet-sieved through 60 μm nylon mesh into ultra-pure water adjusted to pH 7 with NaOH. The supernatant was decanted off and saved for analysis, and the <60 μm fraction was dried at 80°C, and ground to a fine powder for analysis. Analysis of the supernatant showed that only Mn was significantly mobilized during sieving. Digestion and analytical procedures were the same as with bed sediments.

Replicate sampling of the same trench at four sites in the Clark Fork River and one site in the Blackfoot River was employed to test variability in the sampling method. The coefficients of variation (CV) of replicate samples ranged from 0 to 29% depending on the site and metal, but averaged 2 to 16%, depending on the site. At two sites (72.4 and 152.9 km) trenches 5 m apart were sampled to test variability on a small spatial scale. Although this is not a large enough sampling effort to provide quantitative characterization, it appeared that substantial variability was possible on this scale (33% for Ag at 72.4 km). Samples collected at 152.9 km had relatively low variability, ranging from 0 to 15%, and averaging 4.5%.

Eight of the bank samples were collected at close (3–14 km) intervals between 111.9 and 168.3 km to assess variability in metal concentration in a reach where the river channel had been extensively modified. In addition to the shortening of the river channel, two artificial meanders were constructed in this area (between ~115 km and 160 km) during highway construction in the 1960s (Hunt and Graham, 1975). Some of this construction appeared to separate the river from its historic flood-plain, hence samples collected from this reach probably reflect maximum variability in flood-plain metal concentrations.

RESULTS

Tributary reference values

The lowest concentrations of metals in tributary sediments were observed in Rock Creek, the Bitterroot River, and the Blackfoot River within 71 km of the Clark Fork River confluence (Table 2). Because these also represent watersheds subjected to the least historic mining activities or locations >100 km from mining inputs, mean metal concentrations from these five samples were taken as operational reference concentrations or indicators of pre-mining concentrations in the Clark Fork River sediments. The mean reference concentration of Cu, Pb and Zn (but not Ag or Cd) was significantly lower ($p < 0.05$) than concentrations reported for average shale (Turekian and Wedepohl, 1961), which has been suggested as a reference in other studies (Salomons and Forstner, 1984). Concentrations of all five metals in Flint Creek, the uppermost Blackfoot River and the Little Blackfoot River were significantly higher than the mean reference concentration ($p < 0.05$), which is consistent with the history of mining activity in these watersheds.

Large-scale trends in Clark Fork River bank and bed sediments

Bed sediments. Concentrations of Ag, Cd, Cu, Pb and Zn in bed sediments in all five segments of the Clark Fork River (Fig. 1) were significantly higher (Mann–Whitney; $p < 0.05$) than the operationally defined mean reference concentrations from the tributaries (Tables 2 and 3). At 2.7 km, where the highest concentrations were found, sediments were

Table 2. Concentrations of Ag, Cd, Cu, Pb and Zn (μg/g dry wt) in the <60 μm fraction of bed sediment collected in 1986 and 1987 from five major tributaries of the Clark Fork River. With the exception of several sites on the Blackfoot River, all samples were collected within 25 km of the mouths of the tributaries (kilometers upstream from confluence with Clark Fork River are noted in parentheses)

	[Ag]	[Cd]	[Cu]	[Pb]	[Zn]
Tributary stations influenced by mining					
Flint Creek	6.5	2.0	57	190	672
Blackfoot River (173.8 km)	≤0.2	2.8	95	38	845
Blackfoot River (150.4 km)	≤0.2	≤0.3	35	19	113
Little Blackfoot River*	0.6	0.8	39	47	171
Tributary stations least influenced by mining					
Blackfoot River (71.0 km)	≤0.2	≤0.3	27	13	56
Blackfoot River (22.5 km)	≤0.2	≤0.3	21	11	54
Blackfoot River (20.8 km)	0.6	≤0.3	22	9	60
Rock Creek*	≤0.2	≤0.3	14	10	45
Bitterroot River	≤0.2	≤0.3	17	10	48
Main reference concentration†	0.3 ± 0.2	≤0.3 ± 0.0	20 ± 5.0	11 ± 1.5	53 ± 6.1
Av. Shale‡	0.07	0.22	45	20	95

*Concentrations are means for 1986 and 1987 data. Data for individual years are reported in Table 8.
†Mean reference concentrations are the mean concentrations of the five tributary stations that are least influenced by mining.
‡TUREKIAN and WEDEPOHL (1961). These are total concentrations.

enriched 18- (Ag), >67- (Cd), 115- (Cu), 21- (Pb), and 66-fold (Zn) over mean reference concentrations. Downstream at 381.1 km, Clark Fork River sediments were enriched 4-, >6-, 6-, 4- and 8-fold respectively.

Concentrations of all metals decreased exponentially with distance downstream over the 381 km of the study area (Fig. 2). The downstream decrease for each metal followed the equation

$$\ln [\mathrm{Me}_{i,d}] = a + b\,(\mathrm{km}) \qquad (1)$$

where $\mathrm{Me}_{i,d}$ is the concentration of metal i at distance d, a is the y intercept, and b is the slope of the relation.

Table 3. Trace metal concentrations (μg/g dry wt) in <60 μm bed and flood-plain (bank) sediment of the Clark Fork River observed in 1986 and 1987

Site	[Ag]		[Cd]		[Cu]		[Pb]		[Zn]	
(km)	Bed	Bank	Bed	Bank	Bed	Bank	Bed	Bank	Bed	Bank
2.7+	5.6	—	20.0	—	2298	—	235	—	3561	—
10.1	4.4	6.4	12.6	57.8	1558	3069	156	318	2062	6298
21.1*	5.3	15.0	10.1	4.6	1472	3823	181	405	1994	1255
34.6*	4.9	14.0	7.8	6.2	1992	2759	159	496	1597	1849
58.7	3.3	5.8	5.6	17.1	857	2081	112	217	1285	5687
72.4*	3.9	3.9	6.7	6.4	1011	834	127	140	1364	2212
95.8	3.7	3.6	6.7	7.5	859	1156	107	126	1349	3560
107.0	4.8	3.7	5.2	6.8	736	747	133	160	1251	3296
111.9	4.4	3.2	4.8	6.7	696	549	120	114	1171	1568
122.6+*	2.9	0.8	4.8	≤0.3	556	33	100	15	1129	113
125.3	3.0	≤0.2	7.4	≤0.2	735	54	121	21	1441	128
131.1	2.8	3.0	6.8	8.8	631	802	110	169	1430	3878
145.5	2.8	2.4	5.8	1.6	604	683	102	99	1150	435
152.9	2.9	0.7	3.8	≤0.3	417	35	91	13	1497	114
164.5	3.0	2.6	3.5	4.6	442	476	94	116	1162	2734
168.3*	2.3	2.3	5.0	14.8	466	729	84	118	1168	5204
181.2	2.9	2.5	5.2	4.8	561	522	94	102	1161	2126
272.8	2.1	—	2.6	—	293	—	52	—	675	—
327.5	1.8	—	2.2	—	232	—	45	—	580	—
381.1	1.2	—	1.7	—	117	—	44	—	427	—

Means are reported where replicate bed samples were collected; standard deviations or ranges for these are reported in Table 5 (+) and Table 8 (*), respectively.

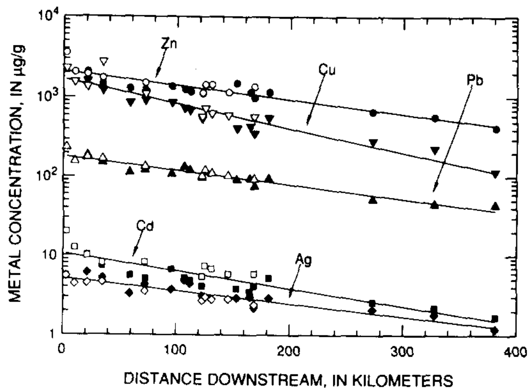

FIG. 2. Regression plot of Zn, Cu, Pb, Cd and Ag concentrations in the <60 μm fraction of bed sediments collected in 1986 (open symbols) and 1987 (closed symbols) from the Clark Fork River. Kilometers are marked as distance downstream from Warm Springs Creek.

The fit of this equation to the data for all metals was highly significant ($p < 0.001$; Fig. 2 and Table 4). The distance necessary for concentrations to decline by 50% (half distance) differed among metals, and was 98 km for Cu, 136 km for Cd, 167 km for Pb, 172 km for Zn and 188 km for Ag. The downstream distribution of sediments with metal concentrations significantly greater than the mean reference concentration was extrapolated from Eqn (1) to be 525 km for Cu, 750 km for Zn, 580 km for Pb, 550 km for Ag and ≥475 km for Cd (this is actually the distance at which Cd concentrations would be significantly greater than twice the detection limit, because all reference tributary concentrations were at or below the detection limit for Cd). This calculation predicts that sediments detectably contaminated with metal originating from the Butte/Anaconda mining and smelting district, are accumulating in Lake Pend Oreille, >550 km from their source. JOHNS and MOORE (1985) reported enriched Pb, Zn and Cu concentrations in non-sieved, fine-grained sediments in a reservoir at 537 km that were within the 95% confidence interval predicted by the exponential model in our study.

Although half-distances differed among metals, only the slope of the downstream trend for Cu differed significantly from the other metals when all metals were considered together (ANCOVA; $p < 0.05$). The differences in downstream dispersion could partly result from differences in initial and reference concentrations (ANDREWS, 1987; LEENAERS, 1989). Copper was most enriched upstream relative to its reference concentration (nearly two times the enrichment factor of the next most enriched metal). The slope of the exponential equation describing the downstream decrease was greater for those metals that were most enriched, relative to reference concentrations, and smaller for those that were least enriched.

Flood-plain sediments. Concentrations of metals were strongly enriched in most cutbank sediments relative to reference concentrations (see Tables 2 and 3; the exceptions are discussed below). However, the downstream distribution of metal was more variable in flood-plain sediments than in bed sediments and downstream trends were complex, as suggested by MOORE *et al.* (1989). No consistent downstream trend was observed for Zn or Cd over the 200 km reach sampled (see Zn profile, Fig. 3a). Concentrations of Ag, Cu and Pb all decreased with distance downstream (see Pb profile, Fig. 3b), and Eqn (1) was used to characterize the decrease. The correlation coefficient was significant ($p < 0.02$) for all three metals (Table 4). As shown by the slopes (Table 4), metal concentrations in flood-plain sediments decreased much more rapidly downstream than in bed sediments.

Modifications of the river channel appear to add to the variability among cutbanks. Some banks as little as 5.7 km apart in the most modified reach (115–160 km) differed by more than 10-fold in their metal concentrations (Table 3; Fig. 3). For example, concentrations of all metals except Zn in banks at 122.6 and 152.9 km were not significantly different ($p >$

Table 4. Experimental fits of the exponential model to Clark Fork River bed and floodplain sediments; intercept (a), slope (b) and coefficient of determination (r^2) for the relation of metal concentration with distance downstream from Warm Springs Ponds

	Bed sediments (n = 25)			Floodplain sediments (n = 16)		
	a	b	r^2	a	b	r^2
Ag	1.64	−0.00368	0.843*	2.44	−0.01165	0.591*
Cd	2.36	−0.00509	0.799*	2.59	−0.00786	0.134
Cu	7.34	−0.00705	0.889*	8.16	−0.01690	0.372**
Pb	5.20	−0.00415	0.916*	5.93	−0.01170	0.353**
Zn	7.65	−0.00404	0.825*	8.05	−0.00741	0.081
Fe	10.40	−0.00191	0.835*	10.71	−0.00358	0.516**
Mn	8.35	−0.00637	0.630*	7.39	−0.00015	0.000

* Denotes significance at $p < 0.001$; ** denotes significance at $p < 0.02$.

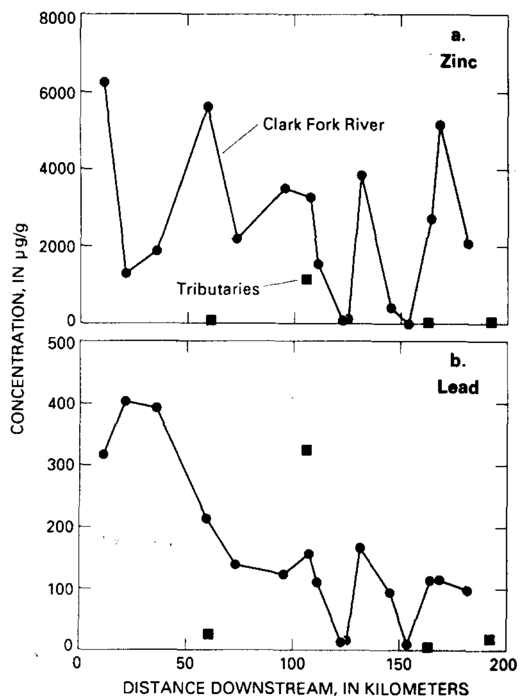

FIG. 3. Downstream distribution of (a) Zn and (b) Pb in the <60 μm size fraction of flood-plain sediment of the Clark Fork River and several main tributaries. Downstream distribution of Cu is similar to Pb; Cd is similar to Zn. Kilometers are marked as distance downstream from Warm Springs Creek.

0.05) than reference bed sediments from tributaries, but banks on either side of these (111.9 and 131.1 km) were strongly metal-enriched. Metal concentrations also were exceptionally low in a bank at 125.3 km. These results suggest that some flood-plain sediments currently exposed in cutbanks along the river do not contain mine wastes, probably because the river was moved into these areas within the last three decades. If flood-plain samples collected in this interval are removed from the regression analysis for downstream trends, coefficients of determination for Ag, Cu and Pb become much more significant ($p < 0.001$); for Ag, $r = 0.874$; for Cu, $r = 0.904$; and for Pb, $r = 0.871$ (compare to Table 4).

Bed sediment trends on 10-km scale

Although significant trends occurred in bed sediments over 381.1 km, mean metal concentrations were seldom significantly different between adjacent segments of the river in the upper 200 km. Variability in concentrations was such that, for the most part, separation of sites by >100 km (midpoint to midpoint of river segments) was necessary before significant changes ($p < 0.05$) in metal concentrations in bed sediments were detectable at the sampling frequency employed. For example, no significant differences ($p > 0.05$) were evident between mean metal concentrations in segment 1 and segment 2, but metal concentrations in segment 1 and segment 3 were always significantly different. Concentrations in segment 4 were never significantly different from concentrations in segment 5, but concentrations in segment 3 were always significantly different from those in segment 5. Clearly, large-scale sampling (hundreds of kilometers) of bed sediments was necessary in this river to determine the overall characteristics of metal dispersion trends due to large site-to-site variability on spatial scales of tens of kilometers.

Within-site variability

Variability of metal concentrations among deposits within a single site differed among stations. At the seven sites where replicate samples were collected, coefficients of variation (CV) for different metals ranged from 0% to 63% of the mean (Table 5). The degree of variability was generally more site-specific than metal-specific. Inputs from banks and variations in sediment composition both appear to contribute to the variability.

Inputs from banks. Within-site variability in sediment metal concentrations was greatest at sites adjacent to metal-rich cutbanks. The coefficients of variation for bed sediment Zn and Cd correlated significantly with metal concentrations in banks at the four sites where bank and replicate bed samples were collected (Fig. 4). The highest CV for Cu and Pb also occurred at the two sites where flood-plain concentrations were the highest, and the lowest CVs were observed where bank concentrations were lowest. These results suggest that localized input of particles from adjacent banks affected bed-sediment metal concentrations, and highly contaminated banks added to the variability observed in the river bed.

Metal concentrations in bed sediments were not determined solely by local bank inputs. Bed sediments adjacent to banks with very low metal concentrations did not always have especially low metal concentrations (see km 122.6, 125.3 and 152.9 in Table 3).

Composition of sediments. Variability in metal concentrations at some sites was also related to variability in the composition of sediments collected from different deposits. Concentrations of some metals correlated significantly ($p < 0.05$) with concentrations of Fe in replicate samples at km 2.7, 21.1, and 168.3. Total organic C correlated significantly with Ag, Cd and Cu at km 122.6.

Effect of tributaries on local metal concentrations

Metal concentrations above and below Flint Creek were employed to estimate small-scale tributary influences on metal concentrations in Clark Fork River sediments.

Flint Creek was chosen because sediment metal concentrations showed a distinctly different signature compared to the Clark Fork River (Tables 2 and 3). Flint Creek also is a relatively large tributary with a watershed similar in character to the Clark Fork River. Total water discharge from Flint Creek in water years 1985, 1986 and 1987 was 30%, 27% and 28%, respectively, of Clark Fork River discharge upstream of the confluence of the two (SHIELDS *et al.*, 1985, 1987, 1988).

Copper and Pb were employed as tracers because of the large differences in their concentrations in the two streams (Tables 2 and 3). The relative proportions of Clark Fork River and Flint Creek sediment were estimated from

$$X[\mathrm{Me}]_{\mathrm{CFa}} + (1 - X)[\mathrm{Me}]_{\mathrm{FC}} = [\mathrm{Me}]_{\mathrm{CFb}} \quad (2)$$

where X is the per cent contribution of sediment from upstream of Flint Creek, $(1 - X)$ is the per cent contribution of sediment from Flint Creek, and $[\mathrm{Me}]_{\mathrm{CFa,\,CFb,\,FC}}$ are the Pb or Cu concentrations in Clark Fork River sediments above Flint Creek (CFa), below Flint Creek (CFb) and in Flint Creek (FC). Concentrations of other metals in the downstream site were then predicted using the calculated mix of sediments, and compared to observed concentrations, as a test of the accuracy of the tracer.

In 1986, the calculation using Pb as a tracer suggested that the sample collected at 107 km on the Clark Fork River, 1.0 km below the confluence of Flint Creek, consisted of ~70% Clark Fork River sediment and 30% Flint Creek sediment (Table 6). Calculations using Cu as a tracer suggested a slightly larger contribution of Clark Fork River sediment (~85% Clark Fork River sediment and 15% Flint Creek sediment). Detailed sediment load data are not available to verify these suggestions (see, for example, dilution mixing estimates in MARCUS, 1989), but the metal signature calculated with either Pb or Cu agreed closely with that observed (Table 6). In 1989, mean Pb concentrations for the three sites within 1.5 km above and below the confluence were not different, however, Cu was used as a tracer to approximate the change in metal concentrations below the confluence (Table 6). Thus a Flint Creek signature appears to have been imposed on Clark Fork River sediments within 1.5 km of the confluence in both years, although changes in absolute metal concentrations were sometimes small.

To determine the influence of Pb inputs from Flint Creek farther downstream of the confluence, Pb concentrations determined at individual sites in 1989 were plotted with the regression line and 95% confidence intervals from Eqn (1) for the combined 1987 and 1988 data set (Fig. 5). Mean concentrations at each site within 0.8 km of the confluence fell outside the 95% confidence interval, but 1.5 and 5.0 km below Flint Creek concentrations were again within

Table 5. Comparison of coefficient of variation (CV) among replicate bed sediment samples collected at six sites on the Clark Fork River and one site on the Blackfoot River either during August 1987 (2.7 and 122.6 km) or July 1988. (Kilometers under Blackfoot River indicate distance from confluence with the Clark Fork River)

km		*n*	Aq	Cd	Cu	Pb	Zn
2.7	mean	5	5.5	20.1	2298	235	3561
	std		0.9	8.1	582	28	1003
	CV		16	40	25	12	28
21.1	mean	5	4.6	11.2	1430	194	2033
	std		0.8	1.5	223	39	517
	CV		17	13	16	20	25
111.9	mean	5	3.4	5.9	789	137	1398
	std		0.4	1.0	36	6	200
	CV		12	17	5	4	14
122.6	mean	5	2.7	5.4	582	102	1139
	std		0.1	0.4	31	4	43
	CV		4	7	5	4	4
168.3	mean	5	1.9	4.1	452	88	1339
	std		0.4	1.2	97	16	845
	CV		21	29	21	18	63
327.5	mean	7	0.7	1.2	144	38	361
	std		0.0	0.1	9	3	19
	CV		0	17	6	8	5
Blackfoot River 173.8	mean	5	bd	3.3	102	51	1106
	std		—	0.2	6	2	189
	CV		—	6	6	4	17

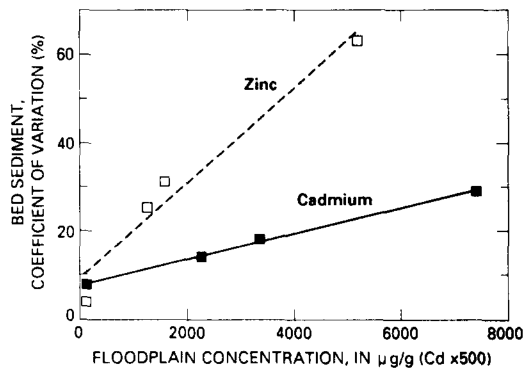

FIG. 4. Correlation plot of variability (CV—coefficient of variation), within a site, in Cd and Zn concentration in the <60 μm bed sediment with concentrations of Cd and Zn in the <60 μm fraction of flood-plain sediment collected from adjacent cutbanks.

the 95% confidence interval for the 1986 and 1987 data.

Effect of sediment composition on downstream trends

Direct influences of Mn and Fe on downstream trends in metal concentrations could not be separated from the effects of physical dilution on all elements in the Clark Fork River sediments because both Fe and Mn were enriched in the Clark Fork River sediments as a result of mining activities (Table 7). Although concentrations of all trace metals correlated strongly and significantly with Fe and to a lesser extent with Mn (also see ANDREWS, 1987), all decreased exponentially with distance downstream. Variability in Mn concentration among sites and among years was higher than for most metals. The rate of downstream decrease in concentration of Mn also was different ($p < 0.05$) between 1986 and 1987, in contrast to results with other metals.

Flood-plain Fe concentrations also were enriched upstream relative to tributary concentrations, and decreased rapidly with distance downstream (Table 7). Flood-plain Mn concentrations were much more variable than Fe concentrations and no downstream trend was evident (Table 7). The downstream Mn profile was very similar to that of flood-plain Cd and Zn. The high variability in concentrations of Mn from site-to-site in both beds and banks and its unusual year-to-year variability in bed sediments might reflect the sensitivity of the element to localized chemical processes, especially changes in reducing/oxidizing conditions or pH.

Year-to-year variability

Metal concentrations in sediments collected at low flow from the upper 168.3 km of the Clark Fork River did not differ greatly (<30%; with two exceptions) between 1986, 1987 and 1988 (Table 8). The slopes of the downstream trends observed in 1986 and 1987 were not significantly different (ANCOVA; $p > 0.05$). The range of CVs for means among years was similar to the range at the six sites where replicate samples were collected (compare Tables 5 and 8). Year-to-year differences in metal concentrations were not significantly different ($p > 0.05$) from within-site variability in nearly all cases where comparisons were possible.

Despite these similarities, year-to-year differences in sediment metal concentrations and the slope of downstream trends cannot be discounted. Significant differences between 1986 and 1988 were observed downstream. Concentrations of Ag, Cd, Cu and Zn in 1986 were significantly higher ($p < 0.01$) than the mean concentration in 1988 at km 327.5 (Table 8). The difference at this site also caused the slope of the trend in 1986 to differ significantly ($p < 0.05$) from that in 1988. Sensitive determination of year-to-year changes is limited by the relatively large site-to-site and within-site variability inherent in the system. Preliminary data suggest some changes in the slope of the downstream trend might have occurred in 1989, a year with more precipitation and higher peak flows (AXTMANN and LUOMA, unpublished data).

Table 6. Metal concentrations in the Clark Fork River near the confluence of Flint Creek (F.C.) in August 1986 and July 1989

		[Ag]	[Cd]	[Cu]	[Pb]	[Zn]	[Fe]	[Mn]
1986	Above F.C.	3.7	6.7	859	107	1349	2.670	1890
	In F.C.	6.5	2.0	57	190	672	2.290	3560
	Below F.C.	4.8	5.2	736	133	1251	2.560	1210
	Predicted$_{Pb}$	4.6	5.2	610	—	1139	2.550	2408
	Predicted$_{Cu}$	4.1	6.0	—	119	1247	2.613	2140
1989	Above F. C.	—	4.9 ± 1.1	784 ± 81	130 ± 8	1354 ± 130	3.127 ± 0.091	2262 ± 691
	In F.C.	—	≤0.5	66	189	644	2.809	4406
	Below F.C.	—	2.5 ± 1.5	455 ± 57	129 ± 16	1052 ± 176	2.834 ± 0.115	3216 ± 778
	Predicted$_{Cu}$	—	2.6	—	157	1027	2.981	3248

Predicted concentrations were calculated using either Pb or Cu as a tracer. In 1989, concentrations above and below Flint Creek are mean concentrations for three sites within 1.5 km of the confluence of Flint Creek.

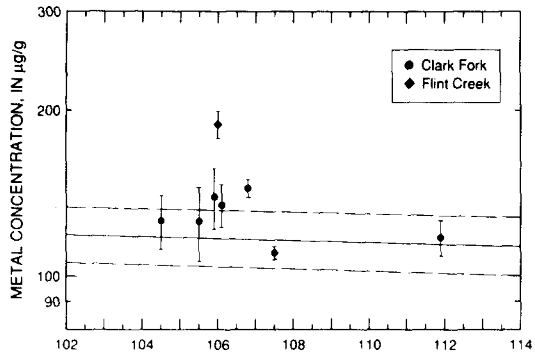

FIG. 5. Means and standard deviations for Pb concentrations in the <60 μm fraction of bed sediment collected from the Clark Fork River and Flint Creek in 1989, plotted against the regression line and 95% confidence interval for 1986 and 1987 data.

DISCUSSION

Historical discharges from the mining and smelting complex at the head-waters of the Clark Fork River have resulted in elevated Ag, Cd, Cu, Pb and Zn concentrations in the <60 μm fraction of bed sediments. This contamination extends, for some metals, >550 km from the mining and smelting district to Lake Pend Oreille.

Bed-sediment metal concentrations declined exponentially with distance downstream from the contamination source, as observed on smaller scales in some other rivers (WOLFENDEN and LEWIN, 1978; CHAPMAN *et al.*, 1983; MANN and LINTERN, 1983; PRUELL and QUINN, 1985; RYBICKA and KYZIOL, 1987; LEENAERS *et al.*, 1988). Chemical processes in the Clark Fork River were not investigated directly, but differential mobilization among metals was not evident in bed sediments. Although some differences among metals were observed in the slope of the downstream decline, the differences corresponded roughly to the degree of enrichment. LEENAERS (1989) reported similar findings for flood-plain sediments of the River Geul. Such results suggest physical dilution is more important than chemical mobilization in explaining the downstream decline in concentrations in such systems (LEENAERS, 1989; ANDREWS, 1987). The dominant importance of physical processes is not surprising in a river with near-neutral pH (pH 6.4–8.8) and where metal input is dominantly in particulate form.

Chemical processes do, however, appear to be important in the flood-plains. The downstream distribution patterns of Cd, Zn and Mn in flood-plain sediments were all very similar, and all three showed no detectable trend away from the source. Silver, Cu, Pb and Fe, on the other hand, decreased with dis-

Table 7. Iron and Mn concentrations (wt%) in <60 μm bed and flood-plain (bank) sediment collected in 1986 and 1987 from the Clark Fork River

Site (km)	[Fe] Bed	[Fe] Bank	[Mn] Bed	[Mn] Bank
Clark Fork River				
2.7+	3.98 ± 0.42	—	1.244 ± 0.398	—
10.1	2.78	7.08	0.833	0.501
21.1*	3.32 ± 0.16	3.14	0.422 ± 0.777	0.876
34.6*	2.90 ± 0.08	3.16	0.374 ± 0.322	0.781
58.7	2.81	3.96	0.253	2.651
72.4*	2.64 ± 0.13	2.99	0.189 ± 0.089	1.846
95.8	2.67	3.62	0.189	1.444
107.0	2.55	2.71	0.121	3.466
111.9	2.61	2.51	0.154	1.767
122.6+*	2.35 ± 0.04	2.58	0.150 ± 0.047	0.509
125.3	2.53	3.10	0.255	0.628
131.1	2.31	3.01	0.169	3.878
145.5	2.46	3.07	0.133	0.652
152.9	2.16	2.50	0.197	0.403
164.5	2.40	2.36	0.154	3.247
168.3*	2.17 ± 0.21	2.63	0.127 ± 0.002	3.185
181.2	2.32	2.41	0.167	3.438
272.8	2.03	—	0.075	—
327.5	1.90	—	0.039	—
381.1	1.50	—	0.083	—
Mean reference concentration	1.53 ± 1.4		0.026 ± 0.013	

Means and standard deviations are reported at sites where replicate bed samples were collected (+) or sites where bed samples were collected in both 1986 and 1987 (*). The bed sediment mean reference concentrations for Fe and Mn are also reported.

Table 8. Comparison of trace metal concentrations in the <60 μm fraction of Clark Fork River bed sediment collected in August 1986, August 1987, and July 1980

km	Year	[Ag]	[Cd]	[Cu]	[Pb]	[Zn]
21.1	1986	6.1	10.2	1591	186	2062
	1987	4.5	10.0	1352	176	1925
	1988	4.6	11.2	1430	194	2033
	CV	16	6	8	5	4
34.6	1986	5.2	7.4	1221	150	1460
	1987	4.6	8.1	2763	168	1733
	1988	3.7	4.6	845	120	1050
	CV	18	27	63	16	24
72.4	1986	4.3	5.1	917	120	1223
	1987	3.5	8.2	1105	134	1505
	CV	15	33	13	8	15
111.9	1986	4.4	4.8	696	120	1171
	1988	3.4	5.9	789	137	1398
	CV	18	15	9	9	13
122.6	1986	3.1	4.1	550	97	1118
	1987	2.7	5.4	582	102	1140
	CV	10	19	4	4	14
168.3	1986	2.2	4.1	357	75	985
	1987	2.4	5.9	575	93	1350
	1988	1.9	4.1	452	88	1339
	CV	9	21	24	11	17
327.5	1986	1.8	2.2	232	45	580
	1988	0.7	1.2	144	38	361
	CV	67	41	33	12	33
Blackfoot River	1987	≤0.2	2.8	95	38	845
(173.8)	1988	≤0.2	3.2	102	51	1106
	CV	—	10	5	20	19
Rock Creek	1986	≤0.2	≤0.3	14	10	53
	1987	≤0.2	≤0.3	13	9	36
	CV	—	—	5	7	27
Little Blackfoot	1986	≤0.2	0.7	38	40	161
River	1987	0.9	0.9	40	53	180
	CV	—	13	3	19	8

Coefficient of variation (CV) also is shown. Mean values and standard deviations for years where replicate samples were taken are shown in Table 5.

tance downstream. The difference in distributions might be a function of mining activities, but more likely it is a function of preferential, post-depositional mobilization of Cd, Zn and Mn because these metals are more susceptible to diagenetic processes than Cu or Pb (SCOKART *et al.*, 1983; CALMANO and FORSTNER, 1983). Sediment deposition and erosion processes, as well as modification of the channel during highway and railroad construction all may add complexity to downstream trends in metal concentrations in the flood-plains.

The extensive and persistent contamination of the bed sediments of the Clark Fork River is at least partly the result of storage and re-introduction of contaminated sediments from flood-plains. Several observations support this suggestion. First, the occurrence of contaminated sediments in actively eroding cutbanks is extensive, as is contamination of the flood-plain in general (MOORE, 1985; RICE and RAY, 1985; MOORE *et al.*, 1989). Elevated concentrations of Ag, Cd, Cu, Pb and Zn were observed downstream 181 km in the <60 μm fraction of sediments sampled from cutbanks along the edge of the river. Second, slumping bank material appears to affect metal concentrations locally, as suggested by the correlation of localized variability in bed-sediment metal concentrations with high concentrations in nearby cutbanks. It is likely that during periods of high flow, such inputs are integrated downstream. Bank inputs may be especially important in the Clark Fork River because of unusually thick overbank deposits (ANDREWS, 1987) that presumably resulted from the large historical sediment releases from the minerals extraction activities.

Contamination of flood-plain sediments is not unique to the Clark Fork River. It is estimated that one-third of the tailings originally released from mining operations into Whitewood Creek, South Dakota are stored along 121 km of flood-plain downstream (MARRON, 1987). Contamination of flood-plain sediments has been observed in the River Elbe (MIEHLICH, 1983), the River Geul (LEENAERS, 1988) and in rivers draining the lead-mining districts in mid-Wales (WOLFENDEN and LEWIN 1977; BRADLEY and LEWIN, 1982). In all such systems proportionately small contributions (in terms of sediment load) of material from highly contaminated banks could enhance bed sediment contamination locally and expand the downstream extent of contamination.

Although tributaries probably add significant loads of uncontaminated sediment to the Clark Fork River, contaminant dilution expected from inputs of clean sediments is not as evident as observed elsewhere (SALOMONS, 1988). The study near Flint Creek suggests that tributary inputs add to the local variability of metal concentrations in Clark Fork River sediments, but their downstream influences are reduced as other processes (perhaps flood-plain inputs) come into play. The limited range of specific tributary influence is further supported by the lack of significant differences in metal concentration between adjacent segments of the river. ANDREWS (1987) drew a similar conclusion, suggesting that although the non-contaminated Bitterroot River contributed 50% of the suspended load of the Clark Fork River, no comparable decrease in metal concentration of bed sediments occurred below the confluence of the two. Tributaries may influence the large-scale dilution of metal concentrations downstream in ways that cannot be determined from our study, however.

Although site-to-site variability is large, data from the three low flow years sampled demonstrate that general, large-scale trends are clear over hundreds of kilometers in contaminated rivers. Such trends may be relatively stable, year-to-year, in rivers like the Clark Fork River, although multiple-year studies over a range of flow conditions are important for precise characterizations. Smaller scale trends (<100 km) may be obscured by the large variability, however. Several factors may contribute to this small-scale variability which is commonly observed in contaminated river systems receiving particulate waste (MOORE, 1985; RICE and RAY, 1985; WOLFENDEN and LEWIN, 1977; MOORE *et al.*, 1989):

1. Input of contaminated sediments from highly variable bank deposits appears to increase variability in bed sediment metal concentrations. In the Clark Fork River, CVs for bed sediment metal concentrations corresponded to the degree of bank contamination.

2. Association of metals with discrete, highly enriched particles such as specific mineral grains can lead to variability in sediment metal concentrations unless sample sizes are very large (CLIFTON *et al.*, 1967, 1969; MORIARTY *et al.*, 1982). Discrete particles of iron sulfide, mineral oxide and devitrified smelter slag containing exceptional concentrations of Cu, Zn and Pb have been observed upstream in Clark Fork River bed sediments (FITZPATRICK and ANDREWS, in prep.; J. N. MOORE, University of Montana, pers. commun.). In our study, metals in replicate samples of bed sediment from one site correlated best with Fe where the banks were most metal-enriched and bed sediment concentrations most variable. Such correlations could reflect metal-rich Fe-sulfide particles entering the bed from deposits stored in the flood-plain. The correlations between metals and Fe also could result from metal associations with Fe-oxide coatings, but then significant correlations would be expected throughout the river.

3. Sediment samples can vary widely in total organic C content and Fe concentration, both of which appeared to affect metal concentrations at some Clark Fork River sites. Although particle size biases may affect variability, such an effect is less likely with <60 μm sieved sediments.

Understanding spatial and temporal variability in sediment metal concentrations is fundamental to interpreting processes and distributions of metals in fluvial systems. Replicate sampling at individual sites, or composite sampling, is necessary to improve sensitivity in determining small-scale variability among sites. Sampling over long reaches of the river, at least in this system, is imperative in determining longitudinal trends.

Acknowledgements—Discussions with Edmund D. Andrews, U.S. Geological Survey, were instrumental in initiating this project and have been valuable since. We also thank Johnnie N. Moore, University of Montana, who has been an ongoing source of important ideas and inspirational enthusiasm.

Editorial handling: Brian Hitchon.

REFERENCES

ANDREWS E. D. (1987) Longitudinal dispersion of trace metals in the Clark Fork River, Montana. In *The Chemical Quality of Water and the Hydrologic Cycle* (eds R. C. AVERETT and D. M. MCKNIGHT), Chap. 13, pp. 1–13. Lewis Publishers.

BOETTCHER A. J. and GOSLING A. W. (1977) Water resources of the Clark Fork Basin upstream from St. Regis, Montana. State of Montana Bureau of Mines and Geology Bull. 104.

BRADLEY S. B. and COX J. J. (1986) Heavy metals in the Hamps and Manifold Valleys, North Staffordshire, U.K.: distrubution in flood-plain soils. *Sci. Total Environ.* **50**, 103–128.

BRADLEY S. B. and COX J. J. (1987) Heavy metals in the Hamps and Manifold Valleys, North Staffordshire, U.K.:

partitioning of metals in flood-plain soils. *Sci. Total Environ.* **65**, 135–153.

BRADLEY S. B. and LEWIN J. (1982) Transport of heavy metals on suspended sediments under high flow conditions in a mineralized region of Wales. *Environ. Pollut.* **4**, 257–267.

BROOK E. J. and MOORE J. N. (1988) Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in bed sediment from the Clark Fork River, Montana (USA). *Sci. Total Environ.* **76**, 247–266.

BROSTEN T. M. and JACOBSON M. A. (1985) Historical water-quality data for the Clark Fork (River) and the mouths of selected tributaries, Western Montana. U.S. Geol. Surv. Open-file Rept. 85–168.

CALMANO W. and FORSTNER U. (1983) Chemical extraction of heavy metals in polluted river sediments in Central Europe. *Sci. Total Environ.* **28**, 77–90.

CHAPMAN B. M., JONES D. R. and JUNG R. F. (1983) Processes controlling metal ion attenuation in acid mine drainage streams. *Geochim. cosmochim. Acta* **47**, 1957–1973.

CLIFTON H. E., HUBERT A. and PHILLIPS R. L. (1967) Marine sediment sample preparation for analysis for low concentrations of fine detrital gold. *U.S. Geol. Surv. Circ.* **545**.

CLIFTON H. E., HUNTER R. E., SWANSON F. J. and PHILLIPS R. L. (1969) Sample size and meaningful gold analysis. U.S. Geol. Surv. Prof. Paper 625-C.

DINGMAN O. A. (1932) Placer mining possibilities in Montana. State of Montana Bureau of Mines and Geology Mem. No. 5.

FITZPATRICK J. and ANDREWS E. D. (1990) The mineralogic association of heavy metals in the bed sediments of the upper Clark Fork River, Montana (in prep.).

GEESEY G. G., BORSTAD L. and CHAPMAN P. M. (1984) Influence of flow-related events on concentration and phase distribution of metals in the lower Fraser River and a small tributary stream in British Columbia, Canada. *Water Res.* **18**, 233–238.

GIBBS R. J. (1973) Mechanisms of trace metal transport in rivers. *Science* **180**, 71–73.

HOROWITZ A. J., ERLICK K. E. and CALLENDER E. (1988) The effect of mining on the sediment-trace element geochemistry of cores from the Cheyenne River arm of Lake Oahe, South Dakota, USA. *Chem. Geol.* **67**, 17–33.

HOUBA C., REMACLE J., DUBOIS D. and THOREZ J. (1983) Factors affecting the concentrations of cadmium, zinc, copper and lead in the sediments of the Vesdre River. *Water Res.* **17**, 1281–1286.

HUNT W. A. AND GRAHAM R. O. (1975) Evaluation of channel changes for fish habitat. Meeting preprint 2535, Fall National Convention of the American Society of Civil Engineers, 3–7 November, 1975, Denver, Colorado.

JACKSON T. A. (1978) The biogeochemistry of heavy metals in polluted lakes and streams at Flin Flon, Canada, and a proposed method for limiting heavy-metal pollution of natural waters. *Environ. Geol.* **2**, 173–189.

JENNE E. A., KENNEDY V. C., BURCHARD J. M. and BALL J. W. (1980) Sediment collection and processing for selective extraction and for total trace element analyses. In *Contaminants and Sediments* (ed. R. A. BAKER), Vol. 2, Chap. 10, pp. 169–190. Ann Arbor Science Publishers.

JENNETT K. C. and FOIL J. A. (1979) Trace metal transport from mining, milling and smelting watersheds. *Water Poll. Control Fed.* **51**, 378–405.

JOHNS C. and MOORE J. N. (1985) Metals in bottom sediments of Lower Clark Fork River reservoirs. Montana Water Resources Research Center.

JOHNSON H. E. and SCHMIDT C. L. (1988) Clark Fork Basin Project: Draft Status Report and Action Plan. Clark Fork Basin Project, Office of the Governor, Capitol Station, Helena, Montana.

JONES K. C. (1986) The distribution and partitioning of silver and other heavy metals in sediments associated with an acid mine drainage stream. *Environ. Pollut. Ser.* **12**, 249–263.

LEENAERS H. (1989) Downstream changes of total and partitioned metal concentrations in the flood deposits of the River Geul (The Netherlands). *Geojournal* **19**, 37–43.

LEENAERS H., SCHOUTEN C. J. and RANG M. C. (1988) Variability of the metal content of flood deposits. *Environ. Geol. Water Sci.* **11**, 95–106.

LEWIS D. M. (1977) the use of ^{210}Pb as a heavy metal tracer in the Susquehanna River system. *Geochim. Cosmochim. Acta.* **41**, 1557–1564.

LUOMA S. N. and BRYAN G. W. (1981) A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Sci. Total Environ.* **17**, 165–196.

LUOMA S. N., AXTMANN E. V. and CAIN D. J. (1989) Fate of mine wastes in the Clark Fork River, Montana, USA. In *Metals and Metalloids in the Hydrosphere: Impact through Mining and Industry, and Prevention in Tropical Environments*, pp. 63–75. International Hydrological Programme, UNESCO.

MANN A. W. and LINTERN M. (1983) Heavy metal dispersion patterns from tailings dumps, Northampton District, Western Australia. *Environ. Pollut. Ser.* **B6**, 33–49.

MARCUS W. A. (1989) Dilution mixing estimates of trace metal concentrations in suspended sediments. *Environ. Geol. Water Sci.* **14**, 213–219.

MARRON D. C. (1987) Flood-plain storage of metal-contaminated sediments downstream of a gold mine at Lead, South Dakota. In *The Chemical Quality of Water and the Hydrologic Cycle* (eds R. C. AVERETT and D. M. MCKNIGHT), Chap. 14, pp. 193–209. Lewis Publishers.

MIEHLICH G. (1983) Schwermetallanreicherung in Boden und Pflanzen der Pevestorfer Elbaue (Kreis Luchow-Dannenberg). *Abh. naturwiss. Ver. Hamburg* **25**, 75–89.

MILLER R. N. (1973) Production history of the Butte District and geological function, past and present. In *Guidebook for the Butte Field Meeting of Society of Economic Geologists* (ed. R. N. MILLER), Chap. F. Anaconda Company.

MOORE J. N. (1985) Source of metal contamination in Milltown Reservoir, Montana: An interpretation based on Clark Fork River bank sediment. Report to the USEPA: District VII, Helena, MT.

MOORE J. N., BROOK E. J. and JOHNS C. (1989) Grain size partitioning of metals in contaminated, coarse-grained river floodplain sediment: Clark Fork River, Montana. *Environ. Geol Water Res.* **14**, 107–115.

MORIARTY F., BULL K. R., HANSON H. M. and FREESTONE P. (1982) The distribution of lead, zinc and cadmium in sediments of an ore-enriched lotic ecosystem, the River Ecclesbourne, Derbyshire. *Environ. Pollut. Ser.* **B4**, 45–68.

NORDSTROM D. K. and BALL J. W. (1985) Toxic element composition of acid mine waters from sulfide ore deposits. In *Mine Water, Int. Mine Water Symposium*, Granada, Spain, pp. 749–758. Asociacion Nacional de Ingenieros de Minas, Internat. Mine Water Ass.

PAGENKOPF G. K. and CAMERON D. (1979) Deposition of trace metals in stream sediments. *Water Air Soil Pollut.* **12**, 429–435.

PARKS J. W., SUTTON J. A. and LUTZ A. (1986) Effect of point and diffuse source loadings on mercury concentrations in the Wabigoon River: Evidence of a seasonally varying sediment-water partition. *Can. J. Fish. Aq. Sci.* **43**, 1426–1444.

PERRY E. S. (1932) *The Butte Mining District, Montana.* International Geological Congress XVI Session, Guidebook 23-Excursion C2. Washington D.C.

PRUELL R. J. and QUINN J. G. (1985) Geochemistry of organic contaminants in Narragansett Bay Sediments. *Estuarine Coast. Shelf Sci.* **21**, 295–312.

REECE D. E., FELKEY J. R. and WAI C. M. (1978) Heavy metal pollution in the sediments of the Coeur d'Alene River, Idaho. *Environ. Geol.* **2**, 289–293.

RICE P. M. and RAY G. J. (1985) Heavy metals in flood plain deposits along the upper Clark Fork River. *Proceedings-Clark Fork Symposium* (eds. C. E. CARLSON and L. L. BAHLS), Montana Academy of Sci. Montana College of Mineral Sciences and Technology April 1985.

RIVER MILE INDEX (1976) Clark Fork-Pend Oreille River—Washington, Idaho, Montana and British Columbia. Hydrology and Hydraulics Committee, Pacific Northwest River Basins Commission.

RYBICKA E. H. and KYZIOL J. (1987) Soil pollution with lead in the region of the domestic glassware plant "Irena" in Inowroclaw, Poland. *Environ. Technol. Lett.* **8**, 43–52.

SALOMONS W. (1988) Impact of metals from mining and industry on the hydrosphere. In *Workshop on Metals and Metalloids in the Hydrosphere: Impact through Mining and Industry and Prevention Technology* (ed. G. STRIGEL), pp. 1–44. Technical Document in Hydrology SC.88/WS/68. Intl. Hydrological Programme, UNESCO.

SALOMONS W. and FORSTNER U. (1984) *Metals in the Hydrocycle*. Springer.

SCOKART P. O., MEEUS-VERDINNE K. and DE BORGER R. (1983) Mobility of heavy metals in polluted soils near zinc smelters. *Water Air Soil Pollut.* **20**, 451–463.

SHIELDS R. R., KNAPTON J. R., WHITE M. K., BROSTEN T. M. and KASMAN M. L. (1985) Water Resources Data, Montana, Water Year 1985. U.S. Geol. Surv. Water Data Rept. MT-85-2.

SHIELDS R. R., KNAPTON J. R., WHITE M. K., BROSTON T. M. and LAMBING J. H. (1987) Water Resources Data, Montana, Water Year 1986. U.S. Geol. Surv. Water Data Rept. MT-86-2.

SHIELDS R. R., KNAPTON J. R., WHITE M. K., BROSTEN T. M. and LAMBING J. H. (1988) Water Resources Data, Montana, Water Year 1987. U.S. Geol. Surv. Water Data Rept. MT-87-2.

SOKAL R. R. and ROHLF F. J. (1969) *Biometry*. W. H. Freeman and Co.

TESSIER A., CAMPBELL P. G. C. and BISSON M. (1980) Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). *Can. J. Earth Sci.* **17**, 90–105.

TESSIER A., CAMPBELL P. G. C. and BISSON M. (1982) Particulate trace metal speciation in stream sediments and relationships with grain size: Implications for geochemical exploration. *J. Geochem. Explor.* **16**, 77–104.

TUREKIAN K. K. and WEDEPOHL K. H. (1961) Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.* **72**, 175–192.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA). (1983) Color aerial photographs, 8305b, 1:8000 scale, LN68, RN1, 8-23-89.

WOLFENDEN P. J. and LEWIN J. (1977) Distribution of metal pollutants in flood-plain sediments. *Catena* **4**, 309–317.

WOLFENDEN P. J. and LEWIN J. (1978) Distribution of metal pollutants in active stream sediments. *Catena* **5**, 67–78.