Copper, Zinc, and Arsinic in Bottom Sediments of Clark Fork River Reservoirs: Preliminary Findings

Carolyn Johns and Johnnie Moore

Geology Department University of Montana Missoula, MT 59812

Abstract

Acetic acid extracts of sediments from four Clark Fork River reservoirs,--Milltown, Thompson Falls, Noxon Rapids, and Cabinet Gorge--indicate that mining and smelting operations in the upper drainage have enriched metal concentrations throughout the river. Milltown Reservoir contains metal values over 10 times the background levels for copper, zinc, and arsenic. Enrichment over background decreases downstream where the lower reservoirs contain copper and zinc concentrations 4 to 10 times over background values. In the lower reservoirs arsenic is not elevated over background. These trends suggest that contaminants have been transported over 350 miles from the major source of metals in the upper drainage and very likely reside in the sediments of the Clark Fork River delta in Lake Fend Oreille.

Introduction

The Clark Fork River originates in the Anaconda-Butte region from the confluence of Silver Bow Creek, Mill Creek, Willow Creek, and Warm Springs Creek. Silver Bow Creek has received wastes from mining activities in Butte and a series of three settling ponds were built on its lower reach to contain smelting wastes from ore processing at the Washoe copper smelter in Anaconda. Until the settling ponds were constructed in 1954-55, mining and smelting operations discharged wastes directly into the creek and these wastes moved into the Clark Fork River unimpeded and untreated. Over the interval from the 1880's until the mid-1950's, many thousands of tons of effluent found their way into the upper Clark Fork River drainage. Since the onstruction of the settling ponds and the subsequent liming treatment of the industrial wastes, contaminant input to the river from the ponds decreased dramatically except for a few occasions when the dikes were breached.

In addition to the mining and smelting wastes transported downstream in the river, river-borne tailings have been deposited across the flood plain in the Deer Lodge Valley, causing significant impacts to riparian systems (for example, 7,8). Remobilization of contaminated flood plain sediments may provide a-source of continued contaminant input to the Clark Fork River (6). The extent of the impacts to the river and adjacent riparian areas downstream have not been fully delineated.

In November 1981 the Montana Department of Health and Environmental Sciences discovered elevated arsenic levels in water from four community drinking wells in Milltown, Montana. Arsenic concentrations ranged from 0.22 to 0.51 mg/L in the wells. These levels caused immediate concern on the part t~ State and local health officials since the Federal Safe Drinking Water standard for arsenic specifies 0.05 mg/L as the upper safety limit. A reconnaissance hydrogeological study identified four possible sources of the arsenic contamination: (1) a wood products mill north of the wells, (2) an abandoned industrial dump southeast of the wells, (3) the adjacent Milltown Reservoir containing an unknown quantity of smelting and mining sediment from upriver, and (4) a deep bedrock ground water system underlying the contaminated reservoir (13).

Noting previous work on heavy metal concentrations in the accumulated reservoir sediment (1), we thought that the reservoir would be the most probable source of the well contamination and obtained four grab samples of Pediment in February 1982 by cutting through the ice. These sediment samples contained from 54 to 135 ug/g arsenic, 5 to 95 ug/g lead, 259 to 1357 ug/g manganese, and 66 to 2880 ug/g zinc. As a result of the hydrologic work and the sediment metal levels, the Environmental Protection Agency (EPA) ranked the Milltown Reservoir as site 198 of the initial 400 Superfund sites. In July 1983 we began a study of Milltown Reservoir sediments as part of a Remedial Investigation funded by EPA and the Montana State Solid and Hazardous Waste Bureau to evaluate the sediments as the likely source of arsenic contamination of the ground water in Milltown. We found arsenic, copper, zinc, and other heavy metal concentrations to be highly and significantly elevated in the Clark Fork arm of the Milltown Reservoir as compared to both the Blackfoot arm of the reservoir and levels reported in the literature (5, 6, 14).

Milltown Reservoir is the first major impoundment below the smelting and mining districts in the Anaconda-Butte area and may have trapped most of the sediment-carried metals. However, occasional releases from the Warm Springs settling ponds have occurred and eyewitness reports tell of the Clark Fork River "running red" with sediment (R.C. Averett, USGS Water Resources Division). If the "red" sediment contained large amounts of heavy metals and arsenic, some portion may have continued to repositories downstream from Milltown Reservoir. Addition of sediment from other large tributaries (Bitterroot, Flathead, Jocko, and Thompson Rivers) below Milltown may have diluted the metals passing through Milltown so that the reservoirs downstream may be relatively uncontaminated. To explore for the lower boundary of mining and smelting impacts to the Clark Fork River, we sampled bottom sediments from three downstream impoundments--Thompson Falls, Noxon, and Cabinet Gorge Reservoirs--to see whether the sediments contained elevated heavy metal and arsenic levels.

The objectives of this paper are threefold: (1) to summarize findings at Milltown Reservoir for comparative purposes; (2) to present early findings from sediment extracts from the three downstream reservoirs; and (3) to examine some preliminary downriver trends in arsenic, copper, and zinc concentrations in the reservoir bottom sediments.

Physical Setting

Milltown Reservoir, the first major impoundment on the Clark Fork River, lies approximately 115 river miles downstream from the Warm Springs Ponds (fig.1). The reservoir is formed by a small dam built in 1907-08 at the confluence of the Clark Fork and Blackfoot Rivers and is currently owned by the Montana Power Company. The dam presently contains five turbines, which produce from 2.5 kW at low flow to a maximum of 3.4 kW at high flow (Phil Smith, 1985, Montana Power Company, Missoula). The Milltown Reservoir itself is small, only about 1.23 miles in total length. The reservoir is full of sediment and is therefore quite shallow throughout except for the two main channels of the Clark Fork and Blackfoot Rivers. Due to the large quantities of sediment already accumulated, the reservoir probably no longer stores much new sediment and most of the recent suspended sediment load of the Clark Fork probably passes through the reservoir and on downstream.

The second major impoundment on the river is the Thompson Falls Dam, also owned and operated by Montana Power Company. It lies approximately 280 river miles downstream from the Warm Springs Ponds. The reservoir formed by the dam is also relatively small, approximately 2 miles in effective

length. The deep Clark Fork channel bisects the reservoir into shallower southern and northern portions. Most of the sediments are sandy; small areas of medium to fine silt deposition occur along the banks.

Noxon Rapids Dam lies roughly 320 river miles downstream from the Warm rings Ponds. Built in 1959. it has a maximum generating capacity of 554.000 kW and is owned and operated by Washington Water Power Company (WWPC). The reservoir behind the dam covers 8.000 surface acres and can exceed 150 feet in depth Sediments in the mainstem of the reservoir are predominantly medium define silts with little sand and very little clay. Broader areas of the reservoir are accumulating more sediment than the narrow portions.

The final hydroelectric impoundment above Lake Pend Oreille is the Cabinet Gorge Dam, which lies 25 miles downriver from Noxon Rapids Dam and approximately 345 river miles downstream from the Warm Springs Ponds. Also owned and operated by WWPG, the facility was constructed in 1952 and has a generating capacity of 230,000 kW. In the lower 15 or 16 miles of the reservoir, sediment is accumulating in only the broad areas of the reservoir.

Methods

Sample Collection

Grab samples of bottom sediment were taken in each reservoir to assess the presence or absence and lateral distribution of arsenic and other metals. Each grab sample was collected with a Peterson dredge. The sediment that had contacted the interior metal surface of the dredge was discarded; the remaining sediment was scooped into a previously acid-washed plastic quart container. The full container was capped and stored in ice for transport to the laboratory. At Milltown Reservoir 27 grab samples were collected in the Clark Fork arm of the reservoir; 10 grabs were collected from the Blackfoot arm of the reservoir (fig. 2). At Thompson Falls Reservoir seven grab samples were collected (fig. 3). Fourteen grab samples were collected from Noxon Reservoir due to its larger size and the a priori judgment that most fine sediments would accumulate there (fig. 4). These grab sample sites included two sites for local background: the upper mouths of Vermilion Creek and Trout Creek. Seven grab samples were taken from Cabinet Gorge Reservoir between the town of Noxon on the upstream end and the Rock Islands toward the downstream end of the reservoir (fig. 5). One sample was taken within the mouth of the Bull River as a local background reference.

Due to the shallow depth of the Milltown Reservoir. core samples were taken there with a handemplaced coring tube of PVC. The inner core tube liner consisted of acid-washed, fitted 10-cm long sections of PVC tube. When the corer was removed, the individual inner core tube sections were removed and capped, then stored in ice for transport to the lab (for details see 14). The lower reservoirs, being considerably deeper, necessitated using a gravity corer. The corer was lined with a clear acetate tube, which was acid rinsed then rinsed with reservoir water before each use. This corer could sample up to 45 cm depths. Most cores collected were 25 cm long. Several cores hit gravel at approximately 35-40 cm. Each core was extruded and divided into 5-cm intervals, stored in acid-washed plastic containers and kept on ice for transport to the lab. Three cores were collected in the Thompson Falls Reservoir in the shallow embayment near the highway (fig.3). Five cores were collected from Noxon Reservoir (fig. 4).

Sample Preparation

All sediment samples were prepared in the laboratory using one of two 3-step extraction schemes. Milltown and Blackfoot samples were centrifuged, in the case of the grab samples, to remove interstitial water. Core samples had the interstitial water removed by nitrogen gas displacement followed by filtration through a 0.45-micron millipore filter (see 14). Samples from the lower reservoirs were subjected to longer transit times between collection and preparation, so instead of displacing the interstitial water, an ammonium acetate (1 M) extraction was used to remove metals held on the ion exchange sites of the sediment (4,10). This extraction was performed by shaking dried, powdered sediment with 1 M ammonium acetate (sediment: solution ratio equaled 1:20) for 2 hours. The mixtures were then centrifuged, the supernatant decanted and filtered through a 0.45-micron millipore filter. The extract was acidified with nitric acid to pH 2 for preservation.

In the second step of both 3-step schemes, residual sediment was dried, repowdered and extracted with 25% (v/v) acetic acid (3,10) to remove metals held in amorphous iron oxides, some manganese hydrous oxides. and some organic fractions. Samples were shaken with 25% acetic acid for 12 hours, centrifuged and the supernatant filtered through a 0.45-micron millipore filter.

In the final step, "total" metals were determined and represent those metals held in the most resistant fractions, including organic components and silicate lattices. For Milltown Reservoir samples, including the Blackfoot arm samples, arsenic and copper were extracted by 4-hour digestion in hot aqua regia (3:1 HC1: HNO3). Zinc was determined on lithium metaborate fusions of the sediment (2,14). "Total" metal digestions on the lower reservoir sediments are done utilizing hot refluxing nitric acid. These digestions have not been completed and are not discussed here.

Quality Assurance

Quality assurance activities included

- 1. reagent blanks analyzed blind for each extract type,
- 2. replicate extractions or digestions,
- 3. digestion of NBS sediment standards (SRM 1645 River Sediment and SRM 1646 Estuarine Sediment),
- 4. splits of sample extracts submitted blind for analysis,
- 5. duplicate analyses of extracts by the laboratories, and
- 6. spike recoveries for each element in each matrix.

Metal concentrations in acetic acid blanks were uniformly low. Arsenic averaged 1.7 IJg/L in the Milltown study blanks and <0.005 mg/L in the blanks from the lower reservoir study. Copper concentrations in the reagent blanks averaged 0 mg/L and <0.01 mg/L for the Milltown and lower reservoir studies, respectively. Zinc averaged 0 mg/L in the Milltown study blanks and <0.02 mg/L in the lower reservoir study blanks.

For the Milltown study, duplicate acetic acid extracts of the sediments were performed. The average percent differences from the mean of these duplicate extracts were 7.3% for arsenic (n=14), 5% for copper (n=13), and 11.1% for zinc (n=16). Triplicate acetic acid extracts were performed on the lower

reservoir sediment samples. The average relative standard deviations were 10.5% for arsenic, 2.4% for copper, and 5.5% for zinc (n=3 for each).

Duplicate analyses of acetic acid extracts performed by the laboratories resulted in average percent differences from the means of 4.9%, 2.1%, and 2.5% for arsenic, copper, and zinc in the Milltown study. The average percent differences from the means of duplicate analyses in the lower reservoir study were 2.1% (n=9), 0.6% (n=9), and 3.3% (n=9) for arsenic, copper, and zinc, respectively.

Spike recovery analyses performed on the acetic acid extracts showed high percent recoveries and low matrix interference effects. For the Milltown study, average percent recoveries for arsenic, copper, and zinc were 97% (n=12), 100% (n=9), and 109% (n=9), respectively. Average percent recoveries for the lower reservoir study samples were 91% (n=9), 105% (n=9), and 97% (n=9) for arsenic, copper, and zinc.

Results and Discussion

Table 1 summarizes total and acetic acid extractable concentrations of arsenic, copper, and zinc in the surface grab samples from all reservoirs long the Clark Fork River. Total copper in the Clark Fork arm of Milltown Reservoir ranged from 250 to 1000 ug/g, averaging 449 ug/g. The acetic acid extractable copper, which represents copper held on sites in amorphous iron oxides and some of the manganese hydrous oxides, averaged 241 ug/g and ranged from 100 to 550 ug/g in the Clark Fork portion of Milltown Reservoir. In contrast, total copper in sediments of the Blackfoot arm of Milltown Reservoir averaged only 23 ug/g, with a range of 11 to 32 ug/g. For comparison, table also reports average total copper values for shales and shallow water sediments. Total copper in the Blackfoot arm of Milltown Reservoir is less than the 45 and 56 ug/g reported for shales and shallow water sediments. Total copper in the Clark Fork arm of Milltown Reservoir sediments clearly greatly exceeds these average expected concentrations and concentrations found in the adjacent Blackfoot arm of the reservoir. Acetic acid extractable copper in the Blackfoot arm averaged 5 ug/g with a range of 3 to 8 ug/g. In both arms of Milltown Reservoir the acetic acid fraction of sediment copper constitutes only 25% to 50% of the total copper present.

In the lower three reservoirs for which only acetic acid extract data are presently available, the extractable copper averages 40, 42, and 19 $^{\circ}g/g$ at Thompson Falls, Noxon, and Cabinet Gorge, respectively. While considerably lower than Milltown Reservoir concentrations, the acetic acid fraction copper in these lower reservoirs exceeds the average Blackfoot arm concentrations by four to eight times. At Thompson Falls Reservoir, acetic acid extract copper concentrations ranged from 32 to 65 ~g/g (Table 2). In the mainstem of the Noxon Reservoir, acetic acid extractable copper ranged from 31 to 52 $\gamma g/g$ in the surface sediments (Table 3). Two sites (N1 and N5), located in the upper mouths of tributary creeks and away from the influence of sediment carried down the mainstem of the reservoir, showed acetic extractable copper concentrations of 4 and $0.3 \sim g/g$. This suggests that local background concentrations for copper in Noxon Reservoir are lower than the Blackfoot arm of Milltown Reservoir upstream. In Cabinet Gorge Reservoir copper concentrations in acetic acid extracts of surface grab samples are lower than at Thompson Falls or Noxon Reservoirs (Table 4) and range from 10 to 26 $^{\circ}g/g$ in the main- stem of the reservoir. As at Noxon, two sites located in the mouths of tributary creeks had very low acetic acid extractable copper concentrations of 2 and 0.3 ug/g, strongly indicating elevated copper levels in the mainstem reservoir sediments compared both to local sediment as well as the Blackfoot upriver.

In the Clark Fork arm of Milltown Reservoir, total zinc concentrations were highly elevated, ranging from 623 ug/g to 5320 ug/g and averaging 1770 ug/g (table 1). These zinc concentrations greatly exceeded both expected zinc concentrations in average shales and shallow water sediment (95 and 92 ug/g, see table 1) and the concentrations found in the Blackfoot arm of Milltown Reservoir.' In the Blackfoot arm, zinc levels ranged from 60 to 134 ug/g but averaged 103 ug/g and so approximated expected normal concentrations of zinc. Acetic acid extractable zinc in the Clark Fork portion of Milltown Reservoir formed a large portion of the total zinc present. Zinc concentrations in these extracts ranged from 510 to 3820 ug/g and averaged 1330 ug/g. However, in the Blackfoot arm of the reservoir acetic acid extractable zinc averaged only 11 ug/g, ranging from 2 to 21 ug/g.

Further downriver, acetic acid extractable zinc averaged 145 ug/g (table 1) at Thompson Falls Reservoir, while ranging from 110 to 213 ug/g in the seven mainstem sites. These zinc concentrations are almost 10 times less than those in the Clark Fork arm of Milltown Reservoir but still tenfold greater than acetic acid extractable levels of zinc in the Blackfoot arm of the reservoir. In Noxon Reservoir acetic acid extractable zinc averaged 135 ug/g (table 1) and ranged from 106 to 201 ug/g in the mainstem reservoir grab samples (table 3). The two sites in upper portions of the mouths of Vermilion and Trout Creeks evidenced very much lower acetic acid extractable zinc concentrations--7 and 10 ug/g, respectively. It is not likely that either of these two sites receives much sediment, if any, from the Clark Fork River influenced mainstem of Noxon Reservoir so we consider these zinc levels to represent local sediment input rather than Clark Fork River sediment. Also, the zinc levels at these two sites are comparable to the levels found in the Blackfoot arm of Milltown Reservoir. For both these reasons we are confident that the concentrations of acetic acid extractable zinc at these two sites represent background levels for the area. In Cabinet Gorge Reservoir zinc concentrations in the acetic acid extracts averaged 111 ug/g (table 1), ranging from 80 to 137 ug/g (table 4). In the two sites, which represent pre- dominantly local sediment input, zinc concentrations in the acetic extracts were 21 and 3 ug/g. Although levels of zinc in the acetic acid extracts in these lower reservoirs are approximately 10 times lower than the levels in the Clark Fork of the Milltown Reservoir, zinc levels are nevertheless 10 times greater than levels at sites representative of local sediment and levels in the uncontaminated Blackfoot arm of Milltown Reservoir.

Total arsenic concentrations in the Clark Fork arm of Milltown Reservoir averaged 58.6 ug/g (table 1). In the Blackfoot arm, arsenic concentrations averaged 7.2 ug/g. Salomons and Forstner (9) cite 13 and 5 ug/g as representative averages for shales and shallow sediments worldwide, respectively. Acetic acid extractable arsenic averaged 16 ug/g in the Clark Fork arm and only 1 ug/g in the Blackfoot arm of Milltown Reservoir. In the lower three reservoirs, acetic acid extractable arsenic concentrations were low, averaging 2.4. 1.9. and 1.5 at Thompson Falls. Noxon and Cabinet Gorge. Ranges of arsenic extracted in the acetic acid were also small in these reservoirs (tables 2. 3. and 4). The arsenic levels observed are comparable to those in the Blackfoot arm and to those found at the local background sites in Noxon and Cabinet Gorge Reservoirs. Arsenic does not appear to be significantly elevated in sediments of these lower three reservoirs.

Concentrations of total and acetic acid extractable metals in a single deep core from the Clark Fork arm of Milltown Reservoir are contrasted in figures 6 and 7 for copper and zinc. Total copper in this core varied with depth in the sediment. Concentrations ranged from 1050 ug/g in the surface 3 cm to 10800 ug/g at 78 cm. Acetic acid extractable copper concentrations ranged from 600 to 1900 ug/g. increasing and decreasing in the same pattern as the total copper levels (fig. 6). As a percentage fraction of the total t per present. the acetic acid extractable copper varied from 60% of the total copper at the lower copper concentrations to less than 20% where total copper was highest.

Total zinc in this core ranged from 3900 ug/g to 10900 ug/g (fig. 7). Greatest acetic acid extractable zinc concentrations occurred in the surface 40 cm and declined to lowest levels at greatest depth. As a proportion of the total zinc present, 50% to 70% of the zinc could be removed by acetic acid in the upper 40 cm of the core. Less than 15% could be extracted by acetic acid in the lower 50 cm of the core.

Cores taken at Thompson Falls and Noxon Reservoirs were shorter than cores from Milltown Reservoir. In several cores from Noxon Reservoir, the corer tip contained gravel when withdrawn from the reservoir bottom, leading us to conclude that the corer had penetrated to the gravel bed and had sampled the entire sediment profile. Copper, zinc, and arsenic concentrations in acetic acid extracts from a core taken at Thompson Falls Reservoir are presented in table 5. Both copper and zinc concentrations varied with depth in the profile. The concentration of each metal was greatest in the deepest sediment, declined to lowest levels between 15 and 20 cm, then increased again near the surface. Arsenic levels demonstrated a similar pattern, but these differences through the profile were small and may not be significant. The zinc and copper concentrations in this core represent elevated levels of both elements compared to Blackfoot grab and core sample extracts.

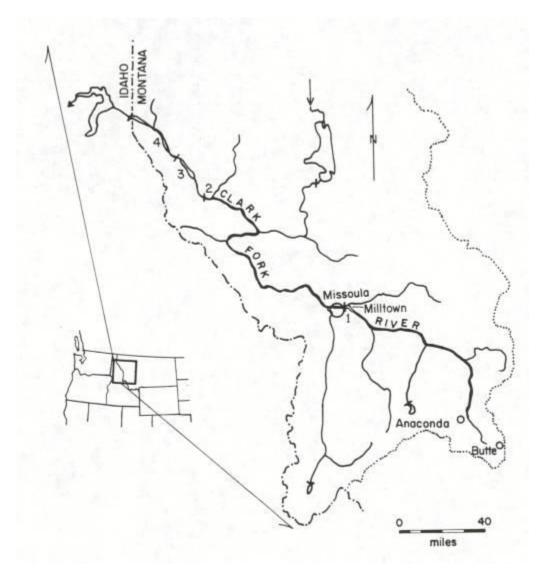
Similarly, copper and zinc in acetic acid extracts from a core in Noxon Reservoir also vary with depth and are elevated with respect to levels of these metals found in acetic acid extracts from the Blackfoot arm of Milltown Reservoir (table 6). This was the deepest core obtained from Noxon Reservoir. Concentrations of all three elements decrease dramatically below 38 cm. The levels of arsenic, copper, and zinc observed in this core between 28 and 41 cm fall within the range found both in the Blackfoot samples and the local back- ground sites for surface sediment in Noxon and Cabinet Gorge Reservoirs. The -sediment above 28 cm in depth probably represents fine sediment deposited from the Clark Fork River since construction of Noxon Rapids Dam. Arsenic levels in the acetic acid extracts show the same general pattern as zinc and copper, but again, such low levels are present that arsenic is probably not significantly elevated in these sediments.

Average copper and zinc concentrations for each reservoir, treating the Clark Fork and Blackfoot arms of Milltown Reservoir as separate reservoirs, are plotted in figures 8 and 9. Acetic acid extractable copper and zinc concentrations in the lower three reservoirs show dramatic decreases with distance downriver from the Clark Fork arm of Milltown Reservoir. But, compared to levels in the Blackfoot arm of Milltown Reservoir and to levels at local background sites within Noxon and Cabinet Gorge Reservoirs, copper and zinc concentrations in the acetic acid extractable fraction of the sediment in the three lower Clark Fork reservoirs are elevated. Although copper concentrations are similar at both Thompson Falls and Noxon Reservoirs, zinc levels appear to be slightly lower at Noxon Reservoir. Levels of both metals appear to be lower in sediment of Cabinet Gorge Reservoir. If the acetic acid extractable copper and zinc represent similar portions of the total copper and zinc present in the sediment, as are present in the Clark Fork arm of Milltown Reservoir, total copper and zinc in these lower reservoirs may be twice the levels found in the acetic acid extracts. We expect the total metal concentrations, in combination with the extractable metals reported here, to provide further evidence for influence of mining and smelting activities in the Butte- Anaconda region on metal content of river-transported sediments 280 to 345 miles downriver. To date, we know of no studies of metal content in sediment in the Clark Fork River delta within Lake Pend Oreille. But, based on our findings so far, metal-enriched sediment may have been transported through Cabinet Gorge and into the lake.

Literature Cited

- 1. Bailey, A. K. 1976. Concentrations of heavy metals in a hydroelectric impoundment. Proceedings Montana Acad. Sci., Vol. 36: 165-170.
- Cantillo, A.Y.; Sinex, S.A.; and Helz, G.R. 1984. Elemental analysis of estuarine sediments by lithium metaborate fusion and direct-current plasma emission spectrometry. Anal. Chem. 56(1): 33-37.
- 3. Chester, R.; and Hughes, M. 1967. A chemical technique for the separation of ferromanganese minerals, carbonate minerals and absorbed trace elements from pelagic sediments. Chemical Geology, Vol. 2: 249-262.
- 4. Luoma, S.N.; and Jenne, E.A. 1976. Estimating bioavailability of sediment-bound trace metals with chemical extractants. In: Hemphill, D.D., ed., Trace substances in environmental health. University of Missouri, Columbia.
- Johns, C.; Moore, J.M.; and Sullivan, M.L. 1984. Distribution of heavy metals in surface sediments of Milltown Reservoir, Montana: source of contaminants for surface and ground water. Abstract. Progr. and Proceed. of Northwest Scientific Assoc.-Montana Academy of Sciences Conf., March 21-24, 1984.
- Moore, J.M.; and Johns, C. 1984. Occurrence, distribution and fractionation of metals in contaminated sediments originating from mining and smelting operations along the Clark Fork River, Montana. Invited paper to Special Session: Fluvial transport of sediment- associated contaminants, American Geophysical Union. Fall meeting, Dec. 3-7, 1984, San Francisco.
- 7. Rice, P.M.; and Ray, G.J. 1984. Floral and faunal survey and toxic metal contamination study of the May 1884 Grant Kohrs Ranch, Nat. Hist. Site: Final report NPS Res. Center, Laramie, WY.
- 8. Rice, Peter M; and Ray, Gary J. Heavy Metals in flood plain deposits along the upper Clark Fork River. Proceedings, Clark Fork River symposium.
- 9. Salomons, w.; and Forstner, U. 1984. Metals in the hydrocycle. Springer-Verlag. New York.
- Thomson, E.A.; Luoma, S.N.; Cain, D.J.; Johansson, C. 1980. The effect of sample storage on the extraction of Cu, Zn, Fe, Mn, and organic material from oxidized estuarine sediments. Water, Air, & Soil Pollution, 14: 215-233.
- 11. Turekian, K.K.; and Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. Bull, GSA, 72: 175-192.
- 12. Wedepohl. K.H. 1969. 1978. Handbook of Geochemistry. Springer-Verlag New York.
- 13. Woessner, W.W.; and Popoff, M.A. 1982. Hydrologic survey of Milltown, Montana and vicinity. Prepared for the Montana Water Quality Bureau, Helena, MI, and Ecology and Environment, Inc., Denver, CO. 36 p.
- Woessner, W.W.; Moore, J.N.; Johns, C.; Popoff, M.A.; Sartor, L.C.; and Sullivan, M.L. 1984. Final Report, Arsenic source and water supply remedial action study, Milltown, Montana. Prepared for the Montana Department of Health and Environmental Sciences, Solid Waste Bureau, Helena, MT. 447 p.

Figure 1: Location map. 1, Milltown Reservoir; 2, Thompson Falls Reservoir; 3, Noxon Rapids Reservoir; 4, Cabinet Gorge Reservoir



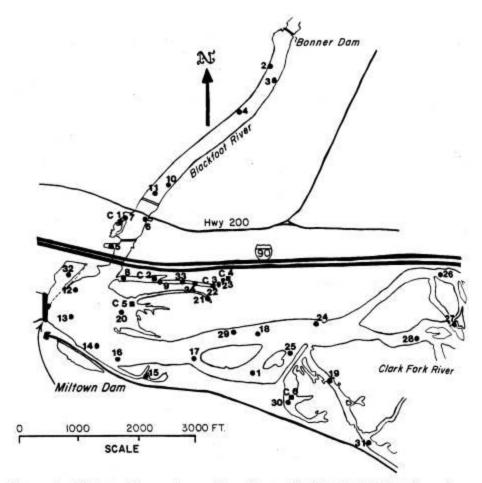


Figure 2. Milltown Reservoir sampling sites. Circles represent grab samples; squares represent cores.

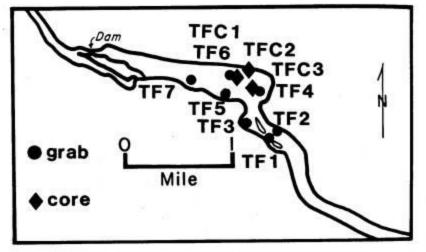


Figure 3. Sampling sites at Thompson Falls Reservoir.

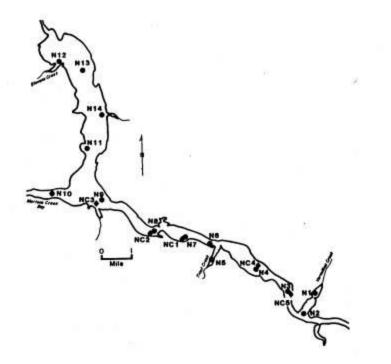


Figure 4. Sampling sites at Noxon Rapids Reservoir. Circles represent grab samples; diamonds represent cores.

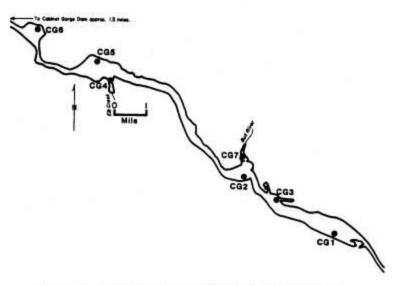


Figure 5. Sampling sites at Cabinet Gorge Reservoir.

Elevent	Туре	Milltown	Blackfoot Arm	Thompson Falls	Noxon	Cabinet Gorge	*Ave. Shale	Shallow Water **Sediment
Cu	Total	***449(177)	23(7)			•	45	56
	Acetic	241(121)	5(2)	47(12)	43(6)	19(7)	-	-
Zn	Total	1770(1430)	103(23.3)	-	•		95	92
	Acetic	1330(1100)	11.0(6)	145(33)	135(27)	111(22)	-	-
As	Total	58.6(22.2)	7.2(1.2)	873	6753	5 7 3	13	5
	Acetic	16.0(4.4)	1.0(0.5)	2.4(0.5)	1.9(0.6)	1.5(0.3)	-	-

Table 1.--Average metal concentrations in reservoir sediments along the Clark Fork River (all as ug/g dry weight basis)

-----Values from Turekian and Wedepohl (1961) as cited by Salomons and Forstner (1984)
** Values from Wedepohl (1969, 1978) as cited by Salomons and Forstner (1984)
*** Hean (Standard Deviation)

Table 2.--Metal concentrations in acetic acid extracts of Thompson Falls Reservoir sediments (all reported as µg/g dry weight basis)

lement	TF1	TF2	TF3	TF4	TF5	TF6	TF7
Cu	32	-*	41	65	45	55	42
Zn	125	117	110	213	146	180	126
As	2.1	1.9	1.9	3.3	2.3	2.9	2.1

Mainstem Reservoir Sites

Table 3.--Metal concentrations in acetic acid extracts of Noxon Reservoir sediments (all as µg/g dry weight basis)

	2015/10/06			Mainstem of Reservoir Sites							*Intermediate Sites		**Local Background Sites	
Element	N2	КЗ	314	196	N7	N8	N9	N1 1	N13	N14	N10	N1 2	NI	NS
Cu	31	52	49	39	38	46	43	42	39	47	26	22		<0.3
Zn	130	201	149	132	120	149	128	123	106	115	88	90	7	10
As	2.3	3.1	2.4	1.5	1.0	2.4	1.8	1.6	1.6	1.7	1.9	1.8	0.8	0.6

 Intermediate Sites: N10 at the mouth of Martens Creek N12 at the mouth of Stevens Creek

** Local Background Sites: N1 in the upper mouth of Vermillion Creek N5 in the upper mouth of Trout Creek

Table 4.--Metal concentrations in acetic acid extracts of Cabinet Gorge Reservoir sediments (all reported as µg/g dry weight basis)

		Mainstem		*Local Background Sites			
Element	CG1	CT2	CG3	CG5	CG6	CG4	CG7
Cu	16	25	10	26	19	2	<0.3
Zn	137	123	80	117	97	21	3
As	1.2	1.7	1.3	1.8	1.6	0.9	0.3

* Local Background Sites: CG4 is the mouth of Elk Creek CG7 is the upper mouth of the Bull River

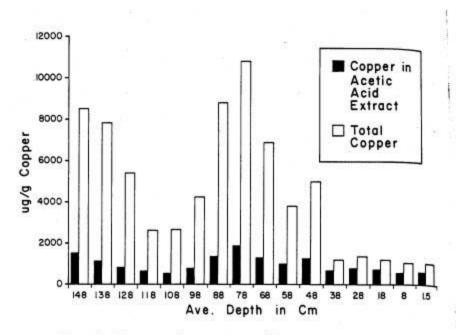


Figure 6. Histogram of copper in core #3 at Milltown Reservoir.

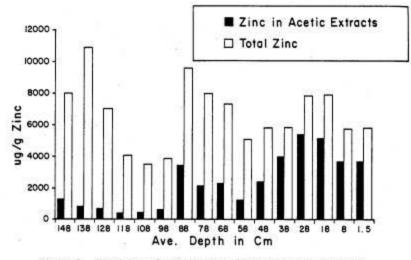


Figure 7. Histogram of zinc in core #3 at Milltown Reservoir.

3 3
l Depths ev.)
1)
9)
(1.0)

Table 5.--Metal concentrations in acetic acid extracts of sediment core #1 from Thompson Falls Reservoir

* All concentrations are ug/g dry weight basis

Table 6.--Metal concentrations in acetic acid extracts of sediment core #3 from Noxon Reservoir

	Sediment Depth in Cm											
Element	0-3	3-8	8-13	13-18	18-23	23-28	28-33	33-38	38-41	Ave. 0-28		
		******		*********	********	*********		*****	*******			
Cu	*52	68	44	53	75	69	0	0	0	60(12)		
Zn	145	166	136	164	237	236	11.9	3.9	3.9	181(44)		
As	2.2	2.7	2.3	2.7	3.3	3.4	1.2	1.9	2.4	2.7(0.5)		

* All concentrations are ug/g dry weight basis

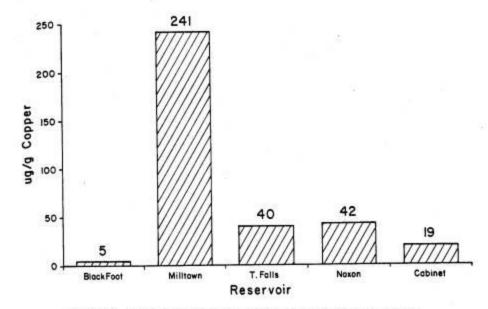


Figure 8. Downriver trends in acetic acid extractable copper.

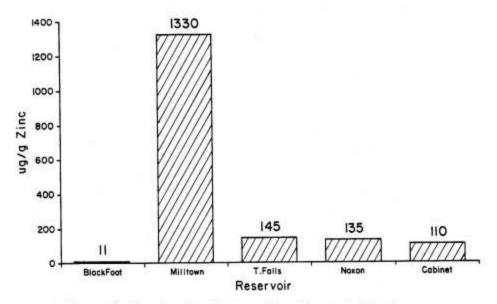


Figure 9. Downriver trends in acetic acid extractable zinc.