

# Sediment Metal Concentrations In A Southwestern Montana Stream Impacted By Smelter Emissions Deposition

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**Abstract**—Historic smelting activities by the Anaconda Copper Mining Company's smelter in Anaconda, Montana emitted large quantities of metals and metalloids which fell to the ground downwind of the smelter. Cabbage Gulch is located 4.5 km south of the smelter site, so it was severely impacted by the fallout of metals and metalloids. Stormwater runoff carried these contaminants into Cabbage Gulch where some of the contaminants that are in a particulate form settled to the bottom in depositional areas such as floodplains and beaver ponds. Stream bed and stream bank samples were taken along the length of Cabbage Gulch. Near-surface stream bed sediment concentrations averaged 60 mg/kg (dry weight) arsenic (As), 3 mg/kg cadmium (Cd), 100 mg/kg copper (Cu), 53 mg/kg lead (Pb), and 120 mg/kg zinc (Zn), while deeper stream bed sediment concentrations averaged 82 mg/kg As, 6 mg/kg Cd, 120 mg/kg Cu, 59 mg/kg Pb, and 170 mg/kg Zn. Near-surface stream bank sediment concentrations averaged 120 mg/kg for As, 8 mg/kg Cd, 250 mg/kg for Cu, 92 mg/kg for Pb, and 290 mg/kg for Zn, while deeper stream bank sediment concentrations averaged 85 mg/kg for As, 4 mg/kg Cd, 130 mg/kg for Cu, 65 mg/kg for Pb, and 160 mg/kg for Zn. Metal concentrations tended to be the highest in the headwaters region, with the exceptions of three depositional areas – an abandoned beaver pond, an inactive beaver pond, and a flat area subject to stream channel braiding. Stream bed contaminant concentrations were compared to stream bank contaminant concentrations; there was no difference in contaminant concentrations in deep sediments (5 to 15 cm deep) but the near-surface stream bank sediments (0 to 5 cm deep) had higher Cu and Zn concentrations than did the near-surface stream bed sediments. Contaminant concentrations did not vary over depth in the stream bed sediments, but they did vary in the stream bank sediments with near-surface sediments having higher Pb and Zn concentrations than did the deep sediments. Cabbage Gulch, which was contaminated solely through airborne deposition of smelter emissions, had lower metals concentrations than did comparative mining-impacted streams where the

source of contamination was solid particles such as mine tailings. Seven of the 21 sediment samples from Cabbage Gulch had high or medium-high risk of toxicity to sediment-dwelling organisms.

**Keywords**—*sediments, metals, arsenic, cadmium, copper, lead, zinc, beaver pond*

## I. INTRODUCTION (*Heading 1*)

Historic smelting activity by the Anaconda Copper Mining Company's smelter in Anaconda, Montana emitted contaminants into the air with the flue gas from the smelter stack, which were then deposited on the land downwind from the smelter. Some of these contaminants of concern (COCs - arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn)) fell in the Mill Creek drainage (Deer Lodge County, Montana), from where they enter surface water in stormwater runoff. Steep topography and a lack of vegetation cause large quantities of sediment to enter surface waters, where some of the COCs that are in the solid phase settle to the bottoms of and flood plains surrounding the streams.

The Anaconda Copper Mining Company began copper concentrating and smelting operations on the east side of Anaconda, MT in 1884. This facility, called the Upper Works, had two smokestacks measuring 35 and 53 m in height [1]. Another smelter, called the Lower Works, was built in 1897 and was located 1 mile east of the Upper Works. The need for increased smelting capacity led to the construction of the Washoe Reduction Works in 1902. The Washoe facility originally had a capacity of 4800 tons of ore per day and produced 600,000 pounds of copper in 1908. This facility started operation with four small smokestacks, which were replaced by one taller 91 m stack in 1904. In 1919, a 178 m tall smoke stack was put into operation, and an electrostatic precipitator was installed to remove some of the metals- and arsenic-contaminated particulate matter from the emissions. The Anaconda Smelter ceased operations in 1980 [2]. The smelter site along with a surrounding 78,000 ha area was placed on the Superfund National Priorities List by the U.S. Environmental Protection Agency in 1983 because of its large volumes of mine

waste and soil, ground water, and surface water contaminated by metallic elements in the flue dust that deposited downwind of the smelter [3].

A number of beaver dams have been built over time on the streams in the Mill Creek drainage. Beaver ponds effect sediment chemistry by creating conditions conducive for particle sedimentation [4] [5] [6] [7] [8] [9]. Sedimentation of particulate COCs can contaminate the sediments in the stream bottoms and flood plains. Sediments in the stream channels that run through beaver ponds are scoured away after beaver dam breaching because of the high water velocity that occurs when the pond is drained, while sediments that lie in the flood plain tend to stay in place [10].

The objectives of this study were (1) to measure COCs in stream bed and stream bank sediments along the length of Cabbage Gulch, (2) to evaluate the level of contamination over sediment depth, (3) to compare stream bed sediment COC concentrations to stream bank sediment COC concentrations, and (4) to evaluate the level of sediment contamination in Cabbage Gulch.

## II. STUDY AREA

Cabbage Gulch is a small stream (1 to 2 m wide and 5 to 10 cm deep during base flow) that is a tributary of Mill Creek, Deer Lodge County, Montana (Fig. 1). Cabbage Gulch is approximately 4.5 km south of the old Anaconda Company smelter smokestack and is within the Anaconda Smelter Superfund site. More than three decades after the smelter ceased operations, the water in Cabbage Gulch is still contaminated with copper (Cu) and arsenic (As) during storm runoff events [11] [12] [13] [9]. A number of beaver dams have been built on Cabbage Gulch. These dams have been abandoned and all but one have breached.

## III. METHODS AND MATERIALS

We collected sediment samples from near the mouth of Cabbage Gulch to its Upper West Branch (Fig. 1). A sampling event was performed in August 2013, when we obtained a sediment core from an inactive beaver pond (IBP). We drove a 5 cm diameter, 30 cm long stainless steel pipe tip with removable plastic insert into the sediment with a pipe pounder apparatus [14]. We divided this core into top, middle and bottom segments of 10 cm each. In sampling events performed in May 2014 and June 2014, we collected grab samples of stream bed, stream bank, and abandoned beaver pond (ABP) sediments from a depth of zero to 7.5 cm with a trowel. During October 2014, we collected stream bed and stream bank samples from seven sites – one from the surface of the sediments to 5 cm deep (near-surface sediments), and the other from 5 to 15 cm

deep (deep sediments). After excavation, we placed sediment samples into individual plastic bags.

The difference between the inactive beaver pond and the abandoned beaver pond was in the amount of water in the ponds. The dam on the inactive beaver pond had not breached although the beavers no longer lived at the pond. Thus, this pond was still full of water and the sample (IBP) was taken where the sediments were covered with water. The dam on the abandoned beaver pond had breached, draining the pond. The ABP sample was taken on dry land immediately upstream of the beaver dam within the confines of the old beaver pond, approximately 50 m away from the stream channel. This location had been covered with water when the pond was full.

Sediment samples were analyzed for As, Cd, Cu, Pb, and Zn. The sediments were digested per EPA Method 3050B. Metals analyses on the filtrates followed EPA Method 200.8. All analyses were performed by the Montana Bureau of Mines and Geology (MBMG) Analytical Laboratory.

## IV. RESULTS

Contaminant concentrations varied greatly among the different sampling locations, and among the different COCs (Table 1). The standard deviations of the stream bed concentrations exceeded the means in eight of the ten groups. Zinc had the highest concentrations and Cd the lowest concentrations in both stream bed and stream bank sediments.

Contaminant concentrations in near-surface stream bed sediment samples are shown longitudinally along Cabbage Gulch in Fig. 2. Metal and metalloid concentrations decrease, in general, from upstream to downstream. There are two notable exceptions. Contaminant concentrations at sampling station ABP were high compared to concentrations upstream and downstream. Sampling station SB16, which was immediately above the Mill Creek Road crossing, also had high concentrations compared to samples taken up to 0.8 km above SB16. Contaminant concentrations in deep stream bed sediment samples are shown longitudinally along Cabbage Gulch in Fig. 3. Contaminant concentrations were relatively constant, except that concentrations at sites IBP and SB16 were relatively high.

Contaminant concentrations in both near-surface and deep stream bank samples showed pronounced variability over the stream length (Figs. 4 and 5). The most downstream sampling site (SBK17) had the highest Cd, Cu, and Zn concentrations in both the near-surface and deep sediments.

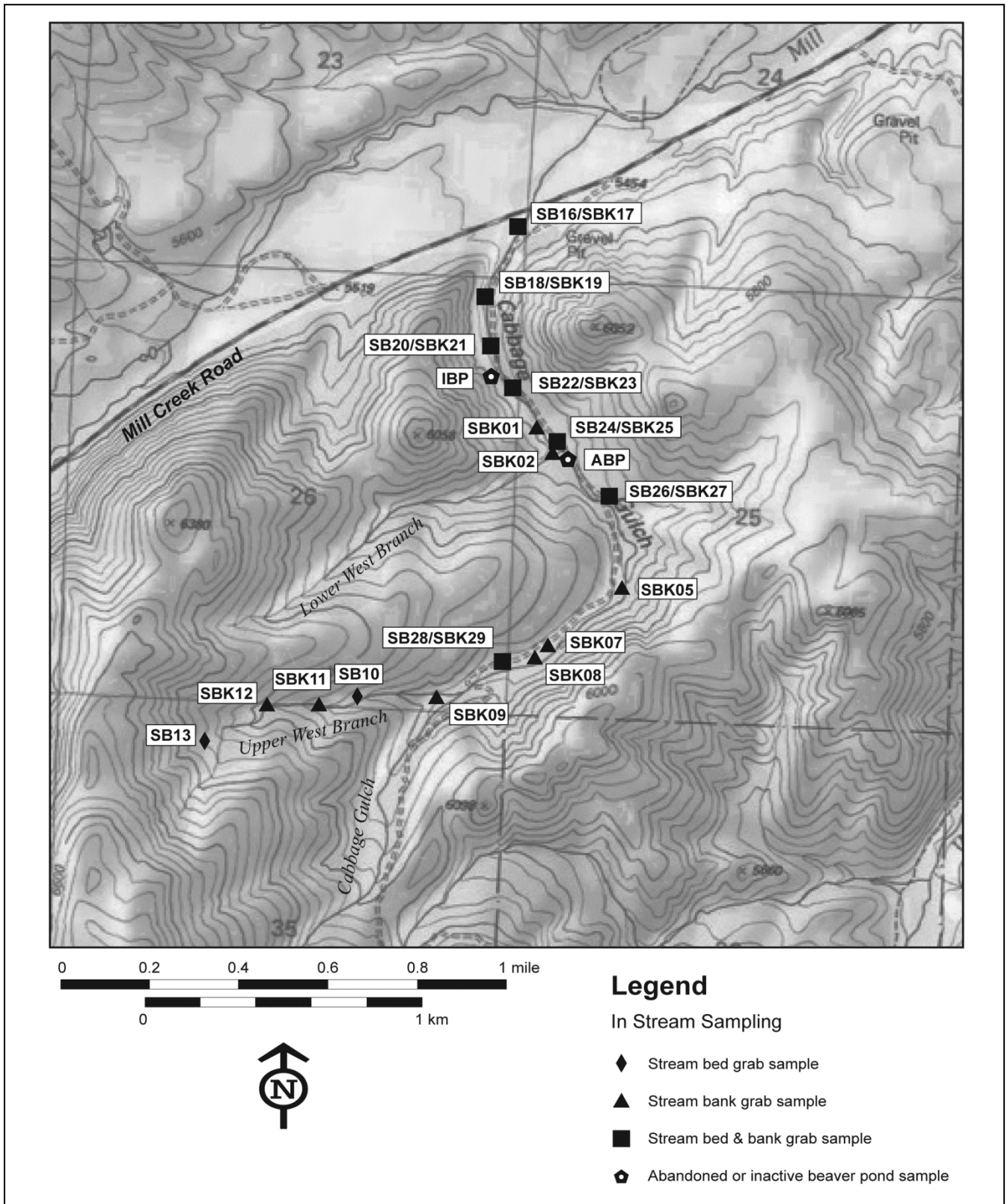


Fig. 1. Cabbage Gulch showing sampling locations.



TABLE I. SUMMARY OF CONTAMINANT CONCENTRATIONS IN CABBAGE GULCH SEDIMENTS, MONTANA, USA (MG/KG DRY WEIGHT)

Near-surface stream bed or beaver pond sediments (12 samples)					
Contaminant	Mean	Standard Deviation	Median	Maximum	Minimum
As	60	65	34	230	17
Cd	3	3	1.2	9	0.6
Cu	100	133	26	414	15.6
Pb	53	58	21	190	13
Zn	120	83	76	280	51

Deep stream bed sediments (9 samples)					
Contaminant	Mean	Standard Deviation	Median	Maximum	Minimum
As	82	100	28	265	13
Cd	6	14	1	40	0.5
Cu	120	203	19	520	10
Pb	59	95	16	270	8.0
Zn	170	240	69	680	36

Near-surface stream bank sediments (8 samples)					
Contaminant	Mean	Standard Deviation	Median	Maximum	Minimum
As	120	50	110	180	47
Cd	8	9	6	30	1.7
Cu	250	220	210	740	50
Pb	92	48	94	180	28
Zn	290	200	270	720	71

Deep stream bank sediments (8 samples)					
Contaminant	Mean	Standard Deviation	Median	Maximum	Minimum
As	85	36	95	120	12
Cd	4	3	3	11	0.7
Cu	130	81	150	270	24
Pb	65	43	57	150	23
Zn	160	74	175	260	54

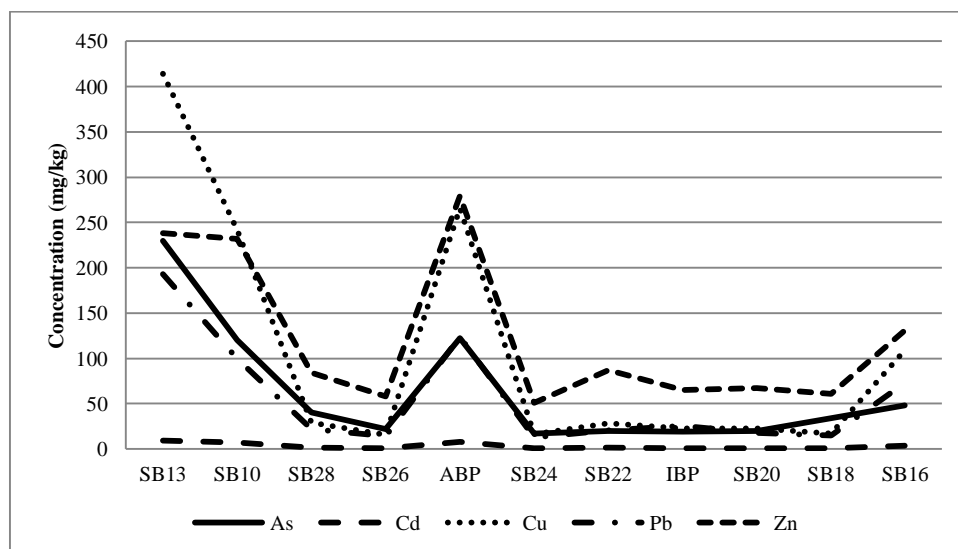


Fig. 2. Near-surface stream bed contaminant concentrations (mg/kg dry weight). Sampling stations (e.g., SB13) are sequenced from the most upstream site (left) to the most downstream site (right).

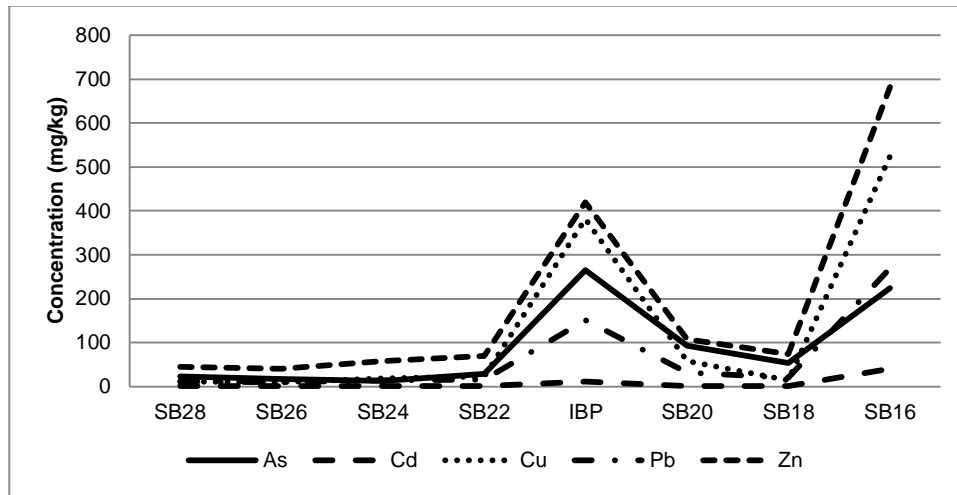


Fig. 3. Deep stream bed (5 to 15 cm or 10 to 30 cm depth) contaminant concentrations (mg/kg dry weight). Sampling stations (e.g., SB28) are sequenced from the most upstream site (left) to the most downstream site (right).

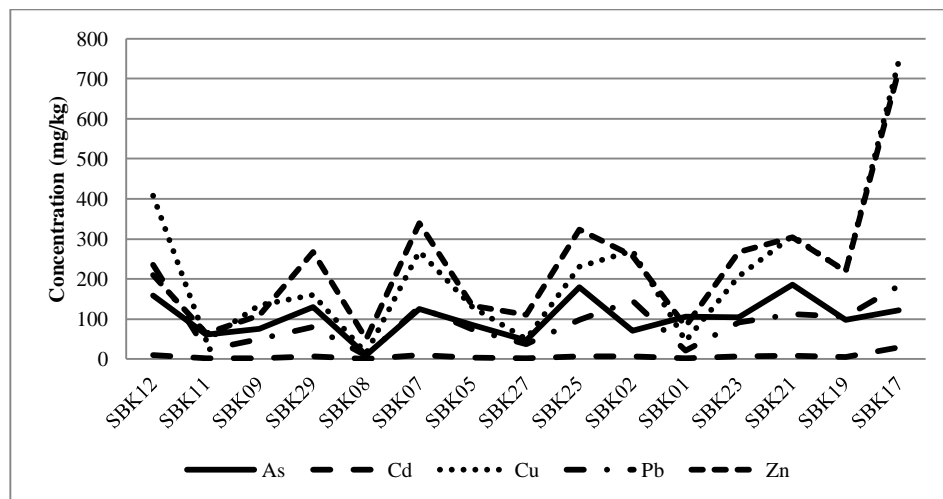


Fig. 4. Near-surface (0 to 5 cm) stream bank concentrations (mg/kg dry weight). Sampling stations (e.g., SBK12) are sequenced from the most upstream site (left) to the most downstream site (right).

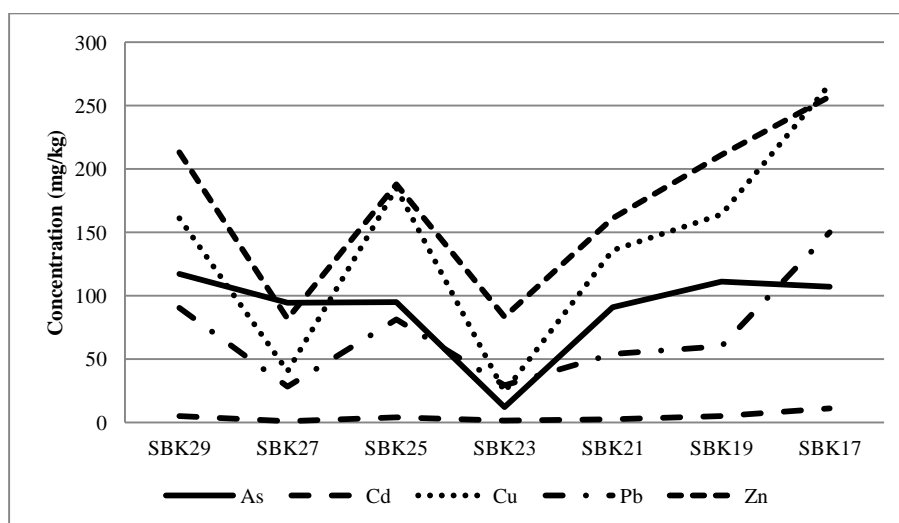


Fig. 5. Deep stream bank (5 to 15 cm depth) concentrations (mg/kg dry weight). Sampling stations (e.g., SBK29) are sequenced from the most upstream site (left) to the most downstream site (right).

## V. DISCUSSION

Contaminant concentrations in the stream bed sediments were highest in the Cabbage Gulch headwaters, in old beaver ponds, and above the Mill Creek Road crossing (Figs. 2 and 3). Sediments accumulated in beaver ponds because the ponds created excellent conditions for particle sedimentation. In the headwaters region, the near-surface sediments were more contaminated than the deep sediments. This could show that soil eroding into the headwaters region of Cabbage Gulch is still a major source of sediment contamination.

The near-surface stream bed sediments in the ABP sample had high COC concentrations (Fig. 3). Observation of Google Earth satellite imagery shows that this pond breached between August 12, 2002 and September 19, 2005. Contaminated sediments remained in the formerly inundated area approximately ten years later. This agrees with Levine and Meyer [10] that sediments in a beaver pond that are not in the stream channel remain indefinitely after the pond drains. Therefore, stream drainages with metallic contamination and beaver ponds should have high metal concentrations in the soil where the beaver ponds were.

Copper, Pb, and Zn concentrations in both stream bed and stream bank samples at sampling site SB16/SBK17 were relatively high for both near-surface and deep sediments. This site was in an area with a nearly flat topography, which caused the stream channel to be almost non-existent and disbursed the flow over a wide vegetated area. Water flowing around the beaver dams in this area caused stream channel braiding and overland flow. These are excellent conditions for particle sedimentation in that the water velocity is slow and the particles need settle only a short depth to deposit onto the soil. Not being in the main channel floodway, the sediments were not subject to subsequent scouring by flood flows and, therefore, remained where they settled.

Arsenic concentrations in the sediments were low compared to the concentrations of the four metals (Figs. 2 – 5). In Cabbage Gulch water, As was entirely in the dissolved phase [9] so there was no solid-phase As to settle. Arsenic in the sediments probably came from adsorption of As onto previously-settled sediments.

We compared stream bed concentrations to stream bank concentrations using a paired t-test for assessing the average of differences [15], to see if concentrations differed between the stream bed and the stream bank. This technique was used because the stream bed and stream bank samples were paired, having been taken at the same sampling station at the same time. The comparisons were performed at both sampling depths - near-surface samples (0 to 5 cm deep) and deep samples (5 to 15

cm deep). Average concentrations and standard errors were calculated for the near-surface sediments and, separately, for the deep sediments for the seven instances where samples were collected at two depths (0 to 5 cm and 5 to 15 cm). Concentrations were compared at the 95% confidence level.

The near-surface stream bank samples had higher Cu and Zn concentrations than did the near-surface stream bed samples (Table 2). Arsenic, Cd, and Pb concentrations in the stream bed and the stream bank were not different. The concentrations in the deep stream bed samples were not different than the concentrations in the deep stream bank samples for all COCs.

Concentrations in the near-surface samples were compared to the deeper samples for the seven stream bed sites and the seven stream bank sites where sampling was performed at two depths. The comparison used the paired t-test for assessing the average of differences. There was no difference in concentrations over depth in the stream bed samples. The homogeneity in COC concentrations may be due to scouring episodes during high flows, followed by deposition periods during lower flows, which would have the effect of mixing the stream bed sediments. Stream bank concentrations show some variation over depth with Pb and Zn near-surface sediment concentrations being greater than Pb and Zn deep sediment concentrations (Table 2).

The concentrations in the stream bank sediments would vary over depth if the COC concentrations in the sediments that were deposited varied over time and the sediments remained in place since their deposition. The near-surface stream bank sediments probably contained sediments laid down during and after smelter operation so that the sediments were contaminated with metals, while some of the deep sediments may be from the time before the smelter was in operation and the sediments not contaminated.

We compared contaminant concentrations in the stream bed sediments to COC concentrations in sediments from other mining-impacted rivers in southwestern Montana. The Cabbage Gulch sediments had lower COC concentrations than the other sites (Table 3). The Cataract Creek sediments were taken from a small stream below the abandoned Crystal Mine before any reclamation was performed on Cataract Creek. This stream had become contaminated when solid mine wastes entered the creek with stormwater runoff. The Silver Bow Creek samples were taken downstream of the massive copper mining and processing works at Butte, Montana, also before any reclamation had occurred.

TABLE II. STATISTICAL COMPARISONS OF CONCENTRATIONS FROM PAIRED NEAR-SURFACE AND DEEP SAMPLES.

SB vs. SBK		
As	near-surface	No difference
	deep	No difference
Cd	near-surface	No difference
	deep	No difference
Cu	near-surface	SB > SBK
	deep	No difference
Pb	near-surface	No difference
	deep	No difference
Zn	near-surface	SB > SBK
	deep	No difference
Near-surface samples vs. deep samples		
As	SB	No difference
	SBK	No difference
Cd	SB	No difference
	SBK	No difference
Cu	SB	No difference
	SBK	No difference
Pb	SB	No difference
	SBK	near-surface > deep
Zn	SB	No difference
	SBK	near-surface > deep

TABLE III. COMPARISON OF CONTAMINANT CONCENTRATIONS IN NEAR-SURFACE BED SEDIMENTS IN MINING-IMPACTED WATERS IN SOUTHWEST MONTANA, USA (MG/KG). N/A = NOT AVAILABLE.

Metal	This study	Martin (1992) <sup>1</sup>	Kemble et al. (1994) <sup>2</sup>
As	61	N/A	20
Cd	3	27	2
Cu	100	1400	290
Pb	53	N/A	56
Zn	120	2600	560
Metal	Dodge et al. (2003) <sup>3</sup>	Dodge et al. (2003) <sup>4</sup>	
As	N/A	N/A	
Cd	13	3	
Cu	1600	440	
Pb	280	70	
Zn	3300	630	

Average of nine samples; Cataract Creek drainage below the Crystal Mine, MT, USA

<sup>2</sup> Average of three samples; Upper Clark Fork River, MT, USA

<sup>3</sup> Average of nine samples collected from 1993-2002; Silver Bow Creek below Butte, MT, USA

<sup>4</sup> Average of 70 samples collected at eight sampling sites from 1993-2002; Upper Clark Fork River, MT, USA

Silver Bow Creek sediments can be assumed to consist partially of mine tailings containing Cd, Cu, Pb, and Zn. The upper Clark Fork River is also below the mine workings at Butte, but downstream of the Warm Springs Ponds treatment system on lower Silver Bow Creek. The first of these ponds was built in 1911 to settle mine tailings and other contaminated sediment out of the water (CFRTAC 2014). The upper Clark Fork River below the location of these ponds was contaminated from sediment-laden flood events prior to 1911. While highly-contaminated sediments no longer traveled downstream from Butte to deposit onto the stream bed of the upper Clark Fork River after 1911, the Warm Springs Ponds dampen the peaks of storm hydrographs, reducing the scouring that would occur if the peak flows were higher. Thus, the upper Clark Fork River can be considered to be partially remediated at the times of sampling. Sediments containing solid wastes from mine workings (Cataract Creek and Silver Bow Creek) have the highest metals concentrations and sediments containing historic solid Springs Ponds treatment system on lower Silver Bow Creek. The first of these ponds was built in 1911 to settle mine tailings and other contaminated sediment out of the water [16]. The upper Clark Fork River below the location of these ponds was contaminated from sediment-laden flood events prior to 1911. While highly-contaminated sediments no longer traveled downstream from Butte to deposit onto the stream bed of the upper Clark Fork River after 1911, the Warm Springs Ponds dampen the peaks of storm hydrographs, reducing the scouring that would occur if the peak flows were higher. Thus, the Clark Fork River can be considered to be partially remediated at the times of sampling. Sediments containing solid wastes from mine workings (Cataract Creek and Silver Bow Creek) have the highest metals concentrations and sediments containing historic solid wastes but have been protected by reclamation (the upper Clark Fork River) have the next highest metals concentrations. The lowest sediment COC concentrations were in Cabbage Gulch, which had no input of solid wastes from mining operations but was contaminated only by smelter fallout.

We estimated stream bed sediment toxicity by comparison of COC concentrations with consensus-based sediment quality guidelines for freshwater sediments. The sediment quality guidelines provide simple thresholds for evaluating the risks that toxic contaminants in sediments have to organisms in those sediments [17]. Consensus-based probable effect concentrations (PEC) are 33.0, 4.98, 149, 128, and 459 mg/kg (dry weight) for As, Cd, Cu, Pb, and Zn, respectively [18]. Mean sediment quality guideline quotients (mPECQ) were calculated from the concentrations at each of the near-surface and deep sediment samples and the PECs (equation 1) [19] [20]:

$$mPECQ = \frac{\sum_{i=1}^n \frac{C_i}{PEC_i}}{n} \quad (1)$$

$C_i$  is the concentration of contaminant  $i$  in the sediments and  $n$  is the number of contaminants - in this case, five. A mPECQ provides "a single, easily understood, effects-based numerical index of the relative degree of chemical contamination in sediment samples" [16]. Mean PECQs ranged from 0.13 to 3.96 (Table 4). Mean PEQs have been characterized as having a high risk of toxicity if they are greater than 2.3, having a medium-high risk of toxicity if they are between 1.51 and 2.3, having a medium-low risk of toxicity if they are between 0.11 and 1.5, and having a low risk of toxicity if they are less than 0.1 [17] [21] [22] [23]. Three of the samples had a high risk of toxicity (IBP, deep; SB13, deep; and SB16, deep) and two had a medium-high risk of toxicity (ABP, near-surface; and SB10, near-surface).

Another method for characterizing the risk of toxicity is to assume mPECQs less than 0.5 indicate sediments where adverse biological effects are unlikely, while mPECQs greater than 0.5 indicate sediments where adverse biological effects would be expected [17] [18]. Seven of the 19 samples had mPECQs greater than 0.5 (Table 4). Arsenic had the highest PECQ in six of the seven samples that had high mPECQs; Cd had the highest PECQ in the seventh sample. Areas with high mPECQs were the Upper West Branch of Cabbage Gulch, ABP, IBP (deep sediments only), SB16, and SB20 (located about 0.5 km upstream from the Mill Creek Highway).

## VI. CONCLUSIONS

- Arsenic, Cu, Pb, and Zn concentrations in stream bed and stream bank sediments were higher in the Cabbage Gulch headwaters than in the downstream section of the stream.
- Arsenic, Cu, Pb, and Zn concentrations in stream bed and stream bank sediments were high in depositional areas caused by beaver ponds and stream channel braiding.

TABLE IV. COMPARISON OF CONTAMINANT CONCENTRATIONS IN NEAR-SURFACE BED SEDIMENTS IN MINING-IMPACTED WATERS IN SOUTHWEST MONTANA, USA (MG/KG). N/A = NOT AVAILABLE.

Sampling site	Near-surface sediments	Deep sediments
ABP	1.73	--
IBP	0.22	2.31
SB10	1.57	--
SB13	2.64	--
SB16	0.72	3.96
SB18	0.29	0.35
SB20	0.22	0.61
SB22	0.26	0.24
SB24	0.17	0.15
SB26	0.21	0.13
SB28	0.36	0.16

- Near-surface (0 to 5 cm) stream bank sediments had higher concentrations of Cu and Zn than did near-surface stream bed sediments.
- Deep (5 to 15 cm) stream bank sediments did not have different COC concentrations than the deep stream bed sediments.
- Near-surface (0 to 5 cm) stream bank sediments had higher Pb and Zn concentrations in than in deep (5 to 15 cm) stream bank sediments.
- Cabbage Gulch, whose source of contamination was airborne deposition of smelter emissions, had lower COC concentrations than did streams in the same region that were contaminated by solid mining wastes.
- Seven of the 19 stream bed sediment samples had COC concentrations indicating the probability of toxicity to sediment-dwelling aquatic life.

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