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EFFECTS OF LAND RECLAMATION TECHNIQUES ON RUNOFF WATER QUALITY FROM THE CLARK FORK RIVER, FLOODPLAIN, MONTANA

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ABSTRACT

Persistent fill kills have been recorded in Montana's Clark Fork River below the confluence of Silver Bow and Warm Springs Creeks. The cause of mortality was disputed until changes in river water quality associated with a thunderstorm in 1989 were documented. After this storm it was clear that the source of elevated metal concentrations in the dead fish was a temporary increase in the metal levels in the river. These metals were derived from salts present in crusts deposited on adjacent soil surfaces by evaporation of metal salt laden water. To prevent the recurrence of these fish kills and to remediate the area, revegetation studies have been conducted to assess the feasibility of vegetation establishment on the metal impacted areas within and immediately adjacent to the floodplain. This paper presents the results of water quality investigations associated with this and related studies in the Clark Fork River Basin. In addition, the impact of the technologies developed in the streambank study and implemented on contaminated lands adjacent to the stream in which the fish kills occurred are noted.

INTRODUCTION

Periodic fish kills affecting several species have occurred in Montana's Clark Fork River. It was postulated that metal mining, processing, and smelting activities in the headwaters of the river were responsible, but scientific documentation of the cause of mortality was sparse. During a major thunder-storm in July 1989 a sequence of events that lead to a major fish kill was documented. From analyses of the data collected during this event, it was clear that the fish died because of elevated metal loads in the river water. Since these deaths have been associated with intense summer thunderstorms, attendant soil erosion has been proposed as a major contributing factor in the death of the fishes. While surface soils are contaminated with metals they do not, under most conditions of erosion, provide sufficient quantities of metals to the river to cause large acute toxicity events. Since ground water flushes of metals augmented by the storms would not reach the river until some time after dead fish were identified, this water source is also unlikely as a factor contributing to the fish kills. It is now recognized that soluble and very acid metal salts transported to the river by surface water runoff caused the mortality (Phillips and Lipton 1995). This paper presents arguments for assigning responsibility for the elevated metal levels to the surface salts and examines a method of remediating the movement of metals salts into the river during precipitation events.

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ENVIRONMENTAL SETTING

Butte, Montana, was the center of copper mining in the United States for many years. Wastes from the processing of these pyritic ores still remain along the banks of Silver Bow Creek, downstream from the copper mining area. Numerous waste deposits are also located in and near the city of Anaconda, location of a now demolished world class copper smelter, and other mining and smelting wastes are also found elsewhere along the Clark Fork River (Figure 1). These materials range from pyritic tailings expressing very acid pH values to soils contaminated with metals and arsenic. The main geographic area of concern is located immediately upstream from the confluence of Warm Springs and Silver Bow Creeks. The 1989 fish kill began below the junction of these two creeks.

Background Surface Water Quality

U.S. EPA (1986) water quality criteria values are reported in Table 1, as are typical values measured in water samples taken from Silver Bow Creek and the Clark Fork River between 1985 and 1993 (Lambing et al. 1995). Acute and chronic criteria for copper and zinc are routinely exceeded in Silver Bow Creek which is presently unable to sustain fish life. Chronic criteria values for these metals are also commonly exceeded in the Clark Fork River but water quality is sufficient to support trout, although numbers reported are lower than those in similar streams that are not impacted by metals (Hillman et al. 1995). It is during intense thunderstorms that water quality in the streams degenerate and fish kills occur.

River Water Quality During Fish Kill

On the afternoon of July 12, 1989, a severe thunderstorm occurred over the headwaters of the Clark Fork River when the river was at a low flow (1430 L sec^{-1}). Instream monitoring and collection of water samples were initiated within a few minutes of the onset of the storm. Results of monitoring are reported in Table 2. Within 20 minutes, the pH of the water was reduced from 7.93 to 4.30. In terms of hydrogen ion concentration, this change represents an increase of nearly four orders of magnitude. Alkalinity was reduced from 86 mg L^{-1} to concentrations reported at or below the detection limit (< 10 mg/L), while the hardness of the water increased by a factor of two.

Copper concentrations increased from a prestorm level of 120 μgL^{-1} to a maximum level of 13,300 $\mu g\ L^{-1}$ at 48 minutes. Large increases in concentrations of the other metals and arsenic were also recorded. Concurrent with the water sampling, dead fishes were collected for diagnostic tests. Mean concentrations (dry weight) of cadmium, copper, and zinc in gill tissue from the collected fish were 5.6 mg kg^{-1}, 683 mg kg^{-1}, and 888 mg kg^{-1} respectively, which confirmed that mortality was due to toxic metal concentrations (MDFWP 1989).

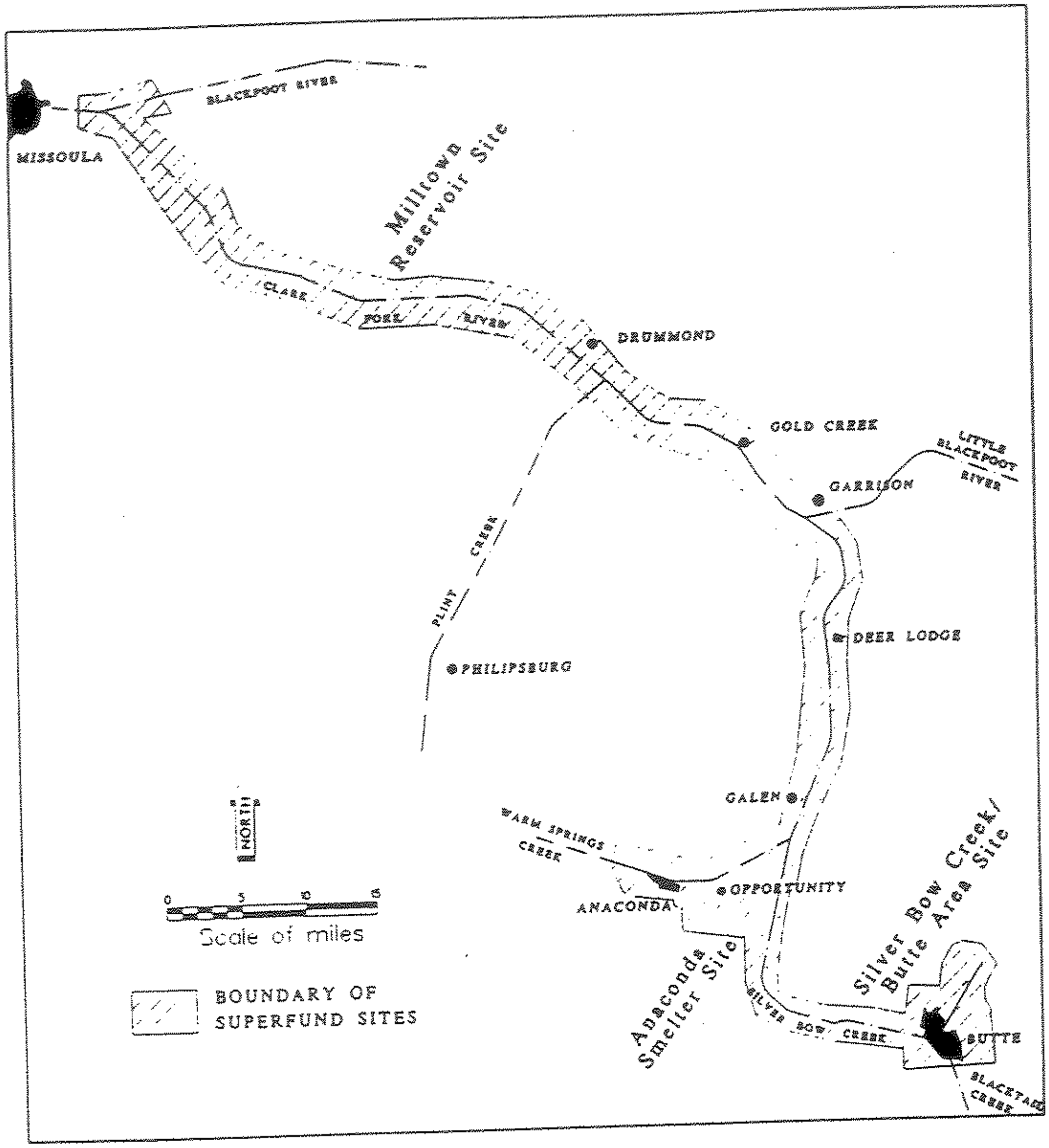

Figure 1. Silver Bow Creek and Clark Fork River in southwestern Montana.

Table 1. Water quality criteria[1] for arsenic, copper, and zinc and range of typical measurements[2] of these metals in Silver Bow Creek and the Clark Fork River, March 1985 to September 1993.

Type of criteria or Location sampled	Metal (µg L^{-1})		
	Arsenic	Copper	Zinc
Water quality criteria			
Acute	360	18	320
Chronic	190	12	47
Range of typical stream measurements (mean values in parentheses)			
Silver Bow Creek			
Below Blacktail Creek (N=8)	11-39 (18)	130-550 (252)	990-1,600 (1,060)
At Opportunity (N=8)	11-140 (32)	100-900 (261)	260-1,400 (566)
At Warm Springs (N=8)	13-29 (20)	23-60 (38)	40-140 (85)
Clark Fork River			
At Galen (N=36)	3-60 (18)	11-240 (46)	20-360 (79)
At Deer Lodge (N=53)	8-200 (26)	12-1,500 (125)	10-1,700 (155)
At Gold Creek (N=8)	11-31 (16)	21-150 (55)	30-180 (69)
At Drummond (N=8)	12-30 (17)	18-140 (55)	30-260 (92)

[1] U.S. EPA (1986); based on hardness of 100 mg L^{-1} as $CaCO_3$.

[2] Lambing et al. (1995); all results reported as total recoverable.

Table 2. Water quality of river samples collected concurrent with fish kill.[1]

Characteristic	Minutes from commencement of thunderstorm						
	0	11	21	33	48	60	113
pH (SU)	7.93	6.52	4.30	4.35	4.14	4.50	4.98
Alkalinity (mg L^{-1})	86	30	<10	<10	<10	<10	<10
Hardness (mg L^{-1})	216	285	357	392	446	394	398
Aluminum (µg L^{-1})	280	7,870	30,600	28,100	37,700	22,100	16,500
Cadmium (µg L^{-1})	3	14	51	55	85	58	46
Copper (µg L^{-1})	120	2,660	8,900	9,280	13,300	8,300	6,000
Lead (µg L^{-1})	2	11	30	10	10	20	10
Iron (µg L^{-1})	410	8,570	29,200	33,400	43,900	29,000	20.3
Zinc (µg L^{-1})	140	3,020	10,400	10,000	14,000	9,900	7,900

[1]Montana Department of Fish, Wildlife and Parks (1989).

Surface Soil Chemistry

Metal levels in contaminated surface soils and wastes along streams in the upper Clark Fork River Basin are reported in Table 3. The sampled materials ranged from well vegetated soils to barren expanses of nonvegetated tailings containing highly elevated levels of metals known to be toxic to plant growth.

Table 3. Metal concentrations and pH of contaminated soils and wastes adjacent to Clark Fork River streams.[1]

Characteristic	pH and metal concentration range
pH (SU)	2.5 - 6.7
Arsenic (mg kg^{-1})	19.3 - 3,140
Aluminum (mg kg^{-1})	227 - 19,700
Cadmium (mg kg^{-1})	2.6 - 108
Copper (mg kg^{-1})	260 - 11,200
Lead (mg kg^{-1})	82.6 - 6,477
Zinc (mg kg^{-1})	19.2 - 22,000

[1]Reclamation Research Unit et al. 1989.

Metal Salts

During dry summer periods salts accumulate on the surface of soil at many sites along the stream. Metals are transported to the soil surface by water and accumulate because of evaporation of the water. During intense precipitation events these salts will rapidly solubilize and are flushed into the river as surface water runoff. The concentrations of metals in salts collected along the banks of the Clark Fork River are reported in Table 4.

Table 4. Concentrations of metals in salts collected from surface of soils along the Clark Fork River.[1]

Metal	Concentration range (dry weight)
Cadmium (mg kg^{-1})	48 - 120
Copper (mg kg^{-1})	70,000 - 98,500
Manganese (mg kg^{-1})	10,000 - 19,700
Zinc (mg kg^{-1})	22,000 - 31,000

[1]MultiTech 1987.

Contaminant Transport

Despite the presence of tailings and contaminated soils adjacent to the river, only a portion of the contaminants are present as water soluble components. Consequently, to achieve the observed concentrations of contaminants in the river (e.g., 13,300 Cu L^{-1} or 23 g Cu sec^{-1} at a flow rate of 1,727 L sec^{-1}), the erosion of huge quantities of sediment from the floodplain would also be required. Since the river flow rate increased by approximately 297 L sec^{-1} following the thunderstorm of July 1989, this 20.7% increase demonstrates the hydrologic linkage of the river to the storm. Using the observed stream flow conditions, known floodplain sediment chemistry and an estimated 1 to 10% solubility of these sediments, extremely high values for total suspended sediment (93.6 to 936 kg sediment m^{-3}) are required to obtain the chemical concentrations reported in the river water. The solubility of copper in tailing material is strongly pH dependent so, typically, soluble concentrations are less than 1% of total levels for the tailing media along these streams during pH conditions in the 4 to 5 range.

Performing the same calculations using the midpoint surface salt concentration for copper at 84,250 mg kg^{-1} (Table 4) and the same 1 to 10% solubility yielded total suspended solids (TSS) estimates from 15.7 to 1.56 kg m^{-3}, respectively. Converting the low end of this range (1.56 kg m^{-3}) to standard units yields a TSS value of 1,563 mg L^{-1} which is similar to other values observed in rainfall simulations performed in support of reclamation studies conducted in the Upper Clark Fork River Basin (RRU 1995). Using 10% solubility for the surface metal salts is a conservative estimate, yet plausible considering the spatial distribution of surface salts which would not comprise 100% of the floodplain immediately adjacent to the river. Sulfate salts and hydrated sulfate salts of copper are known to solubilize readily in water.

It is postulated that these extreme concentrations of metals in readily soluble form were responsible for increases in river metal levels during the July storm. To prevent reoccurrences of fish mortality, several solutions were suggested ranging from total removal of the contaminated soils and tailings adjacent to the streams to chemical treatment of the wastes that would prevent formation of the metal salts.

Phytoremediation Studies

Two large field investigations were initiated, one along Silver Bow Creek (RRU and Schafer & Associates 1993) and one along the Clark Fork River (Schafer & Associates 1995). The objectives of these studies were to test the ameliorative effects of the addition of lime (chiefly $CaCO_3$ and CaOH) to the areas covered with waste materials, followed by revegetation of these areas. The lime would neutralize the acid produced from the wastes, thus reducing the mobility and toxicity of the metals, alter the particle size distribution of the materials, and inhibit the formation of soluble surface salts. The vegetation would reduce wind erosion, limit surface water runoff, and harvest water in the rootzone. It was hoped that this phytoremediation technique, along with streambank stabilization, would prevent fish mortality.

In the Silver Bow Creek study, 100 experimental plots were implemented at five locations along the creek banks and flood plain. The rates of lime application were determined in preliminary laboratory soil column tests. The choice of vegetation type to be seeded into the experimental plots was made based on greenhouse trials. One of the five field sites was a 50 ha tailings area devoid of vegetation. The tailings material had a pH value of 4.8 and concentrations of total arsenic, copper, and zinc were 1,671, 4,579, and 7,194 mg kg^{-1}, respectively. After incorporation of lime, the pH of the amended tailings was in the range of 7.5 to 8.2. Soluble metal levels within the rootzone were markedly reduced. During the third growing season vegetation cover ranged from 55.4 to 62.0%, and the mean above ground biomass ranged from 1,977 to 2,651 kg ha^{-1}. These values are considered to be very good for this geographical area.

Runoff Water Quality - Silver Bow Creek Study

To assess the phytoremediation effects on the quality and quantity of surface water, a series of simulated rainfall-runoff tests were conducted. Water was applied both to the vegetated experimental plot and to a barren area adjacent to, but separated from the plot, at the rate of 3.8 cm hr^{-1} for 2 hours. During the test, surface water runoff was collected from the vegetated plot and from the barren area. The total runoff volume from the barren area was 20.15 L, while the runoff volume from the vegetated plot was only 7.0 L. The quality of these waters was also markedly different (Table 5).

Table 5. Runoff water quality, Silver Bow Creek study.

	Initial Runoff		Composite Runoff	
Characteristic	**Control**	**Treated**	**Control**	**Treated**
Volume (L)	0.50	0.50	20.15	7.0
pH (SU)	4.4	5.4	4.8	6.3
Arsenic (μg L^{-1})	140	49	51	47
Copper (μg L^{-1})	196,000	613	24,500	387
Zinc (μg L^{-1})	563,000	5,700	66,400	2,710
Arsenic mass (mg)[1]			1.08	0.33
Copper mass (mg)[1]			676	11.6
Zinc mass (mg)[1]			1,680	30.5
Total sediment (kg ha^{-1})			478	26

[1]Mass calculations based on total concentrations and sediment load.

The dissolved copper concentration in the initial 0.5 L of runoff water from the barren tailings was 196,000 μg L^{-1}, compared to the copper level of 613 μg L^{-1} in the initial runoff of 0.5L from the vegetated plot. Similar reductions were evident for zinc. The masses of arsenic, copper, and zinc transported in the runoff water were calculated from total concentrations and sediment load. Marked reductions in metal yields were demonstrated by the revegetation treatments. The effect of phytoremediation on the total sediment yield from the rainfall-runoff tests was significant: 478 kg ha^{-1} for the barren, untreated wastes compared to 26 kg ha^{-1} for the treated, vegetated plot.

Runoff Water Quality - Clark Fork River Study

Runoff waters from natural precipitation events were evaluated as part of the phytoremediation study on the Clark Fork River (Schafer and Associates 1995). Two micro-watersheds, one located on untreated mine tailings and one located on an adjacent amended and vegetated area, were identified. From October 1993 until July 1995, 15 runoff events were recorded from the untreated micro-watershed area. Precipitation events as small as 0.30 cm were sufficient to cause measurable runoff. During the same time period, only one runoff event was recorded from the vegetated area as a result of a rainfall of 1.32 cm. Water samples collected during these runoff events were analyzed (Table 6).

Table 6. Runoff water quality, Clark Fork River study.

Characteristic	Amended, vegetated microwatershed[1]	Nontreated, barren microwatershed[2]
pH (SU)	6.2	3.87 - 4.68
Total Arsenic (μg L^{-1})	320	2,900 - 21,100
Dissolved Arsenic (μg L^{-1})	270	13 - 23,000
Total Copper (μg L^{-1})	1,360	10,4000 - 8,380,000
Dissolved Copper (μg L^{-1})	1,330	85,700 - 7,380,000
Total Zinc (μg L^{-1})	800	43,800 - 3,020,000
Dissolved Zinc (μg L^{-1})	790	41,400 - 2,350,000

[1]Data from one runoff event recorded from October 1993 to July 1995.
[2]Range of data from 15 runoff events recorded from October 1993 to July 1995.

CONCLUSIONS

The use of phytoremediation techniques at a series of locations in Montana along Silver Bow Creek and the Clark Fork River have demonstrated significant improvements in the amount and quality of surface water runoff. The formation of soluble metal salts common on non-amended, barren tailings also seems to be inhibited once the wastes have been treated with lime and revegetated. Remediation of large areas of land adjacent to these streams should eliminate fish kills in these waters. However, we caution that erosion of treated soils into streams could potentially have adverse effects on sensitive early life stages of fishes or on adult fishes through the food chain. Hence, lime treatment of contaminated soils should be limited to areas that will not be captured and eroded by the river at some time in the near future.

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