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SILVER BOW CREEK

REMEDIAL INVESTIGATION FINAL REPORT APPENDIX D, PART 1

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SILVER BOW CREEK REMEDIAL INVESTIGATION
DRAFT FINAL REPORT

ALGAE INVESTIGATION

NO. 100-100000
1574 L. CH. 42
HELENA, MONTANA 59620

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MARCH 1986

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PREFACE

Silver Bow Creek originates north of Butte, Montana and is a major tributary to the upper Clark Fork River. Mill tailings and other mining wastes in and near the creek contribute to substantial downstream contamination, particularly by potentially toxic elements: arsenic, cadmium, copper, lead, iron, and zinc. These elements and others were present in the mine ore and remain as by-products of the milling and smelting processes.

The history of mining in the Butte area began with the discovery of placer gold in Silver Bow Creek, in late summer of 1864. Several townsites and camps sprung up among the diggings. However, these operations were short-lived, and most of the miners left by 1869. Those who stayed began prospecting the quartz lode deposits of silver and the associated complex copper ores on the Butte Hill. Their efforts culminated in a silver rush, which began in the mid-1870's and revived the old camp. During that time world-class deposits of copper ore were identified. By 1881, Butte had become one of the nation's major mining centers; the district attained national dominance in copper mining by the mid-1890's and international prominence by the turn of the century. By 1915, Anaconda Copper Mining Company led the industry; but in 1980, in response to a depressed copper market, Anaconda closed all the underground mines and continued active mining only in the Berkeley Pit (established in 1955). In 1977, Anaconda became a subsidiary of Atlantic Richfield Company (ARCO). ARCO closed the Berkeley Pit in 1982 and the East Berkeley pit in 1983.

In addition to mining, various ore processing facilities also operated in the Butte area. The first two mills were erected in 1874 to smelt gold and silver. Ten years later, Marcus Daly, one of the founders of the Anaconda Company, built a copper smelter 27 miles west of Butte and planned the city of Anaconda. The Anaconda Smelter was moved to a new location in the city in 1900, and operated from 1903 to 1980.

The history of over 100 years of continuous mining and related activities changed the area's natural environment greatly. Early mining, milling, and smelting wastes were dumped directly into Silver Bow Creek and transported downstream to the Clark Fork River. In 1911, the first treatment pond was built by Anaconda Company near Warm Springs, Montana, to settle out wastes from Silver Bow Creek before the water was allowed to move on. In 1916 and 1959, two more treatment ponds began operation. Silver Bow Creek continued to receive raw mining and milling wastes until 1972, when a treatment plant was added to the Weed Concentrator in Butte. Creek contamination problems were compounded by urban and domestic sewage, wood products treatment plants, phosphate and manganese production facilities, and chemical factories.

In 1983, the U.S. Environmental Protection Agency (USEPA) designated Silver Bow Creek, contiguous portions of the upper Clark Fork River, and their environs as a high priority Superfund clean-up site. The site extends from Butte to Deer Lodge, Montana, generally following the course of Silver Bow Creek and the upper Clark Fork River. Because the various mining activities interrupted the natural flow of Silver Bow Creek, the beginning of the creek for this investigation was established as the confluence of the Metro Storm Drain and Blacktail Creek, within the city limits of Butte. The site ends at the Kohrs Bridge north of Deer Lodge.

The Silver Bow Creek Remedial Investigation (SBC RI) project consisted of coordinated individual studies to develop data on the extent and severity of contamination within the site. Results of the studies are reported in several volumes. A Summary Final Report discusses the entire project; final reports for each individual study have been issued as appendices to the Summary, as shown below:

- Surface Water and Point Source Investigation, Appendix A, Parts 1-3;
- Ground Water and Tailings Investigation, Appendix B, Parts 1-3;
- Warm Springs Ponds Investigation, Appendix C;
- Algae Investigation, Appendix D, Part 1;
- Vegetation Mapping, Appendix D, Part 2;
- Agriculture Investigation, Appendix D, Part 3;
- Macroinvertebrate Investigation, Appendix E, Part 1;
- Bioassay Investigation, Appendix E, Part 2;
- Fish Tissue Investigation, Appendix E, Part 3;
- Waterfowl Investigation, Appendix E, Part 4;
- Laboratory Quality Assurance/Quality Control Program, Appendix F, Part 1;
- Health and Safety Program, Appendix F, Part 2.

The Solid and Hazardous Waste Bureau (SHWB) of the Montana Department of Health and Environmental Sciences (MDHES) administered the USEPA appropriations to conduct this project. The Montana SHWB program manager was Mr. Michael Rubich. MDHES contracted with MultiTech in October 1984 to perform the SBC RI under contract No. 50341-1202503. The Project Manager at MultiTech was Mr. Gordon Huddleston.

MultiTech was assisted in the SBC RI work by Stiller and Associates of Helena and various other subcontractors. Several state and federal agencies also provided technical information and expertise, including the USEPA bioassay team, the Montana Department of Fish, Wildlife and Parks, the Montana Water Quality Bureau, and the USEPA Montana Field Office.

Information developed in the SBC RI will be used in the next phase of the project, the Feasibility Study, to evaluate options for site remediation.

EXECUTIVE SUMMARY

The principle objective of this investigation was to determine if algae play a significant role in metals transport from the Warm Springs Ponds to the upper Clark Fork River during late winter and early spring. An extensive literature review was conducted which confirmed that several species of algae found in the Warm Springs Ponds are capable of concentrating metals, and one study conducted prior to this remedial investigation concluded that this phenomena was occurring in the Warm Springs Ponds.

Water quality and algal sampling conducted during the Silver Bow Creek Remedial Investigation provided limited, but compelling, evidence that algae in the Warm Springs Ponds reduce the aqueous concentrations of copper and zinc through bioaccumulation of these metals. Under the conditions observed, a portion of these algae appear to be retained in the ponds and the remaining fraction are discharged to the upper Clark Fork River.

The limited nature of this study did not allow a quantitative assessment of metals transport. Two approaches are suggested to provide a more comprehensive evaluation. A field study to more definitively determine if algae play a significant role in metal transport from the Warm Springs Ponds to the Clark Fork River is recommended. Bench-scale tests to quantitatively assess algae metal removal efficiencies are also suggested. These studies are recommended if algae are seriously considered as a remedial control technology for the Silver Bow Creek CERCLA site.

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1.0 INTRODUCTION

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The objective of the Silver Bow Creek Remedial Investigation (SBC RI) was to document the extent and severity of contamination in the Silver Bow Creek/Upper Clark Fork River (see Map 1-1). Past events that have contributed contaminants to this system are shown in Figure 1-1. The data developed by the RI will be used in the Feasibility Study phase to identify potential corrective actions and to evaluate the risk to people from the contaminants. To achieve these objectives, the transport mechanisms for the contaminants of interest must be addressed during the RI phase.

The contaminants of interest in the Silver Bow Creek Site were arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn). These contaminants can be transported through the site by several mechanisms and in several chemical phases: as dissolved species, as suspended sediment (both inorganic and organic), and as bedload sediment. Organisms living within the system can ingest, carry, and release these contaminants.

Because algae have been shown to accumulate metals (Trollope and Evans 1976, Jennett and Wixson 1975, and Jennett et al. 1983) and are found in quantity in the Silver Bow Creek/Upper Clark Fork system, they have long been suspected as a potential transport mechanism for metal contaminants. To address this potential transport mechanism, an Algae Investigation was identified as part of the SBC RI. This report documents the results of the Algae Investigation.

**SILVER
BOW
CREEK**

REMEDIAL INVESTIGATION

MAP 1-1

SILVER BOW CREEK AND UPPER
CLARK FORK RIVER

FIGURE 1-1

HISTORIC CONTAMINATION OF SILVER BOW CREEK

1.1 STUDY PLAN DEVELOPMENT AND OBJECTIVES

After reviewing historical data, a field study was proposed in the SBC RI Work Plan (MultiTech and Stiller and Associates 1984) to evaluate the role of algae in metal transport. This field study was designed (1) to measure the metal content of attached algae, (2) to determine the species composition of attached algae, and (3) to determine if algae were concentrating metals, using the water quality data generated by other RI studies. Sampling stations were located on Silver Bow Creek, the Warm Springs Ponds, and on the Clark Fork River at Deer Lodge.

Due to vandalism and bedload scouring of periphytometer samplers, the proposed approach did not provide any usable data. The Interim Algae Investigation Report, which documents the results of the field studies, is Attachment I to this report (MultiTech 1985).

Following completion of the first sampling episode, a literature report was acquired that cast doubts on the usefulness of the proposed methodology even without vandalism or bedload scouring. Newman et al. (1985) used a similar methodology (algae collection on glass slides) to investigate algae concentration of metals in coal-ash settling basins. They found no correlations between the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), and zinc (Zn) and microfloral cell densities or percent ash free weight. Furthermore, Newman et al. (1985) found by using scanning electron microscopy and X-ray analysis that the

majority of the collected material was abiotic and the elemental levels associated with the abiotic components were generally higher than those of the biotic components. In short, non-biological sediment trapped on the samplers prevented an accurate measurement of the metal content of the attached algae.

To avoid the problems associated with an in situ approach measuring algae metal content, the Interim Algae Investigation Report proposed a laboratory study which would culture collected Silver Bow Creek algae in spiked lab water to investigate algae concentration of metals. However, this approach was not approved by the Montana Department of Health and Environmental Sciences (MDHES). Instead, an approach was approved which utilized the limited algae data on Silver Bow Creek from 1985 and literature data on algae concentration of metals to evaluate the potential for algae transport of metals. This approach was narrowed in scope, to an evaluation of algae in metals transport out of the Warm Springs Ponds during late winter and early spring because (1) the algae data for 1985 were collected during this period and (2) algae have been suspected of playing a major role in metal spikes in the Clark Fork River during this time of year. For discussion of other mechanisms that may account for elevated metals concentrations in the pond discharge, the reader is referred to the Warm Springs Ponds Investigation Report, Appendix C (MultiTech 1985).

This Algae Investigation Report contains the results of an extensive literature review and an analysis of water quality and

phytoplankton data for the Warm Springs Ponds. The MDHES Water Quality Bureau (WQB) collected the phytoplankton data. SBC RI contractors (MultiTech and Stiller and Associates 1985) collected the water quality data. OEA Research performed the literature review and data evaluation. Discussion is based on the relationships between the water quality and phytoplankton data and the results of the literature review.

The revised final objective of the SBC RI Algae Investigation was to assess the role algae play in the transport of metals out of the Warm Springs Ponds into the upper Clark Fork River during late winter and early spring.

1.2 HISTORICAL DATA

Past studies on the algae of Silver Bow Creek and the upper Clark Fork River had included several species and population surveys, and one that addressed algae concentration of metals. Early algae work on Silver Bow Creek included Barry (1956), Spindler and Brinck (1959), Averett and Brinck (1961), and Shinn (1970). These early investigators found few or no algae species present in that stretch from Butte to the Warm Springs Ponds, because during their period of study waste-water treatment from the Butte Operations occurred only at the Warm Springs Ponds. Silver Bow Creek from Butte to Warm Springs was essentially an industrial ditch during this period.

1.2.1 Studies Before Waste Treatment Practice

William T. Barry (1956) studied the algae at 13 stations between Butte and Missoula. Barry reported that Asterionella gracillima, Dinobryon divergens, and Ulothrix zonata showed a tolerance to a wide range of chemical and physical factors. Numbers of species found at stations above contaminant sources decreased abruptly at stations below. The few tolerant species found below contaminant inputs were much more abundant than above the station. Euglena gracilis was found at the contaminated sites of Gregson and Warm Springs. Stigeoclonium subsecundum was found at Warm Springs and at other stations downstream, but was not found upstream of sewage inputs into the system.

1.2.2 Studies After Waste Treatment Practice

Following implementation of waste treatment by the Anaconda Minerals Company in the late 1970's, the biota of the stream began to respond. Algae sampling showed this change (Spindler 1977).

1.2.2.1 Bahls et al. 1979

Silver Bow Creek below Warm Springs Ponds and the Clark Fork River at Deer Lodge were sites of algae collections in August and November 1977 and March 1978 by the MDHES Biological Water Quality Monitoring Program (Bahls et al. 1979). Water chemistry measurements, as well as algal community measurements, were made. The

results of the study indicate that Silver Bow Creek receives nitrogen and phosphorus levels significantly in excess of recommended instream concentrations. The addition of organic material to the stream may enhance the removal of metal species by the formation of organic-metal complexes and by the encouragement of algae growth (Bahls 1983). Diatoms dominated the flora in Silver Bow Creek during the summer and spring. A green alga, Cladophora, was most abundant in the fall. The Clark Fork River site reflected the same dominance.

The major diatom species found by the MDHES in Silver Bow Creek was Achnanthes minutissima in all three seasons. Nitzschia palea, Gomphonema parvulum, Synedra ulna, and Fragilaria vaucheria had high relative abundance also. The Clark Fork River samples were dominated by Achnanthes minutissima in the summer and spring and F. vaucheria in the fall. Nitzschia palea and Navicula minima were other species with high abundance. Diversity index values for the diatom community ranged from 2.48 to 3.58 at the Silver Bow Creek station and 2.89 to 3.04 at the Clark Fork station. Bahls (1979) found that most unpolluted Montana streams support periphyton diatom associations with diversity values ranging from 3.0 to 4.0.

1.2.2.2 Janik and Melacon 1982

Janik and Melacon (1982) made one algae collection in August 1980 at five stations, three above the Warm Springs Ponds on Silver Bow Creek and two below the ponds. Navicula arvensis was the dominant diatom species, contributing over 90% relative abundance at each

of the three upstream stations. A chrysophyte, Phaeodermatium rivulare, was the dominant non-diatom species at two upstream stations; and a green alga, Stigeoclonium tenue, was the dominant non-diatom at the other. This zone was characterized by high levels of arsenic, cadmium, chromium, copper, selenium, and zinc. Mean diatom diversity (Shannon-Wiener index) for the three stations was 0.53. Euglenoids were observed in low abundance.

Mean diversity at the two downstream stations was 2.11. Diatom species diversity increased and species composition changed in the two stations below the Warm Springs Ponds in the Clark Fork River. The dominant diatom species were Achnanthes minutissima, Nitzschia palea, Fragilaria vaucheria, and Gomphonema parvulum. Navicula arvensis was present in much lower abundance than above the ponds. The non-diatom species were dominated by the blue-green species Phormidium sp. and Lyngbya aerugineocarulea. A one-way analysis of variance demonstrated that diatom diversity statistically was significantly higher in the stations below the ponds than above.

Diatom species that indicated tolerance for the existing conditions, both upstream and downstream, were as follows: Cyclotella meneghiniana, Achnanthes minutissima, Navicula arvensis, Nitzschia palea, Surirella angustata, and S. ovata. Species indicating sensitivity to conditions in the upstream stations but not in the downstream stations were as follows: Fragilaria vaucheria, F. crotonensis var. oregona, F. leptostauron var. dubia, and Navicula pupula. Melosira varians was the only species occurring in all of the upstream stations but absent from the downstream stations.

1.2.2.3 Bahls 1983

Bahls (1983) reported an algae collection from four sites in Silver Bow Creek in April 1983. Collections were made upstream of the Colorado Tailings and the Butte Waste Water Treatment Plant, at Rocker downstream of the Colorado Tailings and the Butte Waste Water Treatment Plant, at Miles Crossing downstream of Ramsay, and at Gregson downstream of German Gulch.

Diatoms dominated the aquatic flora upstream of the Colorado Tailings and the Butte Waste Water Treatment Plant, but blue-green algae dominated the collection at the downstream stations. The blue-green species were nondescript, micron sized, coccoid types. Green algae (mostly Stigeoclonium) was represented by a progressively larger ratio of the flora in a downstream direction. Achnanthes minutissima was the principal diatom species upstream of the tailings, and Navicula atomus was the principal species downstream. Diversity of diatom taxa (Shannon index) was low, varying between 0.43 to 1.33.

1.2.2.4 deRuiter 1984

A late season (October 15) collection by deRuiter (1984) gave the following information for the algae community found in the Warm Springs Ponds. Pond 3 contained mainly Cladophora, some Oscillatoria, and diatoms (mainly Navicula and Fragilaria). Pond 2 contained mainly Cladophora, some Oscillatoria, and Ulothrix, and

diatoms (Navicula and Fragilaria). Pond 1 contained mainly Cladophora, some Spirogyra, and diatoms (Navicula and Fragilaria).

These data are in agreement with upstream information (Bahls 1983), where blue-green algae dominate, but diatoms are present.

Preliminary work by deRuiter (1984) on the metal concentration of the algae in the Warm Springs Ponds is presented in Table 1-1.

TABLE 1-1

METAL CONCENTRATION OF ALGAE IN THE WARM SPRINGS PONDS

<u>Pond Number</u>	<u>Metal</u>	<u>ppm</u>
3	Copper	1877
	Cadmium	50
	Arsenic	85.6
2	Copper	316
	Cadmium	16.8
	Arsenic	59.2
1	Copper	171
	Cadmium	2.32
	Arsenic	51.6

Source: deRuiter 1984

2.0 METHODS

This study began with a literature review aimed at several questions:

- o Is there evidence that algae concentrate trace metals out of their aquatic environment?
- o What taxa of algae have shown this trait?
- o What mechanisms were involved?
- o What metals were accumulated?

A review of existing literature is presented in Section 3.0 and is listed in the References.

The next step was to evaluate the data from the literature regarding algal taxa identified in the Silver Bow Creek/Warm Springs Ponds/Clark Fork River ecosystem to see if any of the species that had been shown to accumulate metals are found in the study area. Had the study ended at that point, most of the evidence for the role of algae in metal transport would have been circumstantial. However, in early September 1985, water quality data from spring of 1985 became available that allowed assessment of the role of Chlorella (a taxon known to accumulate trace metals) in early spring transport of metals out of the Warm Springs Ponds system into the Clark Fork River.

Descriptions of the methods used for the collection of data presented in this report are found in the reports and documents cited.

3.0 DATA ANALYSIS AND INTERPRETATION

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3.1 ALGAL TAXA TOLERANT TO TRACE METALS

The earliest literature regarding the relationship between algae and trace metals relates the results of studies of algae inhabiting metal-polluted streams in England. This work began in the early 1920's and has continued sporadically until the present. Much of the work was aimed at determining if some taxa are indicative of specific types of metal pollution. Whitton (1970) reviewed much of this work and concluded that the efforts have been unsuccessful, speculating that other environmental factors (salinity, pH, light, sediment) were confusing the issue. He did, however, conclude that abundant growths of Cladophora indicate that these waters are not subject to repeated pollution by heavy metals. Conversely, a well-illuminated flowing water site with abundant growths of Stigeoclonium tenue, but no Cladophora at all, should be treated as suspect for metal pollution.

Williams and Mount (1965) constructed four outdoor canals which were supplied with running pond water for fourteen weeks. Zinc was added continuously to three of the four canals to yield concentrations of 1, 3, and 9 mg/L. Glass slides (diatometers) were placed in the canals in a horizontal position, allowed to accumulate periphyton for two weeks, and then removed for analysis of standing crop and species identification. Cladophora was abundant in the control canal and found only in that canal.

The authors noted that "organisms producing dominant populations in the largest zinc concentration seemed to have relatively heavy secretions of slime, which may have significance in allowing them to dominate at large concentrations of zinc."

Say et al. (1977) conducted field and laboratory studies on the tolerance to zinc of the filamentous green algae Hormidium rivulare, H. flaccicum, and H. fluitans. All three species were found to be widespread both in waters free of zinc and those zinc-polluted. Various environmental factors were suggested as influencing zinc toxicity in the field. Cadmium and lead appear to increase toxicity, while magnesium, calcium, and hardness appear to decrease toxicity. Populations of the three Hormidium species growing in streams carrying high levels of zinc are adapted forms, being more tolerant of high zinc levels than populations of the same species isolated from unpolluted streams. Say et al. demonstrated that the level of resistance does not change with long-term sub-culture, thus indicating that the adaptation is genetic.

Foster (1982) conducted a study of species associations and metal content of algae from two rivers in the lead mining region of Cornwall, England. While the rivers were polluted, one by copper and the other by zinc, the flora of the two rivers were closely similar. All highly polluted mine sites were characterized by a Microspora community, whereas a Zygnemales community of Spirogyra and Mougeotia species was typical of low metal pollution (see Table 3-1). The author noted that many of the species found at

the metal-polluted sites were mucilaginous. Slime layers may give protection from heavy metals and/or the presence of heavy metals may induce higher levels of mucilage production (Williams and Mount 1965). In addition, the author found that field samples of Spirogyra, Zygogonium, Mougeotia, and Microspora sp. contained metal (copper, iron) concentrations several orders of magnitude greater than ambient levels.

The algal species in these studies found to be tolerant of metals are summarized in Table 3-1.

3.2 ALGAL TAXA CONCENTRATING TRACE METALS

3.2.1 Mining and Smelting Wastes

Trollope and Evans (1976) continued the work on British streams polluted by mining and smelting wastes. They selected waters adjacent, near, and distant (actual distances not provided by the authors) from zinc smelting wastes and collected water and algal samples from these waters. They found a marked difference in species composition between the groups of waters, which compares well with the differences noted by Foster (1982). The authors also calculated concentration factors (CF) for several algae and metals (Table 3-2). Concentration factor is defined as

$$CF = \frac{C}{C_1}$$

Where C = the concentration of the trace metal in the aquatic organism; and

TABLE 3-1

SPECIES FOUND IN FIELD STUDIES TO BE TOLERANT
OF HEAVY METALS

Authors	Taxa	Metal(s) Involved
Williams and Mount (1965)	<u>Anacystis</u> sp. <u>Lyngbya</u> sp. <u>Spirogyra</u> sp. <u>Chlamydomonas</u> sp. <u>Nitzschia linearis</u> <u>Synedra ulna</u> <u>Oscillatoria</u> sp.	Zn
Whitton (1970)	<u>Microspora</u> sp. <u>Ulothrix</u> sp.	Cu, Pb, Zn
Besch <u>et al.</u> (1972)	<u>Achnanthes microcephala</u> <u>Eunotia evigua</u> <u>Pinnularia interrupta</u> <u>Fragilaria virescens</u>	Zn
McLean and Jones (1975)	<u>Hormidium rivulare</u> <u>Ulothrix</u> sp. <u>Spirogyra</u> sp.	Fe, Pb, Mn
Trollope and Evans (1976)	High Pollution Sites: <u>Coccomyxa</u> sp. <u>Mougeotia</u> sp. <u>Tribonema</u> sp. <u>Zygnema</u> sp. Moderate Pollution Sites: <u>Microspora</u> sp. <u>Oscillatoria</u> sp. <u>Ulothrix</u> sp. Low Pollution Sites: <u>Cladophora</u> sp. <u>Oedogonium</u> sp. <u>Spirogyra</u> sp.	Cu, Fe, Pb, Ni, Zn
Say, Diaz, and Whitton (1977)	<u>Hormidium rivulare</u> <u>H. flaccidum</u> <u>H. fluitans</u>	Zn

TABLE 3-1

SPECIES FOUND IN FIELD STUDIES TO BE TOLERANT
OF HEAVY METALS (Continued)

Authors	Taxa	Metal(s) Involved
Foster (1982)	High Pollution Sites:	
	<u>Microspora stagnorum</u>	Cu, Pb, Zn
	<u>M. pachyderma</u>	
	<u>M. willeana</u>	
	<u>Mougeotia parvula</u>	
	<u>Psuedococcomyza adhearans</u>	
	<u>Chlamydomonas vulgaris</u>	
	Moderate Pollution Sites:	
	<u>Zygogonium ericetorum</u>	
	<u>Microspora tumidula</u>	
	<u>Ulotrichiales</u> sp.	
	<u>Hormidium</u> sp.	
	<u>Microthamnion</u> spp.	
	<u>Stigeoclonium tenue</u>	
	Low Pollution Sites:	
	<u>Spirogyra</u> sp.	
	<u>Mougeotia</u> sp.	

TABLE 3-2

TAXA FOUND IN LABORATORY AND FIELD STUDIES
TO CONCENTRATE HEAVY METALS

Author	Taxa	Metals	CF
Polikarpov (in Jennett et al. 1983)	<u>Chara aspera</u> <u>C. fragilis</u>	Zn Zn	2.3×10^3 2.9×10^3
Darnall et al. (in press)	<u>Chlorella vulgaris</u>	Cr, Co, Ni, Cu, Zn, Ag, Pt, Au, Hg, Cd, Pb, Sn, Fe, Be, Al	-
DeFilippis and Pallaghy (in Jennett et al. 1983)	<u>Chlorella</u> sp.	Hg Hg	7.1×10^1 1.6×10^2 - 4.8×10^2 - 1.2×10^3
Coleman et al. (in Jennett et al. 1983)	<u>Chlorella vulgaris</u>	Zn	4.2×10^3 - 9.6×10^4
Polikarpov (in Jennett et al. 1983)	<u>Chlorella</u> sp. <u>Cladophora fracta</u>	Zn Cd Hg Zn	1.4×10^2 1.6×10^4 5.9×10^3 6.1×10^3
	<u>Cladophora glomerata</u>	Cd Hg Zn	1.7×10^4 5.4×10^3 3.9×10^3
Burkett (in Jennett et al. 1983)	"	Hg	6.5×10^1 - 5.6×10^3
Gileva (in Jennett et al. 1983)	"	Zn	3.9×10^3
Trollope and Evans (1976)	<u>Coccomyxa</u> sp.	Ni Zn Cu Pb	1.2×10^3 1.7×10^2 5.0×10^4 3.1×10^4
Coleman et al. (in Jennett et al. 1983)	<u>Euglena viridis</u>	Zn	2.4×10^3 - 1.1×10^5

TABLE 3-2

TAXA FOUND IN LABORATORY AND FIELD STUDIES
TO CONCENTRATE HEAVY METALS (Continued)

Author	Taxa	Metals	CF
Polikarpov (in Jennett et al. 1983)	<u>Mougeotia</u> sp.	Cd Zn	2.8×10^3 3.7×10^4
Trollope and Evans (1976)	"	Cd Cu Pb Ni Zn	2.8×10^3 1.2×10^4 2×10^3 1.6×10^3 1.3×10^3
	<u>Oedogonium</u> sp.	Cu Pb Ni Zn	6.6×10^3 5.7×10^2 1.2×10^3 1.5×10^3
	<u>Oscillatoria</u> sp.	Cu Pb Ni Zn	2.1×10^4 5.6×10^3 9.1×10^2 9.6×10^2
Richardson et al. (in Jennett et al. 1983)	<u>Pediastrum boryanum</u>	Hg	1.8×10^4
Stokes (in Jennett et al. 1983)	<u>Scenedesmus</u> sp.	Cu (lab strain) (from polluted lake) (absence and presence of nickel) Ni	$3.7 - 4.0 \times 10^3$ $2.5 - 3.0 \times 10^3$ $7.6 \times 10^3 - 4.1 \times 10^4$ $1.2 \times 10^3 - 8.2 \times 10^3$

TABLE 3-2

TAXA FOUND IN LABORATORY AND FIELD STUDIES
TO CONCENTRATE HEAVY METALS (Continued)

Author	Taxa	Metals	CF
Polikarpov (in Jennett et al. 1983)	<u>Scenedesmus quadricauda</u>	Zn	7.8×10^2
Gileva (in Jennett et al. 1983)	"	Zn	7.8×10^2
Polikarpov (in Jennett et al. 1983)	<u>Spirogyra crassa</u>	Cd Zn	3.3×10^3 1.9×10^3
Trollope and Evans (1976)	<u>Spirogyra</u> sp.	Cu Pb Ni Zn	3.3×10^3 4.0×10^2 2.5×10^2 $6.6 - 9.0 \times 10^3$ $- 1.4 \times 10^4$ $- 3.8 \times 10^3$ $- 1.7 \times 10^3$
Gileva (in Jennett et al. 1983)	"	Zn	3.2×10^4
Polikarpov (in Jennett et al. 1983)	"	Zn	3.2×10^4
Fujita and Hashizume (in Jennett et al. 1983)	<u>Synedra ulna</u>	Hg	$1.3 - 1.7 \times 10^4$
Trollope and Evans (1976)	<u>Tribonema</u> sp.	Cu Pb Ni Zn	$1.3 - 8.3 \times 10^4$ 3.0×10^3 $1.1 - 3.0 \times 10^3$ 1.7×10^3
	<u>Ulothrix</u> sp.	Cu Pb Ni Zn	1.0×10^4 7.6×10^3 1.4×10^2 7.3×10^2
	<u>Zygnema</u> sp.	Cu Pb Ni Zn	3.5×10^4 2.5×10^3 6.0×10^3 4.0×10^3

C^1 = the aqueous medium metals concentration.

The authors noted that algal blooms appear to regulate uptake of individual metals. For the three groups, mean metal concentrations in the algae were ordered as follows:

Fe > Zn > Pb > Cu > Ni,

while the mean metal concentrations in the water bodies were

distant: Fe > Zn > Ni, Pb > Cu;

near: Zn > Ni > Pb > Fe > Cu;

adjacent: Zn > Pb > Fe > Ni > Cu.

3.2.2 Industrial Wastes

In 1967 a large study was undertaken of industrial treatment of heavy metals to protect aquatic systems (Jennett and Wixson 1975). The new lead belt of southeastern Missouri was developing quickly. High concentrations of lead, zinc, copper, and manganese were found in the streams, and benthic diversity indices were declining. This information caused several mining/milling companies to change their waste water treatment programs. Previous work by Wixson and Jennett had shown that algae effectively removed heavy metals. Because of the capacity of algae to concentrate heavy metals, a series of shallow and meandering channels was constructed and populated by a mixed algae community of which Cladophora was one of the major forms. The smelter effluent was passed through the meander channel prior to discharge to the receiving stream. Algae trapped the metals, and when the algae broke loose

they were trapped in a final sedimentation basin. Based on total heavy metals removed, the system was 99%+ effective.

Darnall (in press) has shown that cultured Chlorella vulgaris may have economic potential for recovery of metal ions. The cultured algae are harvested by centrifugation, dialyzed against de-ionized water, and lyophilized for storage. The algae are then immobilized in polyacrylamide and packed in a column. Various metal-containing solutions are then passed through the column. Several metal ions are bound by Chlorella between pH 5 and 7: chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), silver (Ag), gold (Au), mercury (Hg), cadmium (Cd), lead (Pb), uranium (U), iron (Fe), beryllium (Be), and aluminum (Al). These ions bind to the cell surface and algae and can be selectively eluted from the algae using a medium of increasing acidity.

3.2.3 Factors Affecting Algal Metals Accumulation

Following their earlier work, Jennett et al. (1983) looked at factors which influenced metal accumulation by algae. Table 3-2 is derived in large part from their publication. This table clearly demonstrates a number of algal species are capable of bioconcentration of trace metals.

The authors showed that removals of lead and mercury are rapid phenomena, usually accomplished in three hours or less at room temperature. Metal accumulation was little affected by pH in the

range of pH 5-8 when young cells were employed. Chlamydomonas (a green flagellated form) proved to be vastly superior to all other species tested in its ability to remove lead. Concentration factors of 1.9×10^4 (see Table 3-2) were noted.

In other experiments Ulothrix and Chlorella had concentration factors for cadmium greater than 1×10^4 . The most dramatic removal of mercury was by a strain of Nostoc which, along with Spirogyra, was also most effective at removing zinc. The results of this study show reasonably good agreement with other studies in the literature; most concentration factors between studies agree within a factor between 2 and 4 (see Table 3-2).

3.2.4 Metals Accumulation by Algae in the Warm Springs Ponds

During October 1983 deRuiter (1983) collected algae from shallow water along the dikes of the Warm Springs Ponds. The algae collected were in direct contact or close proximity with the soil. She also collected water samples from the ponds and their associated discharges. Analysis of the samples (algae and water) for copper, cadmium, and arsenic indicated that the algae were concentrating these metals. The author argued that algae were removing the metals from the sediment and mobilizing them into the water column. Thus, she concluded that the ponds are a point source of metals pollution and that algae provide the mechanism for pumping sediment-bound metals into the water system.

Part of deRuiter's reasoning is based on the results of metals analysis of the water samples. The values for dissolved and total cadmium and copper are below detection limits in Pond 2 and its discharge. However, the values for total and dissolved arsenic are higher in the discharge than in water sampled collected near the dikes where the algae were collected.

Two serious flaws appear in this line of reasoning. If the algae growing on the sediment are mobilizing metals from the sediments into the water column, then metals concentrations should be at least as high in water collected in the vicinity of the algae as in water collected from the pond discharge. Secondly, a mechanism whereby algae can mobilize sediment bound metals into the water column has not been documented in the literature to this author's knowledge.

deRuiter's data indicating that algae in the Warm Springs Ponds concentrate metals from the aquatic environment is the only direct evidence from the study area of this phenomenon.

3.2.5 Summary of Metals Accumulation by Algae

The literature provides clear evidence that algae are capable of bioconcentration of heavy metals. Some disagreement appears as to the identification of indicator species, especially Cladophora. Whitton (1970) states unequivocally that the presence of Cladophora indicates the absence of heavy metals. Despite this

statement, Cladophora has been found by other authors to not only be tolerant of heavy metals (Trollope and Evans 1976), but to be an effective bioaccumulator of metals (Jennett and Wixson 1975). Cladophora has also been identified in collections from the Warm Springs Ponds (de Ruiter 1984).

Some disagreement also exists as to the mechanisms involved in bioaccumulation. Darnall's work indicates that bioaccumulation is a simple process of adsorption to the cell wall in the case of Chlorella. Gadd and Griffiths (in Shubert 1984) concluded that the amount of metal taken up by passive mechanisms and bound on the surface of algal cells is quite low in comparison with that taken up by metabolic or energy-dependent processes.

In summary, good evidence appears in the literature for bioaccumulation or bioconcentration of heavy metals by algae. However, a number of questions remain as to the factors which influence bioconcentration as well as the mechanisms involved. These points are summarized in the following paragraphs from Boyle (in Shubert 1984):

The bioaccumulation of environmental contaminants by algae performs three functions of ecological importance. (1) The degree to which a compound bioaccumulates affects the concentrations at the site of action and is an important parameter of the toxic effect on an organism. (2) Bioaccumulation of a toxic contaminant may render it, temporarily at least, unavailable to invertebrates and fish, thus affording some measure of ecological resistance to toxic impact on other organisms. (3) Bioaccumulation of persistent refractory organic chemicals or heavy metals by algae may be an important factor in the physical transport of toxic materials from one place to another and the bioaccumulation

through a food chain to consumer organisms in the upper trophic levels.

The bioaccumulation of a compound is the function of a combination of many factors, which can be classified into three categories: (1) The characteristics of different algae in relation to chemical uptake. (2) The effect of environmental factors on availability of the compound to algae. (3) The physical and chemical properties of the contaminant.

Bioaccumulation can also be considered as the net difference in the ratio of biological uptake and elimination and thus may be related to metabolism or the rate of specific biochemical processes. The physical and chemical differences of various species of algae are important factors in determining uptake of bioaccumulation of chemical contaminants. Differences in the surface area to volume ratio among algal species mean that a small algal species would have a larger exposed surface on which to sorb chemical contaminants than would the same weight of a large species of algae. Large colonial forms present less of their immediate surface to the environment.

There are also gross differences in the surface composition of algae which range from the exposed cell membrane in green algae, to mucilaginous sheaths in blue-green algae, to cellulose tests in some colonial forms, and to the outer specialized cellular layers of macrophytic algae. The cellular contents and morphology also vary from relatively structureless procaryotic blue-green algae to highly structured membraneous cells with large vacuoles and starch inclusions in other phyla to the highly differentiated cells of macrophytic algae.

3.3 ALGAL TAXA FOUND IN THE STUDY AREA

Table 3-3 presents the taxa found in the study area by various investigators. Of the taxa identified, many have been found in field studies to be tolerant of trace metals. Nine have been found to concentrate trace metals:

- Synedra ulna
- Chlorella sp.
- Euglena sp.

TABLE 3-3

SPECIES FOUND IN SILVER BOW CREEK AND CLARK FORK RIVER
BETWEEN BUTTE AND IMMEDIATELY BELOW WARM SPRINGS

Author (s)	Taxa	Location	Sample Date(s)
Barry (1956)	<u>Euglena gracilis</u> <u>Stigeoclonium subsecundum</u>	Gregson to Warm Springs	---
Bahls et al. (1979)	<u>Stigeoclonium</u> sp. <u>Cladophora</u> sp. <u>Oscillatoria</u> sp. <u>Scenedesmus</u> sp. <u>Achnanthes minutissima</u> <u>Nitzschia palea</u> <u>Fragilaria vaucheriae</u> <u>Gomphonema parvulum</u>	Clark Fork River below Warm Springs Ponds	Summer, Fall, Spring Collections 1977-1978
Janik and Melacon (1981)	<u>Navicula arvensis</u> <u>Stigeoclonium</u> sp. <u>Phaedermatium revulare</u> <u>Nitzschia palea</u> <u>A. minutissima</u> <u>Fragilaria vaucheriae</u> <u>Phormidium</u> sp. <u>Lyngbya aerugineo-carulea</u>	Gregson-Crackerville Downstream of Warm Springs	August 1980
Bahls (1983)	<u>Achnanthes minutissima</u> <u>A. lanceolata</u> <u>Cymbella minuta</u> <u>C. sinuata</u> <u>Cyclotella meneghiniana</u> <u>Cocconeis placentula</u> <u>C. pediculus</u> <u>Diatoma vulgare</u> <u>Eunotia curvata</u> <u>Fragilaria construens</u> <u>F. vaucheriae</u>	Silver Bow Creek - various locations	April 27, 1983

TABLE 3-3

SPECIES FOUND IN SILVER BOW CREEK AND CLARK FORK RIVER
BETWEEN BUTTE AND IMMEDIATELY BELOW WARM SPRINGS

Author(s)	Taxa	Location	Sample Date(s)
Bahls (1983)	<u>Frustulia vulgaris</u> <u>Gomphomena</u> sp. <u>G. angustata</u> <u>G. parvulum</u> <u>Meridion circulare</u> <u>Melosira italica</u> <u>Navicula atomus</u> <u>N. minima</u> <u>N. muralis</u> <u>N. arvensis</u> <u>N. viridula</u> <u>N. capitata</u> <u>N. lanceolata</u> <u>Nitzschia</u> sp. <u>N. palea</u> <u>Pinnularia mesolepta</u> <u>Surirella ovata</u> <u>S. angustata</u> <u>Rhoicosphemia curvata</u> <u>Synedra rumpens</u>	Silver Bow Creek - various locations	April 27, 1983
deRuiter (1984)	<u>Cladophora</u> sp. <u>Oscillatoria</u> sp. <u>Navicula</u> sp. <u>Fragilaria</u> sp. <u>Cladophora</u> sp. <u>Oscillatoria</u> sp. <u>Ulothrix</u> sp. <u>Fragilaria</u> sp. <u>Navicula</u> sp.	Warm Springs Pond #3 Warm Springs Pond #2	October 15, 1984 October 15, 1984

TABLE 3--3

SPECIES FOUND IN SILVER BOW CREEK AND CLARK FORK RIVER
BETWEEN BUTTE AND IMMEDIATELY BELOW WARM SPRINGS

Author(s)	Taxa	Location	Sample Date(s)
deRuiter (1984)	<u>Cladophora</u> sp. <u>Spirogyra</u> sp. <u>Navicula</u> sp. <u>Fragilaria</u> sp.	Warm Springs Pond #1	October 15, 1984
Bahls (1985a)	<u>Fragilaria</u> sp. <u>Cymatopleura solea</u> <u>Synedra ulna</u> <u>Chlorella</u> sp. <u>Nitzschia palea</u> <u>Chlamydomonas</u> spp. <u>Flagellated chrysophyte</u> <u>Euglena</u> sp. <u>Surirella</u> sp. <u>Scenedesmus</u> sp. <u>Pediastrum</u> sp. <u>Anabaena</u> sp. <u>Achnanthes</u> sp.	Warm Springs Pond #2 Warm Springs Pond #3	March/April/ May 1985
Bahls (1985b)	<u>Achnanthes minutissima</u> <u>A. lanceolata</u> <u>Cymatopleura solea</u> <u>Cyclotella meneghiniana</u> <u>Cymbella minuta</u> <u>Cocconeis placentula</u> <u>Diatoma vulgare</u> <u>Epithemia sorex</u> <u>Fragilaria construens</u> <u>F. vaucheriae</u> <u>F. crotonensis</u> <u>F. capucina</u> <u>Gomphonema parvulum</u> <u>G. sp.</u>	Silver Bow Creek - various locations	May/June 1985 June 1985 May 1985 May 18-20, 1985

TABLE 3--3

SPECIES FOUND IN SILVER BOW CREEK AND CLARK FORK RIVER
BETWEEN BUTTE AND IMMEDIATELY BELOW WARM SPRINGS

Author (s)	Taxa	Location	Sample Date(s)
Bahls (1985b)	<u>Melosira varians</u> <u>Meridion circulare</u> <u>Navicula cuspidata</u> <u>N. pelliculosa</u> <u>N. arvensis</u> <u>N. decussis</u> <u>N. minima</u> <u>N. cincta</u> <u>N. subminuscula</u> <u>N. fragilarioides</u> <u>N. heufleri</u> <u>N. salinarum</u> <u>N. viridula</u> <u>Nitzschia palea</u> <u>N. paleacea</u> <u>N. gracilis</u> <u>N. frustulum</u> <u>N. linearis</u> <u>N. dissipata</u> <u>N. inconspicua</u> <u>N. amphibia</u> <u>Pinnularia sp.</u> <u>Rhoicosphemia curvata</u> <u>Surirella angustata</u> <u>S. ovata</u> <u>Stephanodiscus hantzschii</u> <u>Synedra ulna</u> <u>S. filitarmis</u>	Silver Bow Creek - various locations	May 18--20, 1985

- Scenedesmus quadricauda
- Pediastrum sp.
- Cladophora sp.
- Oscillatoria sp.
- Ulothrix sp.
- Spirogyra sp.

3.4 ALGAE-TRACE METALS AT WARM SPRINGS PONDS, SPRING 1985

During the spring of 1985 the Montana Department of Health and Environmental Sciences (MDHES) Water Quality Bureau (WQB) and SBC RI investigators intermittently collected algae samples from Warm Springs Ponds 2 and 3 and collections also were made from the discharges of these ponds. The WQB conducted phytoplankton counts on these samples and the results of these counts are shown in Table 3-4.

During this same time period water samples were collected from the Warm Springs Ponds and Clark Fork River on a bi-weekly basis as part of the ongoing SBC RI. Total suspended sediment (TSS), total iron, total copper, and total zinc were included in the water sample analyses. The dissolved fraction also was analyzed; however, concentrations were at or below detection limits for the period of interest. Streamflow measurements were taken on a bi-weekly basis at the appropriate stations.

TABLE 3-4

RESULTS OF PHYTOPLANKTON COUNTS ON WATER SAMPLES
COLLECTED FROM THE ANACONDA COMPANY'S
WARM SPRINGS PONDS 2 AND 3, SPRING 1985

Date Collected	Collecting Agency	Location	No. cells/ml (including microplankton)	No. genera (excluding microplankton)	Dominant Algae
3/25/85	Stiller	Pond 2	*	*	<u>Fragilaria</u>
3/25/85	Stiller	Pond 2 Discharge	24,638	13	<u>Fragilaria</u>
3/27/85	WQB	Pond 2 Discharge	43,650	12	<u>Chlorella</u>
4/16/85	Stiller	Pond 3	15,120	5	<u>Chlorella</u>
4/16/85	Stiller	Pond 3, E. Tower	14,422	6	<u>Chlorella</u>
		Discharge			<u>Chlamydomonas</u>
4/16/85	Stiller	Pond 3, W. Tower	9,450	5	<u>Chlorella</u>
		Discharge			<u>Chlamydomonas</u>
4/22/85	WQB	Pond 2 Discharge	92,228	8	<u>Chlorella</u>
4/24/85	Stiller	Pond 2	37,125	11	<u>Chlorella</u>
4/24/85	Stiller	Pond 2 Discharge	58,275	13	<u>Chlorella</u>
5/8/85	Stiller	Pond 3	27,450	3	<u>Chlorella</u>
5/8/85	Stiller	Pond 3, E. Tower	26,392	4	<u>Chlorella</u>
		Discharge			<u>Chlorella</u>
5/8/85	Stiller	Pond 3, W. Tower	31,140	4	<u>Chlorella</u>
		Discharge			<u>Chlorella</u>
5/30/85	WQB	Pond 2 Discharge	1,200	11	Unknown <u>flagellate</u> <u>Pediastrum</u>

Source: Loren Bahls (Memos to Mike Rubich 1985a, 1985c).

* Sample was left unpreserved for 47 days between collection and analysis, hence a quantitative analysis could not be performed.

Figures 3-1 through 3-5 present the algae, water chemistry, and (where appropriate) flow information for Pond 2, Pond 2 discharge, Pond 3, Pond 3 discharge, and the Clark Fork River at Perkins Lane Bridge. The Perkins Lane Bridge station is located downstream of the confluence of the Mill-Willow Bypass and the Pond 3 discharge, upstream of the confluence with Warm Springs Creek.

The figures show that trace metals at any given station follow the same trend, with very few exceptions (iron at Pond 2 and Perkins Lane Bridge, March 27, 1985). Within the ponds, the total metals concentrations are correlated with levels of TSS. The peak values of metals and TSS in the ponds do not correspond to peak flows from the ponds, but the peaks in metals and TSS at Pond 2 do correspond to peak flow in the Clark Fork River at Perkins Lane Bridge.

The existing algae data are insufficient to determine the actual peaks in algae numbers and the lack of an analysis for organic carbon makes it impossible to determine the organic fraction of TSS. Thus, while the data indicates a relationship between metals and TSS concentrations, no data directly correlates concentrations of algae and TSS.

The best data regarding algae are for the Pond 2 discharge. Algal numbers increased from March 27 through April 22, but the number of algae dropped almost to zero by May 30, the next sampling date. These changes appear to follow the trend of TSS both in the Pond 2 discharge and Pond 2 itself.

FIGURE 3-1

TRACE METALS, TOTAL SUSPENDED SOLIDS, PHYTOPLANKTON
POND 2
(graphic representation of data presented in Table 3-4 and
MultiTech and Stiller and Associates 1985)

FIGURE 3-2

TRACE METALS, TOTAL SUSPENDED SOLIDS, PHYTOPLANKTON AND FLOW (cfs)
POND 2 DISCHARGE

(graphic representation of data presented in Table 3-4 and
MultiTech and Stiller and Associates 1985)

FIGURE 3-3

TRACE METALS, TOTAL SUSPENDED SOLIDS, PHYTOPLANKTON
POND 3
(graphic representation of data presented in Table 3-4 and
MultiTech and Stiller and Associates 1985)

FIGURE 3-4

TRACE METALS, TOTAL SUSPENDED SOLIDS, PHYTOPLANKTON AND FLOW (cfs)
POND 3 DISCHARGE

(graphic representation of data presented in Table 3-4 and
MultiTech and Stiller and Associates 1985)

FIGURE 3-5

TRACE METALS, TOTAL SUSPENDED SOLIDS, AND FLOW (cfs)
CLARK FORK RIVER AT PERKINS LANE BRIDGE
(graphic representation of data presented in Table 3-4 and
MultiTech and Stiller and Associates 1985)

The algal data for Pond 3 and its discharge are more limited. The peak in algal numbers could occur at the same time as the peak in TSS, but with only two samples from each station a conclusive determination is impossible. As with Pond 2 and its discharge, the peak in metals coincides closely with the peak in TSS within Pond 3, but this is not true for the Pond 3 discharge.

There is no apparent relationship among metals concentrations, TSS, and flow at Perkins Lane Bridge.

3.5 INTERPRETATION

The possible role of algae in the loading of trace metals to the Clark Fork River during the spring has been the subject of this study.

The literature review yielded a body of evidence showing that a number of algal species concentrate trace metals from the water column. In fact, periphyton communities can provide treatment of lead smelting waste water that is very effective in meeting federal and state discharge requirements for trace metals. A number of the species shown to concentrate trace metals have been collected by investigators from Silver Bow Creek and the Warm Springs Pond system.

Efforts to determine whether existing data prove that algae in the Warm Springs Ponds accumulate heavy metals and transport them into the river system were hampered by the limited amount phytoplankton data and the lack of a measure of the organic contribution to TSS in the site.

The best evidence that phytoplankton are accumulating trace metals in the Warm Springs Ponds is provided by data from Pond 2 and the Pond 2 discharge. Data from Pond 2 and Pond 3 show a strong relationship between trace metal and TSS concentrations. This relationship could be attributed to high flows within the river system at this time carrying metals-laden sediment, except that in the river system an inverse relationship exists between trace metal concentrations with flow and TSS. Algal data from Pond 2 and its discharge indicate that the peak in algal numbers probably occurs at roughly the same time as the peaks in TSS and trace metals within the pond.

Table 3-5 provides peak concentrations of trace metals and TSS for Pond 2, Pond 2 discharge, and the Clark Fork River at Perkins Lane Bridge. This table points out the close relationship between trace metals and TSS in Pond 2 and the inverse relationship between them in the Clark Fork River. It also shows the much higher concentrations of trace metals within Pond 2.

TABLE 3-5

PEAK CONCENTRATIONS (mg/L) IN TOTAL COPPER, IRON, ZINC AND TSS BY DATE

	Pond 2	Date	Pond 2 Discharge	Date	Clark Fork River at Perkins Lane Bridge		Date
Zinc	0.729	5-8-85	0.322	2-27-85	0.138		4-10-85
Iron	3.71	5-8-85	1.43	3-27-85	0.868		4-10-85
Copper	0.265	5-8-85	0.139	4-8-85	0.122		3-27-85
TSS	45	5-8-85	17	4-22-85	18		5-8-85

A possible explanation for these limited data centers on the phytoplankton within the ponds. The algae may be increasing in numbers during late winter-early spring (accounting in large measure for increases in TSS) and concentrating trace metals from the incoming water, but are being retained to some extent within the ponds. Thus, TSS and metals concentrations in the discharge water are lower than in the ponds. However, algae concentrations are higher in the discharge than in the pond based upon the samples taken on April 24, 1985. Other potential mechanisms such as sedimentation of metal-bearing particulates may account for this phenomenon. The reader is referred to Warm Springs Ponds Investigation Report, Appendix C (MultiTech 1985).

Before the algae can be given serious consideration as a control technology for Silver Bow Creek/Clark Fork River, a more definitive evaluation of their role in metals transport must be made. Two approaches are suggested:

- (1) Through a program of late winter/spring water and algae sampling, develop a metals "budget" for one of the ponds and determine if and how it correlates to changes in the algal population within the pond. This metals budget would reveal if the pond studied is a metals "sink" and whether the removal of metal from the water is associated with blooms of algae;
- (2) Undertake the culturing program described in the SBC RI Algae Investigation Interim Report (Attachment I).

DRAFT

4.0 CONCLUSIONS

The literature shows certain algae species are capable of concentrating metals from the water column, and some of these species have been found in the Warm Springs Ponds. deRuiter (1984) published data indicating that algae in the Warm Springs Ponds have higher concentration of metals than water samples collected from the ponds.

A reasonable argument can be made that during spring 1985 algae in Warm Springs Pond 2 took metals out of the water entering the ponds and that most of the algae were retained within the pond. The data supporting this argument are limited, but the description of the process by which this occurs is reasonable. The evidence from the literature review gives additional credibility to the argument for this process.

Other potential mechanisms such as sedimentation of metal-bearing particulates may account for lower concentrations of total metals in the Pond 2 discharge.

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SBC REMEDIAL INVESTIGATION
ALGAE INVESTIGATION

ATTACHMENT 1
ALGAE INTERIM REPORT

SILVER BOW CREEK REMEDIAL INVESTIGATION
ALGAE INVESTIGATION
INTERIM REPORT

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July 2, 1985

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1.0 INTRODUCTION

The objective of the Algae Investigation portion of the Silver Bow Creek Remedial Investigation (SBC RI) is to assess the role algae play in the transport of metals in the Silver Bow Creek - Upper Clark Fork River System. The SBC RI Work Plan describes two sampling episodes for algae measurements on Silver Bow Creek. This report describes the methods and results of the first sampling period, March 28, 1985 - April 16, 1985, and makes recommendations for the second scheduled sampling period.

2.0 METHODS

The SBC RI Surface Water and Point Source Investigation generates the necessary water quality data for the Algae Investigation. Four other measurements needed to meet the study objective are chlorophyll, biomass, metal content (for As, Cd, Cu, Fe, Pb, and Zn), and species identification. Measurement methods for these parameters are described in the SBC RI Work Plan and briefly reviewed below.

Periphytometers were used to sample for all four parameters; in addition, natural substrate scraping supplemented species identification.

At each stream station sampled, 7 periphytometers (each with 8 acid-washed glass slides) were anchored with 40 lb. test monofilament fishing line and swivels to an eyebolt set in a cement-filled coffee

can. Periphytometers were submerged and drifted in the current approximately 6-8 feet downstream of the anchor. Periphytometers were anchored so that the slide surfaces were perpendicular to the current.

At each pond station, the periphytometers were suspended by the manufacturer-supplied floats, which held the sampler slides approximately 2 inches below the surface of the water. The pond samplers also were anchored with a cement-filled coffee can.

Table 2-1 shows the dates of exposure for each station sampled by periphytometers. After exposure, the samplers were placed in an acid-washed, labeled, light-proof slide box, and the slide boxes were placed in a cooler with ice for transportation to the lab. At the MultiTech lab, the boxes were logged in, sample custody was transferred, and the boxes were placed in a lab freezer. At the time of periphytometer collection, natural substrates such as rocks and pilings were scraped with a small spatula, the scrapings placed in glass vials, and Lugols solution added as a preservative.

Chlorophyll was to be measured by an acetone extraction and spectrophotometric analysis of the scrapings from 5 slides. Biomass was to be measured by an ashing-gravimetric analysis of the chlorophyll analysis residue. Metals content of the algae was to be determined by digesting the scrapings from 10 slides and analyzing by atomic

absorption spectrophotometry or inductively coupled plasma spectrophotometry. Species identification was to be made on glass slide samples and natural substrate scrapings.

To date, the analysis proposed on the samples collected has not been performed. Reasons for this deviation from the work plan are presented in the next section.

3.0 RESULTS

Table 2-1 shows the outcome of the early April sampling episode. Only two stations of the seven planned for sampling produced usable samples; none of the Silver Bow Creek stations produced any algae on the collector slides, Warm Springs Pond No. 3 was not sampled due to ice cover during the sampling period, and no samplers were recovered from the Clark Fork station. The Silver Bow Creek samplers did not have any algae growth on them because they were located on the bottom of the creek, where they were scoured by the unanticipated bedload movement of the sandy bottom material. The samplers had been placed at creek bottom to avoid any vandalism that might occur if the samplers were held sub-merged by floats. Vandalism may have occurred at the Clark Fork station.

The two samples obtained were judged to be insufficient for evaluating the role of algae in metal transport in SBC. As a consequence, none of the samples collected have been analyzed for chlorophyll, biomass mass, or metal content, and the species identification samples have

not been submitted for evaluation. Salvaging any useful data from this first sampling episode may be done by performing only the species identification on the natural substrate scraping as outlined in the next section.

4.0 RECOMMENDATIONS

The objective of this investigation could not be met from the first sampling episode, which uncovered problems in the planned methodologies:

- Risk of no usable sample using floating periphytometers due to vandalism.
- Risk of no usable sample using submerged periphytometers due to bedload scouring.
- Contamination of the glass-slide scrapings by sediments which would invalidate the metals analysis.

In re-evaluating the methodology, two in-situ alternative methods were considered but judged to be inadequate:

- Filtering whole water samples with a plankton net and analyzing the filtrate for metals. This approach does not prevent contamination of algae sample by sediments.
- Scraping natural substrates and analyzing for metals. This approach also does not prevent contamination of the sample by sediments.

The major question of this investigation is: Do Silver Bow Creek algae concentrate metals above ambient levels? A contamination-free

in-situ method for answering this question is not yet available. However, another possibility was suggested by Joe Greene (USEPA, Corvallis, Ore.):

- Collect algae samples from SBC this summer using either floating periphytometers, plankton nets, or natural scrapings (depending on species of interest).
- Culture these collections in lab-prepared, sediment-free water to imitate dissolved water-quality conditions of Silver Bow Creek (or culture in filtered Silver Bow Creek water) using two sets of controls, one with the Silver Bow Creek algae culture in "clean" water (no metals) and one with a similar (in species composition), but geographically separate, algae source population in "dirty" water.
- After an adequate culture period, collect the algae (by filtering on ashless paper), digest the sample, and analyze for the metals; and
- Identify the collections for species composition;
- Analyze the culture water for the metals of interest.

This method allows the comparison of the concentration of the metals of interest in the algae biomass and the ambient water, which would provide a method of evaluating the role the SBC algae play in metal segregation and transport. The controls would serve to increase confidence that any significant differences in metal concentrations would be due to uptake by Silver Bow Creek algae.

Species identification of samples collected in mid-April of 1985, in conjunction with species identification of cultured species, would indicate the possibility that phenomena described by the proposed laboratory experiment were present during the Spring period of sample collection.

With the approval of MDHES, the new procedure described above will be expanded into a proposed Scope-of-Work change for the SBC RI Work Plan. A cost estimate also will be prepared at the same time.