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**SPATIAL AND TEMPORAL VARIATIONS  
IN THE GEOCHEMISTRY OF SEVERAL  
WESTERN MONTANA STREAMS AND RIVERS**

by

Sonia Anita Nagorski

M.S., The University of Montana, 1997

B.A., Amherst College, 1994

Presented in partial fulfillment of the requirements

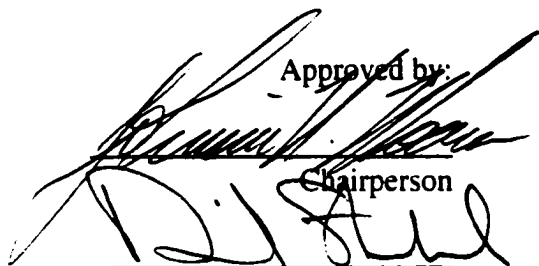
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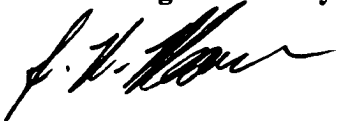
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**Spatial and temporal variations in the geochemistry of several western Montana streams and rivers.**

Director: Johnnie N. Moore



Clean sampling methods were used to examine the solute (operationally defined as  $<0.2$   $\mu\text{m}$ ) and total recoverable geochemistry of the Blackfoot River and Clark Fork River watersheds. The purpose of the first study, conducted in the upper Blackfoot River watershed near a proposed gold mine site, was to measure pre-mining water quality conditions and to characterize the physical relationships between surface water and ground water. Other than for the major elements, most solutes were not well correlated with streamflow. The chemical variations appeared to be a product of the complex interactions among the timing and magnitude of meltwater and rainwater contributions, shifting proportions of the ground water component of the streamflow, and contaminant mobilization in the headwaters of the Blackfoot.

The second study measured both the solute phase and bed sediment in a one-time sampling event of the entire Blackfoot River watershed. The highest metal concentrations were located in the vicinity of the historic mining complex in the headwaters, and these concentrations declined sharply as tributaries joined the mainstem. Comparison of sediment samples with those collected in 1989 and 1995 do not show evidence for basin-scale long-term changes, despite remediation work begun in 1993.

The third project investigated the geochemical responses of the solute and suspended phases to streamflow on bi-hourly, daily, and seasonal timescales. The study was conducted on two rivers and two mountain streams in the Blackfoot and Clark Fork River basins. Generally, the trace element (Al, As, Cu, Fe, Mn, and Zn) patterns were more complicated than those of the major elements (e.g. Ca, K, Mg, Na), which were better correlated with discharge. Suspended sediment, total recoverable trace metals, and some dissolved elements exhibited short-term flushing effects at the onset of high flow conditions associated with spring runoff and a late summer precipitation event. Diel cycling was observed for pH, dissolved oxygen, water temperature, dissolved inorganic carbon, total suspended sediment, and total recoverable metals at some or all sites. For many parameters, short-term variations were small compared with long-term variations. However, the short-term variability of some parameters covered large portions of or exceeded the seasonal variability. These results have important implications for the future design of studies that aim to monitor and characterize the surface water geochemistry of contaminated and pristine watersheds.

## **Acknowledgments**

I am very grateful to numerous people whose guidance, advice, and assistance were critical to the completion of this project. I thank Johnnie Moore, my mentor of 7 years, for generously guiding me through each project with great enthusiasm, insight, and encouragement. The other members of my dissertation committee, Bill Woessner, Ian Lange, Dave Patterson, and Garon Smith, also contributed many great ideas, and I thank them very much for the time and energy they put into my projects.

David Smith of the U.S. Geological Survey in Denver provided the funding that supported all of the work in this dissertation. For this I thank him tremendously. I am also very grateful for his ideas about the various projects and for entrusting me with a large degree of independence in designing and implementing the research.

Numerous folks helped out in the field and in the lab, and I greatly appreciate their hard work and our good times together. They include David Beale, Lynn Biegelsen, Anna Breuninger, Dan Cole, Sarah Day, Justin Harris, Matthew Hiro, Nick Kujawa, Beth Nichols, Jan Shifflett, Nate Stevens, Clara Wheeler, and Amanda Yates. Special thanks goes to Temple McKinnon, who generously shared with me her enthusiastic energy, time, ideas, and friendship while working on most of this dissertation with me in the field and in the lab.

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## **Chapter 1: Introduction**

The mineral extraction industry is a major anthropogenic source of metal and metalloid contamination to waters, soils, and biota. At last report, the metal mining industry was the largest source of toxic releases to the environment in the United States, accounting for 3.5 billion pounds of releases in 1998 alone (EPA, 2000). Some of the consequences of mineral extraction include surface water and ground water quality degradation, aquatic benthos toxification, hydrological and landscape alterations, and air pollution (Honeyman and Santschi, 1988; Moore and Luoma, 1990; Luoma and Carter, 1991; Helgen and Moore, 1996; EPA, 2000). The environmental impacts of resource extraction have become important areas of study in the fields of geochemistry, hydrology and biology.

Due to rising human populations and growing demands for the world's natural resources, environmental problems associated with mining and ore processing will draw increasing regulatory and scientific focus in the future. Though widespread and of great concern to human and environmental health, the impacts by mining activities on water quality have not been well characterized and quantified. Additionally, very limited work has been done to characterize the aqueous geochemistry of pristine systems to which impacted areas need to be compared.

The research to date is so limited largely because the science of freshwater aqueous geochemistry is a relatively young field. Few current and historic mines have adequate records of pre-mining water quality conditions. Historically, pre-impact characterization of watersheds was not required, and early mineral prospectors found metal concentrations in surface water to be of limited use in locating ore deposits due to their fluctuating, low, or undetectable concentrations (Hosking, 1970; Hoffman and Fletcher, 1972; Rose et al., 1979; Runnells et al., 1992). At present, there is little consistency in the sampling designs of water quality studies. Sample processing and analytical methods are continually being revised and are typically incompatible among datasets. In the past decade, several studies have effectively invalidated much of trace metal work done for much of the last century due to the discovery of major contamination problems associated with standard sampling protocols (Benoit, 1994;

Windom et al., 1991; Horowitz et al., 1994; Taylor and Shiller, 1995). These studies have demonstrated that by following meticulous “clean” (or “ultra-clean”) sampling, processing, and analytical techniques, trace metal contamination of water samples can be drastically reduced. The conversion to the use of these new techniques is ongoing, but numerous papers are still being published based on data collected using the problematic older methods.

Based on both conventional and clean data, scientists still have a poor understanding of the spatial distribution and temporal dynamics of the geochemistry of trace metals in surface waters. Most studies examine either spatial or temporal aspects of trace metal geochemistry, but not both, and many of these studies focus only on heavily contaminated areas. In particular, a relatively large amount of work has been done on defining the spatial geochemical trends in streams impacted by acid mine drainage (e.g. Filipek et al., 1987; Moore et al., 1991; Kimball et al., 1994; Schemel et al., 2000). Few such studies have incorporated a temporal dimension to their research. Additionally, there is a lack of research examining the surface water geochemistry at similarly tight spatial and temporal resolutions in uncontaminated systems.

The geochemistry of rivers can vary within short distances due to both physical and chemical dynamics in the watershed. Microbially-mediated, redox and pH-dependent dissolution-precipitation, and sorption-desorption reactions are thought to be the major controls on partitioning of metals and metalloids among the dissolved, colloidal, suspended sediment, and bed sediment fractions (Nordstrom and Ball, 1986; Filipek et al., 1987; Rampe and Runnells, 1989; McKnight and Bencala, 1990; Moore et al., 1991; Smith et al., 1992; Broshears et al., 1996). Metals transported away from a source become physically diluted by tributaries and ground water, while changing chemical conditions continue to rearrange the partitioning between the water column and particulate phases [Chapman et al., 1983; Bencala et al., 1990; Davis et al., 1991; Kimball et al., 1994; Gurrieri, 1998].

In pristine areas, the major controls on the physical and chemical changes to the stream geochemistry include variable contributions from soil zones and vegetation, interactions with groundwater and hyporheic zones, atmospheric deposition of acidic anions, the natural buffering capacity of the local geology, differential weathering rates

within the basin, and the organic carbon concentration in the stream (Campbell et al., 1991; Pinol et al., 1992; Shafer et al., 1997; Meixner et al., 1998; Clow et al., 2000). In a stream impacted by acid mine drainage, additional factors influence the dispersion of the mining contaminants in the watershed. These include the type, size, and grade of the mineral deposit, the mining and ore processing methods, the grain size of the contaminated sediments in the system, the availability of sorption surfaces in the water column, and interactions between the metals and sulfate released from the mine drainage sources (Ficklin et al., 1992; Plumlee et al., 1992, Helgen and Moore, 1996; Schemel et al., 2000).

While the study of seasonal variations in the major element geochemistry of freshwater systems has received a moderate amount of research attention, few studies have included trace metals in their analyses. Even fewer have used clean methods to collect those data. From the available data, little agreement has emerged in terms of the temporal patterns of trace metal concentrations in both contaminated and pristine streams and rivers. In contrast, numerous papers have reported generally consistent inverse relationships between discharge and major ion concentrations (e.g. Hem, 1970; Cossa, 1990; Pinol et al., 1992; Williams et al., 1993).

One type of temporal variation that has increasingly been recognized is that of hysteresis patterns. Hysteresis describes a loop pattern in streamflow vs. concentration plots in which concentrations differ along the rising limb from the falling limb of a pulse of increased streamflow (Whitfield and Schreier, 1981; Johnson and East, 1982; Stottlemeyer and Troendle, 1992; Evans and Davies, 1998.) Yet only a handful of papers have described hysteresis patterns in dissolved or total trace metals (e.g. Whitfield and Clark, 1982; Weatherbee and Kimball, 1991 Sokolov and Black, 1996; Bhangu and Whitfield, 1997). Because trace metals are more reactive in surface waters than are major ions, they are more susceptible to changing conditions in their source areas and to in-stream chemical dynamics (Van der Weijden et al., 1989; Shiller, 1997, Sherrel and Ross, 1999). Hence, their hysteresis patterns are less predictable and more difficult to interpret than those for major ions such as Ca, Mg, and Na.

An adequate collection of reliable water quality research is clearly lacking, despite the vast environmental and economic implications. There are many unanswered



questions regarding the spatial and temporal variation of surface water geochemistry that are of scientific, environmental health, and regulatory importance. In this dissertation I try to answer some of these questions, at least in terms of how they relate to the Blackfoot River and Clark Fork River watersheds in western Montana.

In Chapter 2, I present the results of a temporal and spatial investigation of the geochemistry of a several kilometer-long stretch of the contaminated upper Blackfoot River and one of its pristine tributaries, the Landers Fork. Studying the seasonal variation at sites spaced at approximately 1 km intervals, I found a large degree of physical and chemical variation among sites, over time, and between streams. I discuss hysteresis patterns which emerged for many of the major elements and try to explain some of the differences between the responses of trace elements and major elements to high flow events. The Blackfoot River and Landers Fork come together at the site of a proposed large scale open pit gold mine, and it is for this reason that they were chosen for study by the Mineral Resources Program (MRP) of the U.S. Geological Survey (USGS). This project is part of a larger scale effort by the MRP to investigate geochemical baselines in mineralized, unmined watersheds. The results of this project have been previously reported in the form of two USGS Open File Reports: Nagorski et al. (1998) and Nagorski et al. (2001).

I present a synoptic study of the water and sediment geochemistry of the Blackfoot River basin in Chapter 3. The purpose of this study was to put into context the geochemistry of the study area in chapter 2 into the Blackfoot River basin as a whole, and to characterize the downstream extent of metals contamination originating from the historic Heddleston Mining District in the headwaters. I examine the role of tributaries in influencing the geochemistry of the mainstem, and I identify differences between the water and sediment dispersion patterns for metals of environmental concern. In addition, I compare streambed sediment data from the watershed collected by Moore et al. (1991) in 1989 and Menges (1997) in 1995 with those I collected in 1998. While the historic mining district has been undergoing remediation since 1993, I found almost no differences among metal concentrations in 1989, 1995, and 1998. The data from this research have been published in a U.S.G.S. Open File Report as well (Nagorski et al., 2000).

In Chapter 4, I report the results of a twelve month study on the spatial and temporal variations of the inorganic geochemistry at four sites in western Montana. For this study, I sampled two large rivers and two high elevation streams; two of which were impacted by mining and two not. The smaller streams were the Landers Fork (pristine) and upper Blackfoot River (mining-impacted), which were the focus of the study in chapter 2. Hence, another year of data at two of the sites in the chapter 2 project was added, allowing for multiple year examination of temporal patterns in the watersheds. The two large river sites were the Clark Fork River near Drummond (mining-impacted) and the lower Blackfoot River near Bonner (minimally-impacted). However, unlike the projects in chapters 2 and 3, in this study I analyzed the total recoverable phase in addition to the dissolved phase of the water samples. Because water quality standards are set for the total recoverable content in waters, I monitored the water quality according to aquatic life regulations. In addition to examining the seasonal variations of the geochemistry of these rivers, I conducted two 24 hour studies at each site in the summer, in which I took samples every 2 hours. The purpose of this portion of the project was to compare the diurnal variation to the seasonal variation. A third type of temporal scale examined was that of daily sampling for almost two weeks following the first significant rainfall in September at the end of the summer drought. From these data, I found that short term variations in some parameters captured much of the variation found on much longer time scales. I also report that major ions behaved differently from the trace metals, that clear hysteresis patterns were present for many constituents, and that streamflow values alone were inadequate predictors of the surface water geochemistry in those systems.

The findings from these projects underscore the superiority of the newly developed clean techniques for sampling water, demonstrate that some of the greatest geochemical changes of a water year may occur during the early stages of runoff, and show that the widely held generalization regarding the inverse relationship between streamflow and solute concentrations is largely invalid in these rivers. The results should have significant implications for the sampling design of future monitoring studies and will contribute to the understanding of the chemical dynamics of surface waters in western Montana.

## Chapter 2: Seasonal variations in the solute geochemistry of the upper Blackfoot River watershed, Montana.

### Abstract

Clean sampling methods were used to study the solute (operationally defined as  $<0.2 \mu\text{m}$ ) geochemistry of mining impacted and pristine surface waters in the upper Blackfoot watershed. Five sites along the Upper Blackfoot River and four sites along the Landers Fork were sampled, some more regularly than others, over the course of 18 months in 1997-1998. Samples were also collected from a tributary to the Blackfoot (Hogum Creek) and a tributary to the Landers Fork (Copper Creek). The Upper Blackfoot River, which drains historic mines ca. 20 km upstream of the study area, had higher trace metal concentrations than did the Landers Fork, which drains the pristine Scapegoat Wilderness area. In both rivers, many of the major elements show a seasonal hysteresis effect in which the concentrations were lower on the rising limb of the hydrograph than on the falling limb. However, elements such as As, Cu, Fe, Mn, S, and Zn exhibited more irregular temporal patterns, which included periods of almost no response to changes in streamflow, concentration elevation following a summer storm, concentration surges at the start of snowmelt in the spring, and/or elevation throughout the course of spring runoff. Streamflow values alone were poor predictors of the solute concentrations in the streams, and complex interactions between the timing and magnitude of streamflow appeared to account for the geochemical trends in the study area.

### Introduction

In order to characterize baseline conditions in pristine watersheds and to obtain accurate data in contaminated watersheds, ultra-clean sampling, processing, and analytical methods are necessary (Benoit, 1994; Horowitz et al., 1994). In the past decade, the importance of these methods has been highlighted by studies that cast doubt on the validity of much of the trace metal data collected using standard protocols (Windom et al., 1991; Taylor and Shiller, 1995). Still, only a small number of published research to date has reported on both spatial and temporal trends within river basins using clean sampling techniques (e.g. Hurley et al., 1996; Shafer et al., 1997; Sherrell and Ross, 1999).

Although major USGS water quality programs (NAWQA and NASQAN) have adopted clean sampling and analytical methods (Horowitz et al., 1994; Shelton, 1994; Alexander et al. 1996), they have not focussed on defining geochemical trends at dense spatial and temporal resolutions within individual watersheds.

Based on both clean and conventional studies, little is known about seasonal variations of the inorganic geochemistry of freshwater systems. Storm-scale or seasonal-scale hysteresis, defined as a loop pattern in plots of concentration vs. discharge caused by elemental concentrations differing along the falling limb from the rising limb of a hydrograph, have been reported for decades (e.g. Johnson and East, 1982; Wetherbee and Kimball, 1991; Piñol et al., 1992; Campbell et al., 1995; Droppo and Jaskot, 1995; Sokolov and Black, 1996; Bhangu and Whitfield, 1997). However, the studies present little consistency in the hysteresis patterns and very few provide data on trace elements. Identifying hysteresis cycles is important because their presence violates the assumption that the geochemical variation in rivers is generally based on an inverse, linear relationship between streamflow and chemical concentration (Hem, 1970; Whitfield and Schreier, 1981). Hence, the identification of hysteresis cycles is critical for the accurate monitoring of trace element loads in surface waters. Additionally, hysteresis patterns can help identify which geochemically distinct sources and processes in the watershed are dominating stream chemistry at different times (Hooper et al., 1990; Evans and Davies, 1998).

Much of the hysteresis research has come from regions where seasonal streamflow variations are not dominated by the springtime melting of snowpacks, but by rain events. Such research has generally documented hysteresis patterns with clockwise rotations (concentrations higher along the rising limb than along the falling limb, Figure 1a). This clockwise pattern is typically attributed to flushing effects at the onset of higher flow conditions, when precipitation in a catchment leads to the displacement of ionically concentrated soil and ground water into the stream channel (Piñol et al, 1992; Sokolov and Black, 1996).

In the few studies coming from cold, mountainous regions in North America (Colorado Rocky Mountains; Sierra Nevadas, and Canada), both clockwise and counterclockwise hysteresis (Figure 1b) rotations have been reported (e.g. Whitfield and Whitley, 1986; Campbell et al., 1995; Bhangu and Whitfield, 1997). Clockwise hysteresis patterns in snowmelt-dominated watersheds have been explained by ionic pulses from the snow itself at the start of the melt period that create surges in stream water ionic concentrations (Williams et al., 1993; Campbell et al., 1995) and/ or a piston-effect by meltwater which increases the soil and groundwater contribution to streamflow (Stottlemyer and Toczydlowski, 1990). Counter-clockwise rotation can occur in high elevation watersheds because when thawed in the spring, the snowpack produces overland flow of relatively unaltered meltwater which produces dilute stream water conditions during early runoff (Stoddard, 1987; Stottlemyer and Troendle, 1992; Bhangu and Whitfield, 1997). Following the initial, usually rapid influx of meltwater, soil water and ground water gain larger roles in contributing to flow, as more snowmelt travels through the subsurface before entering the channel.

Almost no work known to the authors has been done on investigating geochemical seasonal hysteresis in the Rocky Mountains, a region where much of the annual streamflow occurs during the spring snowmelt (Campbell et al., 1995). In this report we present the results of a temporal and spatial investigation of the geochemistry of a several kilometer-long stretch of the upper Blackfoot River and the Landers Fork, which are moderately high elevation streams in western Montana (Figure 2). The purpose of the project is to document seasonal geochemical trends along short reaches of a mining-impacted river and its uncontaminated tributary using clean sampling and processing methods. By identifying hysteresis patterns, we establish the usefulness of streamflow as a valid predictor of surface water geochemistry in the two rivers. By comparing and contrasting the hysteresis patterns, we make inferences about the varying sources driving the geochemical seasonal variability in the contrasting drainages.

Several historic mines, which have been linked to water and bed sediment contamination in the watershed, are located in the headwaters of the Blackfoot River, 20 km upstream of this project's study area (Moore et al., 1991; Menges, 1997; Nagorski et al., 2000). In contrast, the Landers Fork largely drains a pristine area, a portion of the rugged Scapegoat Wilderness area. The upper Blackfoot River and the Landers Fork flow adjacent to an undeveloped ore deposit proposed for open-pit gold mining (the McDonald Gold Project area) before joining together to the southwest of the deposit (Figure 2). The elevation at the sampling sites is ca. 1400 m, and the streams drain areas with elevations of up to 2400 m; therefore, the annual hydrologic variability is dominated by snowmelt dynamics in the spring and early summer. Downstream of the study area, the Blackfoot River flows for another 186 km before joining the Clark Fork River, a major tributary to the Columbia River. The complete dataset from this project has been documented in two USGS Open File Reports (Nagorski et al., 1998 and Nagorski et al., 2001). The first Open File Report (OFR) contains data collected from July, 1997 until March, 1998, while the second focuses on data collected between April and December, 1998.

## **Methods**

### **1. Sampling locations and frequencies:**

We selected sites upstream, adjacent to, and downstream of the proposed mine area (Figure 2). The sites were spaced as evenly as possible, considering access limitations in the area, covering approximately 7 km of each river. Between July, 1997, and August, 1998 we sampled at four sites along the Landers Fork (LA, LB, LC, and LD), three sites along the Blackfoot River (BH, BB, and BC), one site at Copper Creek (C) and one at Hogum Creek (HC) 6 to 13 times (Figure 2). We continued sampling at two of the Landers Fork sites (LB and LC) and two of the Blackfoot River sites (BB and BC) monthly through December, 1998 (although sites LB and BC could not be accessed due to heavy snow in December, 1998). An additional two sites (sites BA and BD) were sampled only from

July to September, 1997. We collected samples of seep water emerging from the streambanks near sites LB and LC when possible—in 1/98 and 4/98 near LB, and in 11/97, 1/98, 3/98, 4/98, 10/98, 11/98, and 12/98 at site LC. During the other times, the seeps near LB were not accessed and the seeps at LC were submerged by channel flow.

## 2. Streamflow measurement:

We measured streamflow at each sampling site using a Price AA current meter connected to an Aqua Calc 5000 calculator (Rickly Hydrological Co.) according to standard USGS protocol (Rantz et al. 1982). During the majority of the sampling events, we measured streamflow twice at each site in order to define the measurement precision. Replicate measurements at sites with less than 142 L/s, between 142-991 L/s, and >991 L/s were within 14%, 9%, and 7%, respectively. At sites where we took only one streamflow measurement, the error assigned to the measurement was the maximum precision error found in the appropriate streamflow bracket.

## 3. Water sampling

Two people were present for each sampling event. While one person measured streamflow, the other took measurements of pH, dissolved oxygen (D.O.), conductivity, and air and water temperature in situ, using an Orion model 230A pH meter, an Orion model 820 dissolved oxygen meter, a Hach Conductivity/TDS meter, and a Barnant 100 Thermocouple Thermometer, respectively. The pH and D.O. meter were calibrated at least once per day, and their calibrations were checked and usually redone at each sampling site.

We used clean sampling and processing methods in order to minimize the chances of contaminating the samples. Each sample bottle was stored in double zip-close bags, from which it was removed only moments before sampling. The sampler contacted each bottle wearing new latex or nitrile gloves. With the help of the other person, the sampler wearing the clean gloves contacted nothing but the sample bottle and the inner storage bag.

After rinsing the sample bottle with one volume of stream water, the sampler filled each bottle by width and depth integrating over an area upstream of where we had disturbed the site by measuring streamflow and the other in situ parameters and took three samples per site. In addition, we always collected samples upstream of bridges in order to limit additional sources of contamination. We immediately returned the sample bottles to their zipped double bags and stored them on ice until return to the laboratory.

We extensively pre-cleaned all collection materials (bottles, syringes, etc.) that came into contact with the water samples. One exception to this was the amber glass bottles used for anion and carbon samples; these bottles were washed only by repeated rinsing with Milli-Q water. All other materials were made of LDPE or HDPE plastic or teflon. Their cleaning procedure consisted of a regular wash with warm water and soap, several rinses in deionized water, soaking in 6N HCl for 2 hours, three rinses in Milli-Q deionized water, soaking in a 1 % trace-metal grade HNO<sub>3</sub> bath for 24 hours, another three rinses in Milli-Q, and drying and storing into clean plastic bags under a Class 100 laminar flow hood. At least one field blank was carried through the acid washing stage, transport into the field and exposure to the ambient air, filtration, preservation, and analysis for each sampling event.

#### 4. Lab Methods

We removed the samples from their double bags and filtered them under a Class 100 laminar flow hood at the University of Montana Murdock Environmental Biogeochemistry Laboratory within 30 hours of collection. Studies have shown that standard methods of field filtration can result in high risks of introduction of trace metal contamination into bottles, and that lab filtration, even if not done immediately, does not cause significant sorption onto sample bottles prior to filtration (Struempfer, 1973; Benoit, 1994; Taylor and Shiller, 1995). In addition, we conducted an experiment for this project to test whether sorption onto bottles before filtration was a problem with these samples. Five replicate samples taken from the Blackfoot River were stored on ice for 2, 12, 41, 65,



and 160 hours before being filtered for analysis. Results show that there was no measurable change in elemental concentrations for most constituents over the 160 hours. The only exceptions were Fe and Mn, whose concentration dropped significantly after 65 hours, a time period longer than the holding times used in this project.

We wore clean nitrile or latex gloves whenever handling the sample bottles and any other sample storage or processing materials. We filtered the samples through 0.2  $\mu\text{m}$  syringe filters with glass prefilters (Gelman Sciences Serum Acrodiscs). At least 50 mL of sample material was used to rinse the syringe, filter, and bottle and to reduce the effective pore size (and as a result, the passage of colloidal material) of the filters (Taylor and Shiller, 1995; Horowitz et al., 1996). Following the purging by the 50 mL of sample, we filled a 60 mL amber glass bottle with filtered sample for the purposes of carbon and anion analysis. Finally, we filled a 125 mL plastic bottle with filtered sample material for cation and arsenic analysis, still using the same filter. We stored the amber bottles in a 4°C refrigerator before analysis, whereas we acidified the samples in the plastic bottles to  $\text{pH} < 2$  with ultrapure, double distilled from quartz Optima (FisherScientific) HCl.

We used a Thermo Jarrel-Ash ICP (IRIS) with ultrasonic nebulization (Cetac, U-5000AT+) to measure trace element and major cation concentrations in the water samples according to EPA Method 200.15 (Martin et al., 1994). This method was modified slightly in that we did not add nitric acid or hydrogen peroxide to the samples. Nitric acid was previously determined by the laboratory not to improve analytical performance, and hydrogen peroxide was not necessary because arsenic was not being analyzed by ICAPES.

Using a Shimadzu Carbon analyzer, we measured inorganic carbon concentrations within one week of sample collection according to Standard Method 505A (Franson, 1985a). However, due to technical problems with the Shimadzu Carbon analyzer in the summer and fall of 1998, we were unable to analyze all samples collected in that time period for inorganic carbon.

Arsenic analysis was done using atomic absorption spectroscopy with hydride generation (HGAAS) according to Standard Method 303A (Franson, 1985b). This method was modified by the Murdock Environmental Biogeochemistry Laboratory to optimize analytical performance (Mickey, written communication, 1997). The modifications consisted of adding KI and HCl to the samples and standards to achieve final concentrations of 2% KI and 1 M HCl and of running solutions of 0.35% NaBH<sub>4</sub> (stabilized with 0.5% NaOH) and 6N HCl through the hydride generation during analysis.

##### 5. Quality Assurance/ Quality Control

We conducted sample analysis according to a strict quality assurance/ quality control program. We calibrated each instrument at the start of each day and checked for accuracy and precision with the analysis of every 10 samples. Accuracy was measured through the analysis of internal and external standards, spikes, and blanks. Precision was evaluated by running replicate samples and standards within individual and over multiple analytical events. The practical quantification limit (PQL) was determined as the threshold at which a sample can be reproduced within a maximum variability of 30% (Table 1).

Six different external standards were analyzed 47 times on the HGAAS with the arsenic samples, and each measured within the reported acceptable range. On the ICP, three types of USGS standards (USGS T-107, USGS T-143, and USGS T-145) were run a total of 150 times during sample analyses, and the average measured concentrations of all elements fell within the reported acceptable range except for Sr, which measured up to 4% low on all three standards, and Ag, which was 12% high on USGS T-143. The mean percent difference between known and measured values of internal standards measured on the HGAAS, and carbon analyzer was less than 7.1%. On average, sample duplicates run on all instruments were less than 8% different from one another (Table 1). Mean percent spike recoveries for all measurable elements were between 86 and 112% (Table 1).

Laboratory reagent blanks were all below the PQL on all instruments. Field collected blanks were mostly below the PQL for all elements as well. Exceptions are for Ca, Mg, Na, S, Si, and Zn, which were detectable in up to 23 of the 31 field blanks. The concentrations of Ca, Mg, S, and Si in the blanks were inconsequential, as they were at least an order of magnitude lower than concentrations found in environmental samples. However, the highest Na concentration (0.42 mg/L) detected in the field blanks could explain the noisiness of much of the Na data. The appearance of 3.7 µg/L of Zn in one of the field blanks unfortunately calls into question much of the Zn data. Zinc is one of the most easily contaminating elements due to its presence in many plastics and materials. However, it should be noted that 24 of the 31 field blanks did not have quantifiable Zn (<0.3 µg/L), and the vast majority of samples from the Landers Fork did not have detectable Zn either.

## **Results**

### **1. Streamflow**

Streamflow levels and surface water - ground water dynamics varied seasonally along the studied reaches of the Landers Fork and Blackfoot River. Streamflow decreased between July, 1997 and March, 1998. Between April and December, 1998, there was a more variable streamflow pattern, as would be expected due to the occurrence of spring runoff in this time period. At most sites, streamflow started to rise in April, and runoff lasted through July (Figures 3 and 4).

Streamflow between LA and LB (accounting for Copper Creek, which joins the Landers Fork between LA and LB) either stayed constant or increased during the summer months. However, it was disconnected during the low flow winter period, when LA was dry and C's flow was lost to the subsurface before reaching LB. Streamflow generated

from seeps sustained ice-free flow at LB and LC at all times of the year sampled. The reach between LB and LC was gaining flow during all 17 times that both sites were measured. The reach between LC and LD had no measurable gain or loss on 3 of the 8 times it was measured; otherwise it was losing.

At the Blackfoot River sites, streamflow was present at all sites every time they were visited over the course of the study. The one exception to this is site BB, where the river was frozen on 1/6/98. The ice-free status at sites BH and BC during the cold winter months indicates an important role by ground water in sustaining streamflows in the area. Although the stretch between BH and BB (accounting for Hogum Creek) was a losing reach 5 of the 6 times it was measured, the stretch of river between sites BB and BC was gaining streamflow the majority (10 of 15) of the times the sites were gauged. The reach upstream of site BD, below the confluence of the Landers Fork and Blackfoot River, was at a steady state flow condition 3 of the 5 times measured, and a losing reach in early 7/97 and 8/97.

## **2. Surface Water Geochemistry**

The solute chemistry of the Landers Fork was different from the Blackfoot for most of the constituents measured. Comparisons of mean concentrations show the Blackfoot samples had higher concentrations of Fe, K, Mn, Na, S, Si, Sr, and Zn and lower concentrations of inorganic carbon, As, Ca, and Mg than the Landers Fork, during the study period (based on paired t-tests with p-values < 0.01) (Table 2). The rivers had similar pH values, water temperatures, and dissolved oxygen, Ba, and Li concentrations. Elements that were below the detection limits in some samples (Fe, Mn, and Zn in the Landers Fork only) were assigned a value of one-half the element-specific PQL. Both Cr and Cu were usually but not always below their PQLs in both rivers, and so mean concentration comparisons could not be made. No samples from any sites had detectable concentrations

of Ag (<1 µg/L), Be (<0.05 µg/L), Cd (<0.5 µg/L), Co (<0.5 µg/L), Mo (<1 µg/L), Ni (<2 µg/L), Pb (<6 µg/L), Ti (<2 µg/L), and V (<2 µg/L).

Most solute concentrations increased as discharge decreased in the both the Landers Fork and the Blackfoot River sites through the summer and fall of 1997. Following the start of spring runoff in April, 1998, most of the major ions decreased in concentration and subsequently rose throughout the rest of study period through summer and fall conditions. Few generalizations can be made about the behavior of the trace elements in the Blackfoot River, and they were largely below detection in the Landers Fork. Specific results follow.

### **a) Landers Fork**

#### **Major elements, Ba, Li, and Sr:**

Hysteresis loops with counter-clockwise rotation were present for inorganic carbon, Ba, Ca, K (site LA only), Li, Mg, and Sr at sites C and LA (Figure 5). That is, these elements had lower concentrations along the rising limb than on the falling limb of the hydrograph. At C, these elements (as well as Si) were inversely correlated with streamflow ( $r < -0.85$ ,  $p < 0.01$ ) overall, while at LA only Ba, K, and Sr were ( $r < -0.74$ ,  $p < 0.04$ ). The other elements at LA were inversely related to discharge considering the falling limbs alone, but a single low concentration rising limb datapoint is responsible for much of the loop formation and the lack of good linear correlation (Figure 6).

At LB and LC, the hysteresis loops are not nearly as clear as those seen upstream at C and LA, despite the additional 5-6 months of sampling at the sites (Figure 7). Although inorganic carbon, Ba, Ca, K, Li, Mg, Si, and Sr show an inverse, approximately linear correlation ( $r < -0.64$ ,  $p < 0.01$ ) with streamflow at the sites, hysteresis loops are weakly apparent due to multiple crossovers. At LD, which was not sampled as regularly as LB and LC, the aforementioned elements also have negatively sloping correlations with streamflow ( $r < -0.69$ ,  $p < 0.04$ ), and overall, the geochemistry at LD was very similar to that of LC. At LB and LC, there were wider ranges of solute concentrations during low flow compared to

high flow periods. In fact, once streamflow exceeded baseflow levels by a factor of about 10, concentrations of many major elements reached relatively steady levels (Figures 7 and 8).

An anomalous major element in the Landers Fork was S, which exhibited different patterns at almost every site. At site C, its concentration was higher during runoff in 1998 than during the falling limb of the 1997 streamflow, an opposite trend to those seen for the other major elements. In contrast, S at LA generally followed the counter-clockwise hysteresis loop characteristic of the other major elements, although its concentration failed to rise with the decrease in streamflow at the last sampling event, in July, 1998. At site LB, S concentrations increased with decreases in streamflow in the fall of 1997, and the highest concentration was found on the late April, 1998 sampling date, when streamflow had just begun to rise for spring runoff (Figure 14b). As runoff continued, S concentrations dropped again to levels found the previous summer. Sulfur concentration variation was comparatively small at LC, even during the dynamic streamflow conditions of 1998. The highest S there was found in September, 1997 (Figure 9).

#### Trace elements: Cu, Cr, Fe, Mn, Zn, and As:

The filterable trace metals Cu, Cr, Fe, Mn, and Zn were usually or always below quantifiable levels at Copper Creek and the Landers Fork sites. Copper was never detected, and Cr was found only rarely— at C on 1/6/98, and at LC during the winter (11/16/97, 1/6/98) and during the highest flow in 1998 (6/29/98). Iron was detected at all sites from July, 1997 to January, 1998. At sites LB and LC, which were sampled through the second fall season, Fe did not rise above the PQL (5  $\mu\text{g/L}$ ) as it did in the fall of 1997 (Figure 10). At site C, Mn was at or above its PQL of 0.3  $\mu\text{g/L}$  only during the first several sampling events, through the summer of 1997. However, at LA, LB, LC, and LD, Mn was quantifiable during 1-2 high flow events in 1998 in addition to during the summer of 1997

(Figure 11). Zinc was mostly below the PQL as well, and it was always below the concentration found in the highest field blank.

Arsenic correlated poorly with streamflow at most sites in the Landers Fork, except for at C and LB, where they correlated reasonably well ( $r = 0.66-0.68$ ,  $p < 0.03$ ). The concentration of As wavered little over time at C and LA, except for some increases during high flows in July, 1997. In contrast, As concentrations at LC and LD were highest during the winter low flow period, reaching a maximum of  $1.0 \mu\text{g/L}$  in early 1998, compared to the  $0.4-0.6 \mu\text{g/L}$  found during the rest of the year (Figure 12). During low flow periods, streamflow at LC was dominated by ground water input, and the seeps measured near the site had As concentrations of  $0.9-1.0 \mu\text{g/L}$ . However, during the last two sampling events (11/98 and 12/98), the seep As concentrations were only  $0.5 \mu\text{g/L}$ , and the surface water As concentration also dropped, to  $0.4 \mu\text{g/L}$ .

#### pH:

Although diel pH variations were not considered, as sites were not always measured at a consistent time of day, some general seasonal pH patterns are apparent at most sites. The pH at the site C exhibited counter-clockwise hysteresis, with pH lower ( $\text{pH}=8.0$ ) at spring runoff compared to the previous fall and winter ( $\text{pH}=8.1-8.4$ ) and to the post-runoff sample in July, 1998 ( $\text{pH}=8.4$ ). At LA, pH did not have a clear relationship with streamflow, although measurements were lower ( $\text{pH}=8.0-8.1$ ) during spring runoff in 1998 than they were in the late summers of 1997 and 1998. At LB, the pH was generally higher ( $\text{pH}=8.0-8.4$ ) in the summers of 1997 and 1998 than during other times of the year ( $\text{pH}=7.6-7.9$ ). At LC, pH also followed a counter-clockwise hysteresis pattern (Figure 13). It was generally lower in the winter of 1997 through spring runoff in 1998 ( $\text{pH}=7.7-8.0$ ), than during the summers of 1997 and 1998, when pH levels were in the range of  $7.9-8.3$ . During the winter, when the site was ground water dominated, the seeps at the site had pH levels that were lower than in the surface water ( $7.1 - 7.8$

compared to 7.7 - 8.3), which could explain the lower winter pH levels at the site. Fall measurement of pH at the site were at levels similar to pre-runoff conditions.

#### Spring flushing:

An ionic pulse of some elements was detected prior to spring runoff at LB and LC. In April, 1998, when streamflow had just begun to rise for runoff at LB, concentrations of Ca and S also rose before being diluted by snowmelt in May and June (Figure 14). While Ca concentrations were 33-35 mg/L between November and March, they rose to 40 mg/L on 4/6/98, when streamflow remained unchanged since March, and to 43 mg/L by the end of April, when streamflow had increased 2-3 fold, to 100 L/s. Sulfur concentrations, which were between 1.0 and 1.1 mg/L from November- March, had increased to 1.2-1.3 mg/L in late April, when streamflow had begun rising for runoff. Barium, Li, and Mg also rose during early runoff, although not as convincingly. Barium's concentration was 265 ( $\pm 4$ )  $\mu\text{g/L}$  on 4/26/98, compared with 230-250  $\mu\text{g/L}$  from November through early April. Lithium rose from 2.2-2.4  $\mu\text{g/L}$  in the winter to 2.6-2.7  $\mu\text{g/L}$  in early and late April. Magnesium, whose concentration stayed within the narrow range of 12.8-13.3 mg/L from September through early April, was at 14.0 ( $\pm 0.2$ ) mg/L in late April. The aforementioned ions all dropped in concentration with the subsequent continuation of the rising hydrograph in May and June.

Similarly, a rise in Ca, and Mg is evident at LC in March and early April, 1998, just before spring runoff began at the site (Figure 15). Streamflow was essentially constant (between 610-740 L/s) from January through April at the site, before jumping up to 8100 L/s at the time of the 5/19/98 sampling. The flushing is seen in that Ca at the site was 34-37 mg/L during the two April sampling events, compared with 31-33 mg/L in January and March. Magnesium was not as consistent during the winter as was Ca, although its concentration of  $13.2 \pm 0.2$  mg/L in late April is slightly higher than that in early April



( $12.0 \pm 0.5$  mg/L), and Mg concentrations did not rise above 13.0 mg/L on any of the prior sampling events. Unlike at site LB, no flushing effect for S was seen at LC.

## **b) Blackfoot River**

### **Major elements, Ba, Li, Sr:**

At site BH, counter-clockwise hysteresis loops with negative slopes ( $r < -0.60$ ,  $p < 0.05$ ) to streamflow are seen for inorganic carbon, Ba, Ca, Li, and Si (Figure 16). Potassium and Mg also correlate inversely with streamflow ( $r < -0.78$ ;  $p < 0.01$ ), but the falling and rising limbs are not distinct from one another (Figure 17). Similarly, inorganic carbon, Ba, Ca, Li, Mg, Si, and Sr correlate inversely with streamflow at site BB ( $r < -0.64$ ,  $p < 0.02$ ). These elements follow a counter-clockwise hysteresis pattern as well, except for Ca and Mg, which have cross-over falling and rising limbs. Likewise, inorganic carbon, Ba, K, Li, Si, and Sr exhibit counter-clockwise hysteresis at site BC (Figure 18). Again, they (and Ca and Mg) have an overall negative relationship ( $r < -0.52$ ,  $p < 0.05$ ) to streamflow at the site. Hogum Creek, which was sampled only between November 1997 and August, 1998, had inverse correlations ( $r < -0.82$ ,  $p < 0.03$ ) with streamflows for most detectable elements (Ba, Ca, K, Li, Mg, Mn, and Sr) as well. However, only 2 elements showed hysteresis loops—S, which had clockwise rotation, and Si, with counterclockwise rotation, and neither was linearly correlated with streamflow.

As was noted for sites LB and LC, there appears to be a stabilization of solute concentrations at BB and BC during high flow periods. This observation is based on only two of sampling events, when discharge increased from 1900 and 2800 L/s at sites BB and BC, respectively, on 6/5/98 to the highest flow measured over the study period (6000 L/s at BB and 7000 L/s at BC), on 6/28/98. During this high flow event, concentrations of most measured solutes were almost identical to those taken earlier that month (Figure 18).

This result may indicate that beyond a certain flow threshold, meltwater overwhelms baseflow contributions.

#### Trace elements:

Unlike in the Landers Fork, many of the trace metals in the Blackfoot were well above their detection limits, allowing for characterization of their trends with time. Although hysteresis patterns were not found, S and trace metals such as Cu, Fe, Mn, and Zn regularly were elevated during spring runoff in 1998, and they were also relatively high following a rainstorm the day before the 7/20/97 sampling event. Like at the Landers Fork sites, a haphazard relationship between streamflow and As is seen along the Blackfoot. Because trace metal seasonality varied from site to site, each site is considered separately.

*Site BH:* As, Cu, Fe, and Mn were the most highly concentrated on 7/20/97, the post-storm sampling date, than on any other over the 14 month study at the site. On the seasonal scale, Fe, Mn, and Zn concentrations were elevated during runoff compared to winter and late summer, although hysteresis loops are not apparent (Figure 19). On the contrary, As showed a counter-clockwise hysteresis cycle without a positive or negative trend ( $r=0.12$ ,  $p=0.72$ ) with streamflow (Figure 20). Copper was not detected other than on the post-storm date and in one of the triplicate samples from each sampling date in July and August 1998. Chromium concentrations appeared above the PQL during a few of the low flow events, but not during spring runoff. Zinc concentrations were highest (31-33  $\mu\text{g/L}$ ) in late April, 1998, at the early portion of spring runoff, and overall Zn correlated positively with streamflow ( $r=0.79$ ,  $p<0.01$ ) (Figure 21a). It was also relatively high (20-28  $\mu\text{g/L}$ ) during the two July, 1997 sampling events. Sulfur behaved similarly to Zn, in that its highest value was in late April, 1998 as well (Figure 21b). In late April and May, 1998, its value (24-31  $\text{mg/L}$ ) was 2-4 times the concentrations found during the rest of the

study period. During the 6/5/98 and 7/20/98 sampling, when streamflow was still high due to runoff, S concentrations returned to levels similar to pre-runoff conditions.

*Site BB:* In late July, 1997, the samples at BB dropped in pH and increased in Cu and Fe the day after the large rain event. Iron was at its maximum on that event compared the whole study period (Figure 22). Overall, Fe correlated poorly with streamflow ( $r=0.05$ ;  $p=0.86$ ) although its lowest values were found in the 6/29/98 samples, when streamflow was the highest (Figure 22). Copper was detected above its PQL not only after the storm, but also in some of the late spring and summer samples of 1998 (Figure 23). In fact, its maximum concentration occurred during the highest flows measured, in late June, 1998. Manganese and streamflow had a positive relationship ( $r=0.48$ ;  $p=0.02$ ). Arsenic was higher in the late summers of 1997 and 1998 than during other times of the study, and it roughly followed a counter-clockwise hysteresis pattern as it did at BH.

*Site BC:* This site was first sampled on 7/20/97, the event that immediately followed the summer storm referred to before. These first samples at BC are relatively low in pH and high in As, Fe, Mn, and Zn compared with those collected through the rest of the study period (Figure 24). The highest Fe (46-49  $\mu\text{g/L}$ ) found at the site over the study period was on the first sampling date, the post-storm event (Figure 24). Otherwise, Fe concentrations were approximately uniform during spring runoff, when they exceeded concentrations in the previous winter and subsequent fall. Like at the other sites, As at BC was variable (0.2-0.5  $\mu\text{g/L}$ ) during low flow conditions and it did not have a negative or positive relationship to streamflow overall ( $r=0.04$ ,  $p=0.88$ ). Copper was detected only during the highest flow event at BC, on 6/29/98. Chromium was above its PQL only in the November 1997 and January 1998 samples, as well as in one of the triplicates from 6/29/98. Manganese correlated particularly well with streamflow at site BC ( $r=0.91$ ,  $p<0.01$ ) (Figure 25). The most outlying point on the linear regression between streamflow and Mn was the July 1997 post-rainstorm sample. Concentrations of S and Zn were lower during the peak of runoff than at the start (Figure 26).

*Site HC:* Arsenic was peculiar in that its concentration went from 0.2  $\mu\text{g/L}$  (the PQL) during November, 1997 and January, 1998, to increasing steadily through the end of the sampling period, when it measured 1.1  $\mu\text{g/L}$  on 8/17/98. Iron also did not follow the trends the major elements did. Although it had a negative relationship with discharge for most of the study period, the last sample collected (in August, 1998) was 3-4 times as high in Fe as all the other samples (Figure 27). Clearly, Hogum Creek would need to be sampled at a far finer temporal resolution and over a longer period of time in order to elucidate the details of its temporal variability.

#### pH:

Although diel variations were not determined when sampling the Blackfoot sites either, a few consistent observations were noted. At BH, the pH was always well above neutral (between 7.8 and 8.4), and the lowest pH values occurred on the post-rain storm sampling day (7/20/97), when pH measured 7.9, and during spring runoff in 1998, when the pH was ca. 7.8. The pH values at BB were not clearly correlated with streamflow either, although they were lower at the start of 1998's spring runoff (7.9 - 8.0) than they were before and after (8.1-8.3). The pH levels at BC were variable within the 7.7 to 8.3 range, and pH was clearly lower at the start of runoff than at the end. The pH at HC was between 7.3 and 7.6 from November 1997 to June, 1998, and between 8.0 and 7.8 at the last two sampling events, in July and August, 1998, indicating clockwise hysteresis.

#### Spring flushing:

Sulfur and Zn appeared to be mobilized primarily during the early stages of runoff at all Blackfoot sites. At BH, HC, BB, and BC, these elements peaked during the early stages of runoff and subsequently dropped during periods of higher flow. This flushing of S and Zn are evident in the load plots. While for all other solutes (e.g. Si and Mn), load trends followed streamflow trends almost exactly, S and Zn loads do not follow changes in

streamflow over the course of runoff (Figure 28). For example, at BH the S load did not increase with the second runoff peak sampled on 6/5/98 (Figure 4a). Because its concentration dropped so dramatically after the start of runoff, its load continued to drop as well despite the rise in streamflow (Figure 28a). This same phenomenon is visible for the Zn loads. While the second runoff peak is detectable via the rise in Zn loads, the second peak is not as high as the first one, even though the streamflow level had risen (Figure 28b). This indicates that factors other than discharge accounted for their load variations.

## **Discussion:**

### **1. Hysteresis**

Hysteresis patterns were observed for some elements at most of the study sites, indicating that factors other than the amount of streamflow need to be considered when predicting the solute geochemistry in these streams. The counter-clockwise seasonal hysteresis of many solutes in both the Landers Fork and Blackfoot River is an indication of the important role played by direct runoff of snowmelt into the streams during the early periods of the spring melt. Although snowmelt, soil, and ground water were not sampled in this study, other researchers have shown that shifting proportions of the relative contributions of these various water sources likely drive hysteresis patterns (Stottlemeyer and Toczydlowski, 1990; Piñol et al., 1992; Campbell et al., 1995; Sokolov and Black, 1996).

Additionally, the differences in the widths of the loops are presumably an indication of greater or lesser chemical differences among the various water sources supplying streamflow during different periods along the hydrograph (Johnson and East, 1982; Evans and Davies, 1998). Hence, the lack of hysteresis loops for some major ions may be due to the sources supplying flow along the falling limb and rising limb having indistinguishable chemical signatures. For example, the lack of open hysteresis loops at LB and LC may

have been due to the strong chemical dominance by the relatively large and steady ground water contributions at the sites. In contrast, the open hysteresis loops at sites C and LA, where groundwater played small to insignificant roles in contributing to surface flow, were likely controlled by more dynamic variations in the snowmelt runoff chemistry and the spatial routing of the meltwater,.

Presumably, snowmelt traveling to the stream channel with minimal interaction with ground surface produced a dilution effect during the earlier portion of runoff. Yet, considering that concentrations did not drop by the same factor by which discharge increased, the soil water and ground water must have been contributing a fair amount to flow as well, and/or there was a significant amount of routing of fresh meltwater through the subsurface. The most dramatic example of this is at LB, where flow increased by approximately 400-fold in the spring of 1998 compared to the preceding winter, although concentrations of most ions were diluted by less than 30%. Another example is at BC, where high flow in the spring was 17 times the winter flow levels, although ionic concentrations were still at 70-90% their baseflow levels (other than for the trace heavy metals, which varied more widely). In general, during high flow conditions at all the sites, concentrations of many ions were typically diluted by no more than one half despite the much larger proportional increases in streamflow. Hence, the diluting power of snowmelt was apparently mitigated by substantial contributions from a combination of adjacent soil water and ground water. During the summer and fall, after the snowpack had been depleted, soil and ground waters, with their higher solute concentrations, presumably took on the dominant role in supplying water to the stream channel. Although much of the original source for the soil and ground water may have been the earlier snowmelt, the dilute meltwater likely took up more ions when in contact with soil and aquifer materials on its subsurface journey to the stream channel (Stottlemyer and Toczydlowski, 1990; Campbell et al., 1995; Stottlemyer et al., 1997).

The lack of hysteresis patterns for many of the detectable trace metals is an indication that processes controlling metal loading are different from those controlling loading of major elements. Other studies in the literature have also found that discharge-concentration relationships for filterable trace metals are poorly defined (Wetherbee and Kimball, 1991; Shafer et al., 1997; Shiller, 1997). Because metals such as Fe, Cu, Mn, and Zn are more reactive than major ions such as Ca, Mg, and Na, their concentrations are more sensitive to changing conditions such as varying pH, redox, dissolved organic carbon, availability of sorption surfaces on colloids, and biologically-controlled processes in the watershed (McKnight and Bencala, 1988; Cossa et al., 1990; Kimball et al., 1992; Shafer et al., 1997; Ross and Sherrell, 1999).

## **2. High flow increases in trace metals:**

The increase of several trace metals and arsenic in the Landers Fork basin (As at site C; Mn at LA; As and Mn at LB; and Mn and Cr at LC) and in the Blackfoot (Cu, Fe, Mn, S and Zn at BH, BB, and BC) during high flow events might be due to one or more of the following factors. For one, the higher solute concentrations may simply be an artifact of the sample processing. During high flows, total suspended particulate matter generally increases in rivers, and hence the presence of more colloidal particles may account for the apparent changes. Many recent papers have shown that even 0.2  $\mu\text{m}$  is not an adequate cut-off for separating colloidal material and truly dissolved particles (e.g. Horowitz et al., 1996; Pham and Garnier, 1998; Ross and Sherrell, 1999). With an increased colloidal abundance in the waters, the likelihood of collecting colloids in the filtrate likewise increases. It is well established in the literature that colloids, primarily colloidal iron, are major transport vectors for trace metals such as Cu, Mn, and Zn (Ross and Sherrell, 1999; Schemel et al. 2000).

Another explanation for the high flow increases in metal concentrations is that during the higher flows, water sources which normally do not significantly contribute to

the streamflow may be active. For example, groundwater from deeper or more distant and geochemically distinct portions of the aquifer may be supplying water to the high flows (Rice and Bricker, 1995). Research in other rivers suggest that during high flow events ground water can play dominant roles in influencing the geochemistry of surface waters (Whitfield et al., 1993; Campbell et al., 1995; Sherrell and Ross, 1999). Additionally, as mentioned earlier, the high reactivity of trace metals, both dissolved and colloidal, make them more prone to physical and chemical changes in the watershed that are more difficult to identify than for conservative major ions. The coupling of changes in both the physical and chemical conditions in the watershed makes it difficult to distinguish among the potential processes which may be accounting for the seasonal trace metal variations.

Lastly, the mining contamination in the Blackfoot watershed may help explain the trends in that river. Metals might be released from the upstream mining district or mining-contaminated marshes below the district. Physical and chemical sources could include higher water supplies from groundwater interacting with mine workings, overflowing treatment ponds, or flushing of reduced waters in the contaminated wetlands and soils upstream of the study area. Clearly, more extensive studies are needed to identify the role of colloids and the specific sources and mechanisms potentially supplying solute metals to the streams during high flow conditions.

The same possibilities discussed above to explain the seasonal rises in trace metals may explain the drop in pH and rise in high As, Cu, Fe, Mn, and Zn collected at one or more of the 3 main Blackfoot sites (BH, BB, and BC) following a rainstorm in late July, 1997. Other studies in the literature have reported trace metal surges and drops in pH in rivers during storm periods (Bird, 1987; Soulsby, 1995; Sherrell and Ross, 1999). The data presented here show that a single short term event may cause geochemical changes at least as great as those found over the course of an 18 month seasonal study in which samples were taken approximately once per month. This result has implications for



adequately designing monitoring studies that aim to capture the full range of temporal geochemical variation in streams.

### **3. Spring flushing**

Flushing effects might explain the pre- and early- runoff rise in the concentrations of some solutes in the Landers Fork and Blackfoot River. With this mechanism, elements which have been accumulating on the periphery of snow crystals and in adjacent soil and ground water over the winter are suddenly pulsed into the surface water, creating a brief surge in concentrations, after which they are depleted (Johannessen and Henriksen, 1978; Harrington and Bales, 1998; Marsh and Pomeroy, 1999). Most research on spring ionic pulsing have focussed on the widespread flushing of sulfate and nitrate, which commonly are atmospherically-derived acidic anions. However, studies of cation flushing report more variable results. For example, while Williams et al. (1993) and Meixner et al. (1998) report little or no ionic pulse for cations in streams in the Sierra Nevada, Stottlemyer and Toczydlowski (1990) observed flushing for Ca, Mg, Na, K, and  $\text{NH}_4^+$  in a Michigan stream. These authors have attributed the patterns of variable cation responses to different biogeochemical processes by soils and vegetation which can both release and uptake pulses of ions, variable displacement of ground water by meltwater into the stream, and weathering-related processes in the watersheds.

Sulfur displayed the most prominent flushing at most sites in this study. A probable explanation for the early S surges is its presence in the snow itself. Extensive snow sampling in the basins would be required to determine its concentration distributions, since the geochemistry of snow varies considerably with depth and distance (Brimblecombe et al., 1985). Yet, it is widely recognized in the literature that atmospheric S accumulates in snow packs both near and far from industrial sources (Davies et al., 1984; Schemenauer et al., 1985; Campbell et al., 1991). Many researchers studying the flush of ions in snowmelt have repeatedly shown that sulfate is preferentially eluted from the

snowpack at the nascent stages of the melt period (Davies et al., 1982; Tsiouris et al., 1985; Williams et al., 1993). Additionally, the higher S concentration in the fall compared to the winter at several Landers Fork sites might be explained by fresh S supplies delivered by autumn precipitation events which contribute directly to the stream or which induced flushing of soil and ground waters in which S accumulated over the relatively dry summer period (Williams et al., 1993; Campbell et al., 1995),

The spring surge of S in the Blackfoot River was likely due to a combination of elution from the melting snow as well as to inputs from acid mine drainage processes upstream. While the pulse of S in the Landers Fork was on the scale of several hundred micrograms per liter, the surge in S in the Blackfoot River was on the order of several milligrams per liter. Unless markedly higher S surges in the Landers Fork were missed in the sampling, it is likely that the much larger increases in the Blackfoot S concentrations originated from sources in addition to the snow itself. The obvious candidate for such a source is the sulfide mining complex 20 km upstream of the study area. The increase of S (and trace metals Fe, Cu, Mn, and Zn) following the July rain storm in the Blackfoot River and not the Landers Fork is further evidence that S can be mobilized and transported downstream in anomalously high concentrations.

Possible reasons for the Zn flushing in the Blackfoot are less clear. Several other studies have noted increases in filterable Zn at the onset of high flow events as well (Weatherbee and Kimball, 1991; Sokolov and Black, 1996; Shafer et al., 1997). In general, Zn is thought to be more mobile than other trace elements because the sorption of Zn onto amorphous Fe oxyhydroxides is reportedly favored at higher pH levels than for many other metals (Benjamin and Leckie, 1981; Filipek et al, 1987; Rampe and Runnells, 1989; Schemel et al., 2000). Hence, any releases of Zn into the surface waters from more acidic sources upstream would more likely be captured further downstream than for the more reactive metals. The mining impacted tributaries and wetlands upstream of the

Blackfoot River sites are good candidates for sources of the filterable Zn and lower pH water (Moore et al., 1991; Nagorski et al., 2000).

The lack of ionic flushing at many sites is likely simply an artifact of the sampling design, which tracked early runoff events at too crude of a temporal resolution to capture short-term changes in chemistry (Whitfield and Schreier, 1981; Robertson and Roerish, 1999). Most studies on ionic pulses in the literature are based on sampling designs in which chemical data are collected at least weekly, and often daily, during the melt period (e.g. Stottlemyer and Toczydlowski, 1990; Piñol et al., 1992; Campbell et al., 1995; Harrington and Bales, 1998). In this study, however, we rarely sampled more than once a month at the sites.

### **Summary and conclusions:**

In summary, this report presents the results of up to 18 months of baseline geochemical studies in the upper Blackfoot and lower Landers Fork watersheds which show large seasonal variations in both physical and chemical characteristics of the sites. Streamflow values alone were poor predictors of the geochemistry of many solutes in the Landers Fork and upper Blackfoot River. The location on the side of the hydrograph appears to be at least as important as knowing the streamflow level for many solutes at the sites studied. Many cations exhibited counter-clockwise seasonal hysteresis, indicating that early meltwater produced a dilution effect on the surface water geochemistry, and that soil and ground water played more important roles in supplying water to the stream channel later in the season. Nonetheless, several ions also exhibited surges at the beginning of the melt period, which may be an indication of flushing from the snow itself or from displacement of soil or ground water by early meltwater.

Compared to the Landers Fork, the Blackfoot River had higher mean concentrations of dissolved organic carbon, sulfate, and most trace metals; lower mean concentrations of

inorganic carbon, As, and Ca; and similar pH, water temperature, dissolved oxygen, Ba, Li, and Mg. Within each watershed, the geochemical and physical variability among sites within a short distance of one another were substantial, with highly variable seasonal streamflow patterns, surface water - ground water interactions, and concentration - discharge relationships. These results highlight the value of designing studies with tight spatial resolutions. As found by Whitfield and Schreier (1981), who observed more variable hysteresis patterns among stations within a single river basin in British Columbia than they did at each station over the course of 4 years, it appears that site specific differences in watersheds such as the Upper Blackfoot can be so great as to have important limitations on any generalizations made from monitoring studies about seasonal geochemical variability in the watershed as a whole.

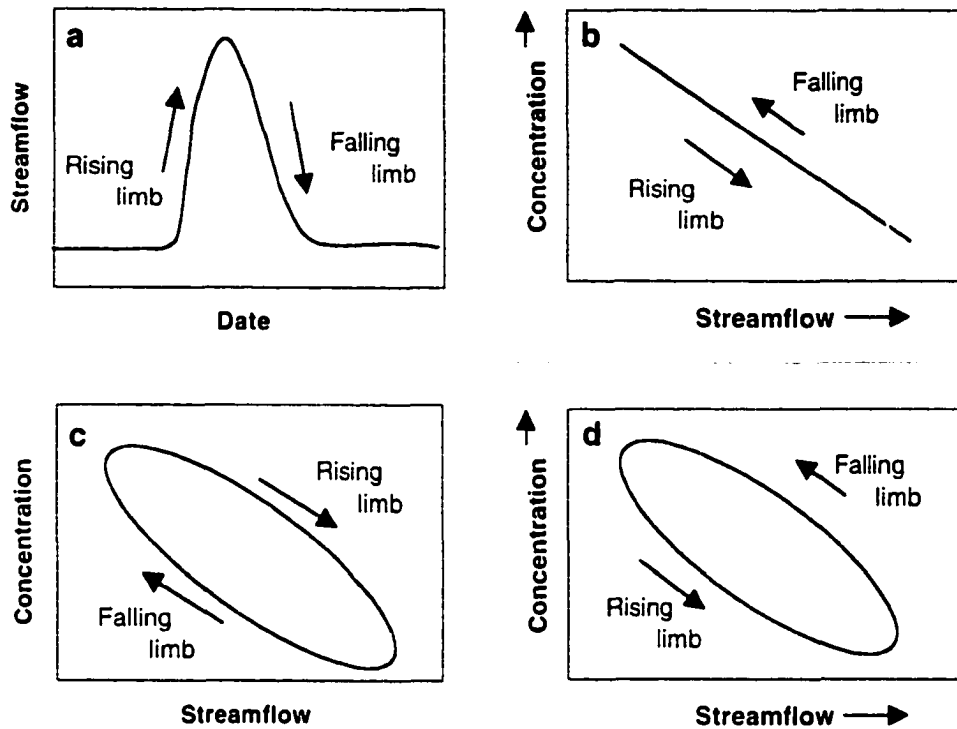
The apparent mobilization of many trace metals during high flow events in the Blackfoot River may be a result of enhanced contributions of the reactive metals from the historic mining district upstream. These results also have implications for the importance of designing sampling and monitoring studies to adequately capture wide variations in streamflow levels. In the Landers Fork, the trace metals were below detection on most sampling events, indicating that more sensitive analysis (e.g. by ICP-Mass Spectrometer) is necessary to detect any ultra-low levels at this site. This result further justifies the use of clean sampling and handling techniques. More detailed temporal studies would be helpful to better understand issues of early spring runoff flushing, storm geochemistry versus spring runoff geochemistry (especially for the trace metals), and the perplexing haphazardness of arsenic concentrations in both watersheds.

Practical Quantification Limits		Instrument precision		Spike recoveries		
Analyte	PQL	Number of replicate sets above PQL	Mean (std. dev.) of % difference btwn. duplicates	Concentration of added spike	Number of spiked samples above PQL prior to spike add'n	Mean (Std. Dev.) percent recovery
Inorg. C	1 mg/L	71	2.0 (2.7)	-	-	-
As	0.2 µg/L	63 (<0.5 µg/L) 39 (>0.5 µg/L)	7.0 (6.1) 3.6 (3.5)	1.0	44	109.8 (7.0)
Ag	1 µg/L	0	-	20	0	-
Al	5 µg/L	0	-	10	0	-
Ba	1 µg/L	55	3.8 (4.0)	200	58	98.0 (9.5)
Be	0.05 µg/L	0	-	-	0	-
Ca	0.01 mg/L	55	3.6 (4.7)	10, 20, 30	40	102.5 (10.3)
Cd	0.5 µg/L	0	-	10	0	-
Co	0.5 µg/L	0	-	-	0	-
Cr	1 µg/L	12	7.4 (4.2)	10	18	100.7 (7.6)
Cu	0.8 µg/L	13	3.3 (4.0)	3, 10, 20	15	106.9 (6.7)
Fe	5 µg/L	36	7.8 (10.0)	20, 30, 50	43	106.0 (16.3)
K	0.10 mg/L	54	4.1 (5.0)	1, 2, 2.5	58	101.3 (5.6)
Li	0.5 µg/L	55	3.4 (4.3)	5, 10	56	103 (6.0)
Mg	0.01 mg/L	55	2.9 (4.3)	5, 10	59	103.8 (6.4)
Mn	0.3 µg/L	31	3.8 (4.8)	10	23	92.0 (4.8)
Mo	1 µg/L	0	-	-	0	-
Na	0.15 mg/L	55	5.4 (6.7)	2.5, 5, 10	58	102.6 (7.5)
Ni	2 µg/L	0	-	20	0	-
Pb	6 µg/L	0	-	80	0	-
S	0.01 mg/L	55	5 (6.7)	2, 5	55	111.8 (8.5)
Si	0.02 mg/L	55	3.3 (4.4)	2, 5	55	111.9 (8.7)
Sr	2 µg/L	55	4.0 (5.2)	50, 100	54	92.5 (8.6)
Ti	2 µg/L	0	-	-	0	-
V	2 µg/L	0	-	-	0	-
Zn	0.3 µg/L	28	7.8 (13.3)	10, 20	37	104.4 (8.1)

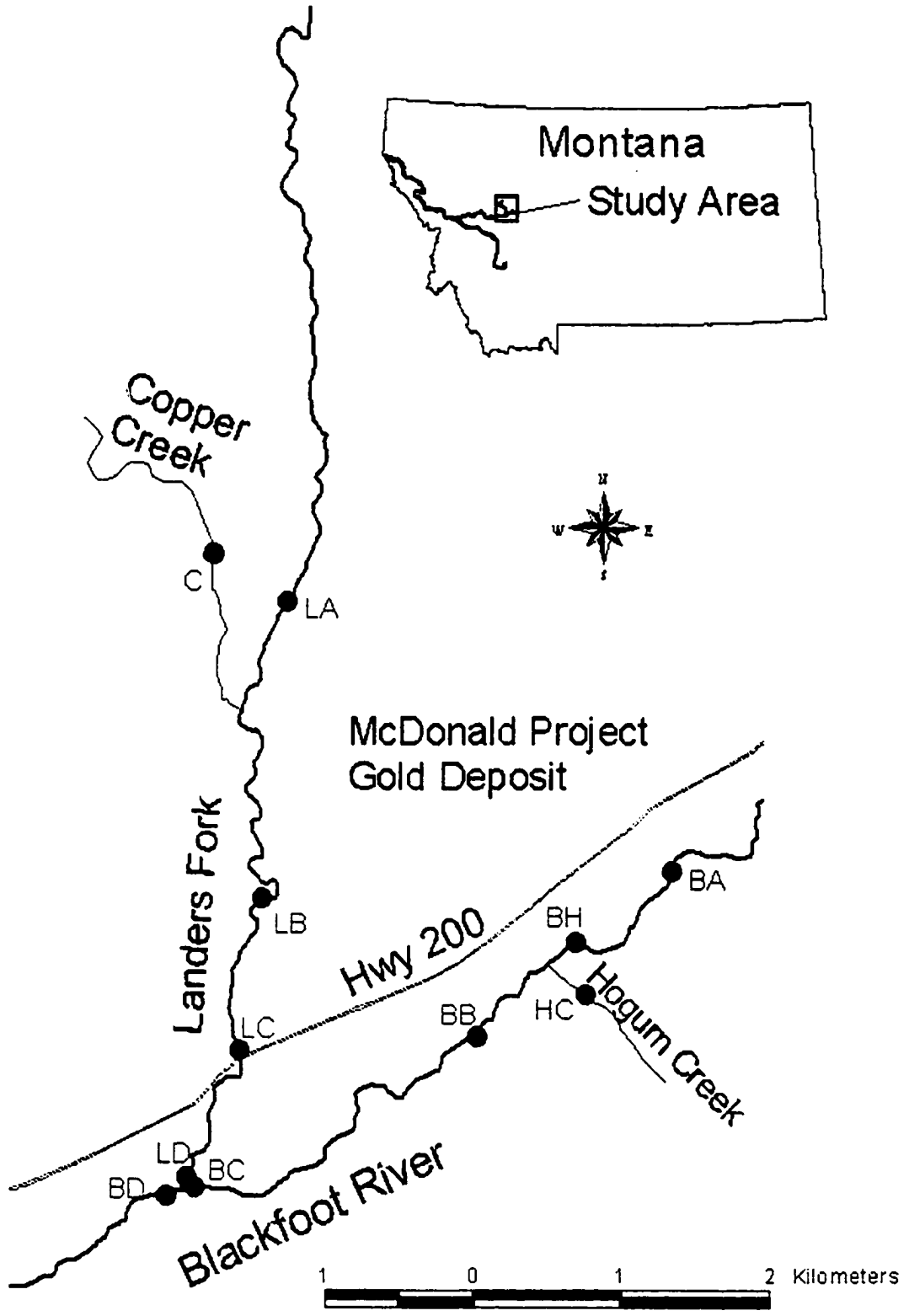
Table 1: PQLs, precision results, and spike recovery results for analysis of water samples.

	LANDERS FORK (Sites LA, LB, LC, and LD)	BLACKFOOT RIVER (Sites BA, BH, BB, BC, and BD)	p-value from two-tailed paired t-test *significant
	overall mean (std. dev.) of all sites on all dates	overall mean (std. dev.) of all sites on all dates	
pH	8.05 (0.25)	8.02 (0.18)	0.912
D.O.	10.5 (2.0)	10.5 (2.1)	0.579
Water temp	7.9 (3.2)	8.3 (5.5)	0.680
Air temp	12.3 (10.3)	13.7 (9.4)	0.775
Inorg.C	32.1 (3.5)	25.1 (3.7)	0.000*
As	0.5 (0.1)	0.35 (0.10)	0.000*
Ba	220 (42)	205 (33)	0.072
Ca	32.50 (3.00)	25.11 (3.11)	0.000*
Cr	0.6 (0.2)	0.6 (0.3)	(BPQL)
Cu	0.4 (0.0)	0.4 (0.2)	(BPQL)
Fe	4 (2)	21.4 (11.6)	0.000*
K	0.5 (0.1)	0.8 (1.0)	0.000*
Li	2.2 (0.3)	2.2 (0.4)	0.158
Mg	11.60 (1.10)	10.97 (1.28)	0.000*
Mn	0.2 (0.1)	3.0 (1.7)	0.000*
Na	1.05 (0.29)	2.31 (0.40)	0.000*
S	0.99 (0.17)	5.32 (2.91)	0.000*
Si	3.60 (0.61)	6.27 (0.68)	0.000*
Sr	19 (8)	114 (24)	0.000*
Zn	0.2 (0.2)	6.5 (7.0)	0.001*

Table 2: Results of paired t-test comparing means in the Landers Fork and Blackfoot River. Mean concentrations from all sites within the Landers Fork were paired by sampling date with the mean concentrations from all sites within the Blackfoot River. Concentrations below the PQL were assigned a value of one-half the element's PQL. Overall mean values that are below the PQL (BPQL) are italicized in the table.



**Figure 1:** a) Simplified hydrograph; b) Simple linear relationship between Q and concentration; c) Idealized hysteresis cycle for clockwise rotation; and d) counter-clockwise rotation.



**Figure 2: Site Locations**

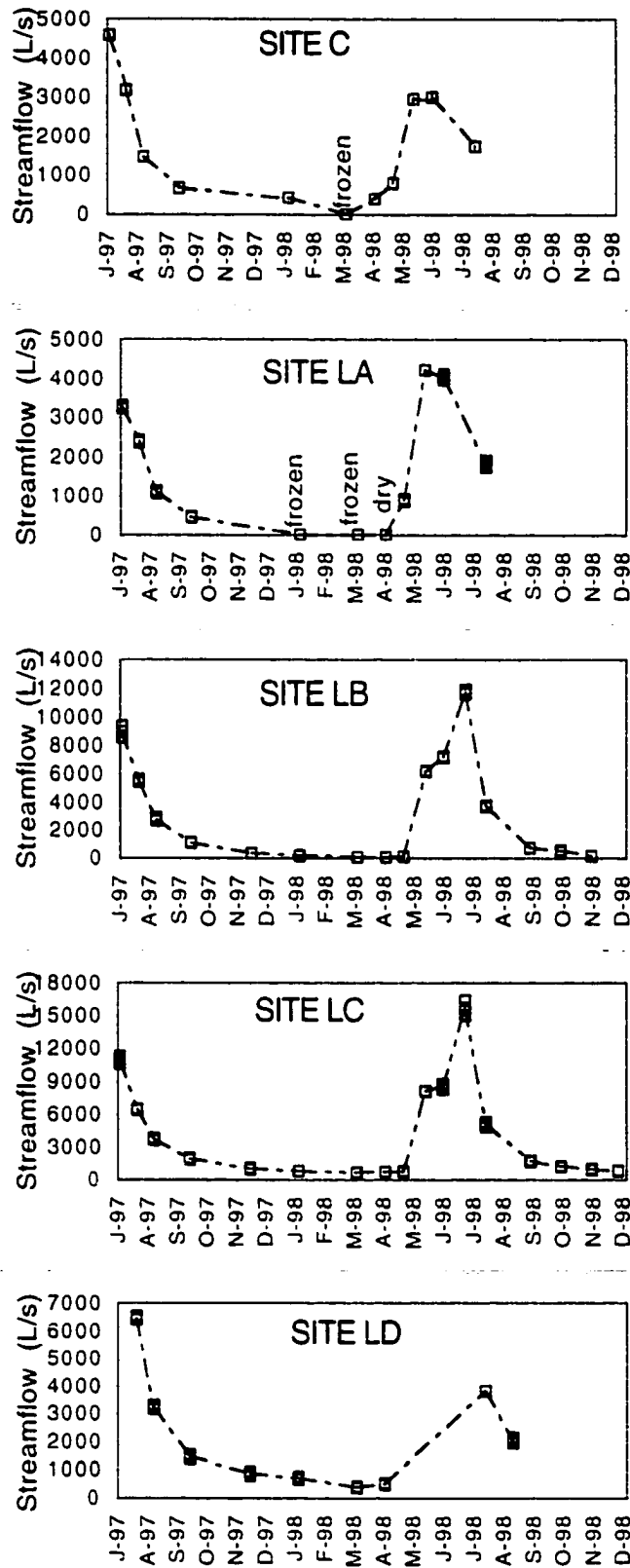
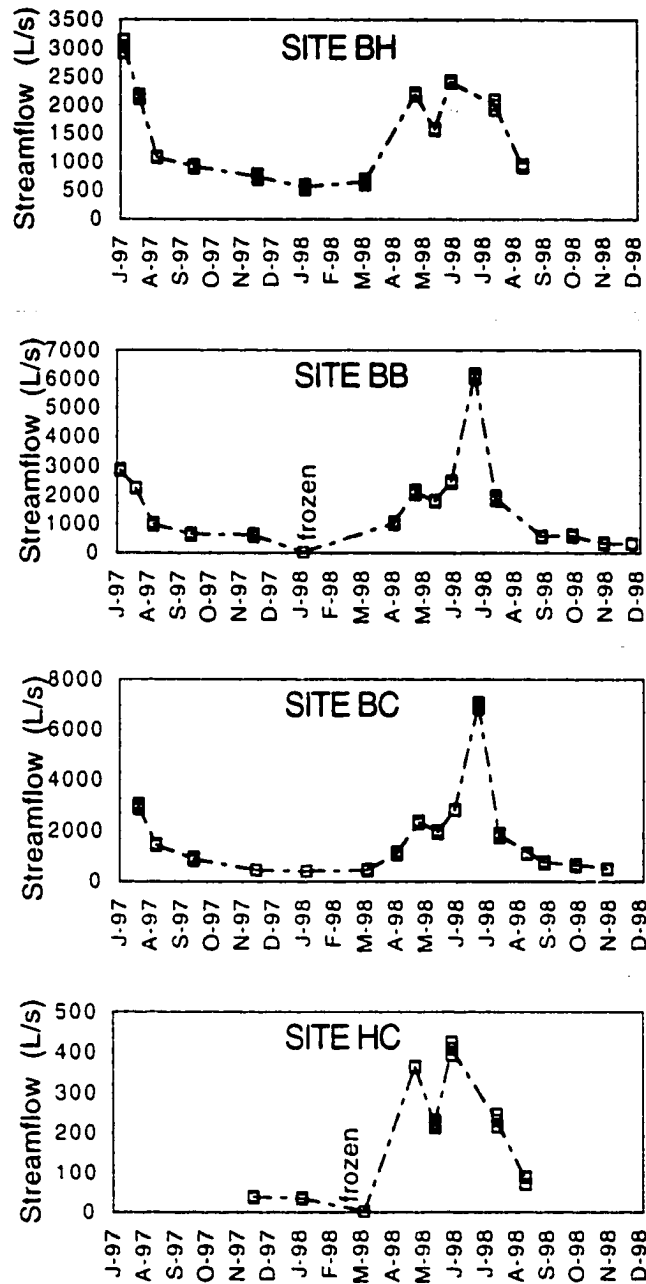
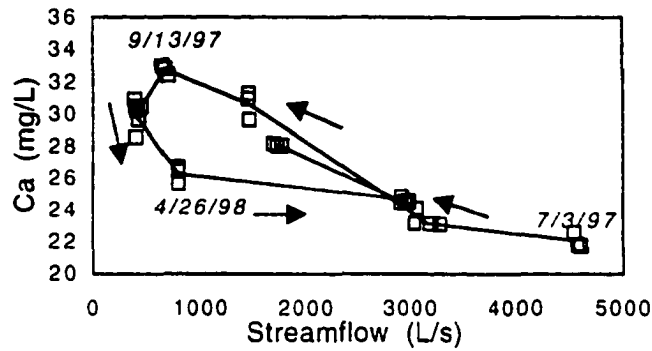


Figure 3: Steamflow at sites a)C, b)LA, c)LB, d)LC, and e)LD on the sample dates.

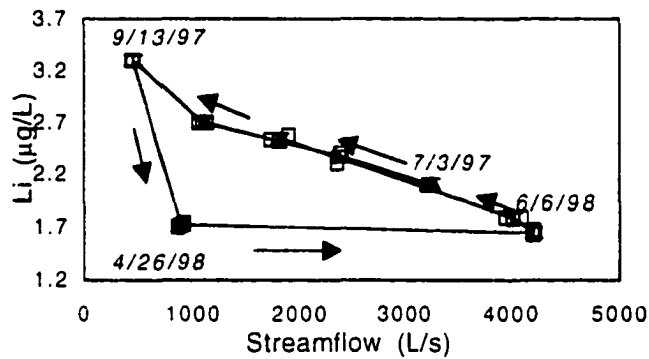




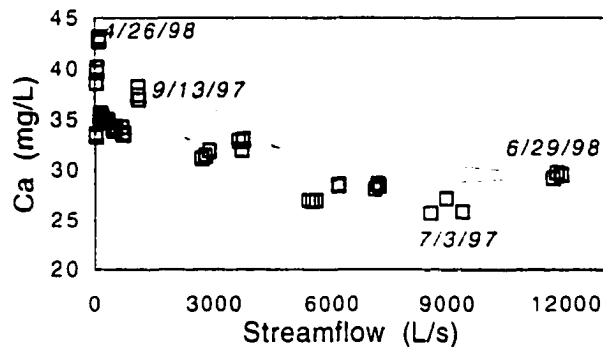
**Figure 4:** Streamflow at sites a)BH, b)BB, c)BC, and d)HC on the sample dates. Multiple squares per date indicate replicate streamflow measurements.



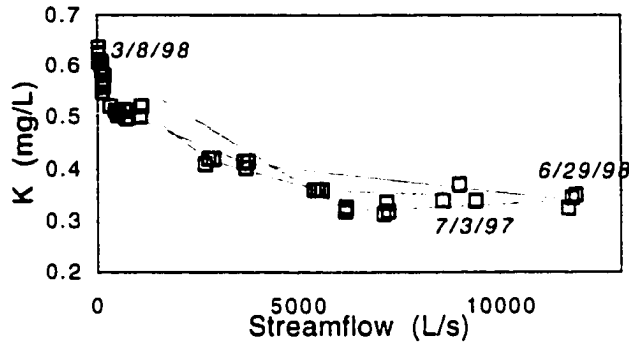
**Figure 5:** Streamflow vs. Ca concentration at Copper Creek (site C). Triplicate samples were taken on each sampling event, and each is represented by a square. The lines connect the mean concentrations at each sampling date. Similar hysteresis was seen for Ba, Li, Mg, and Sr.



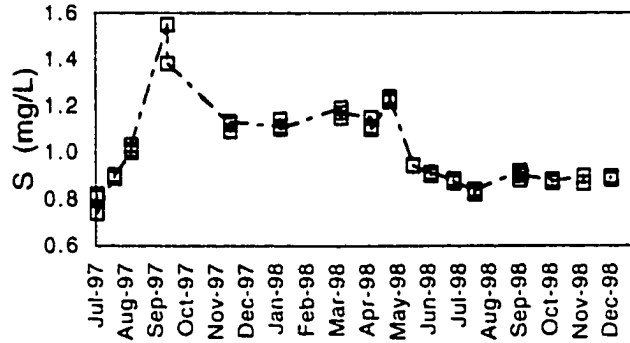
**Figure 6:** Streamflow vs. Li concentration at site LA. Similar hysteresis was seen for inorganic carbon, Ba, Ca, K, Mg, Si, and Sr.



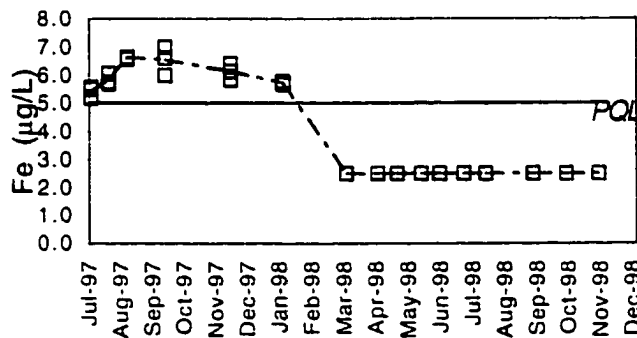
**Figure 7:** Streamflow vs. Ca concentration at site LB. Similar patterns for Ba, K, Li, Mg, Na, Si, and Sr.



**Figure 8:** Streamflow vs. K concentration at site LB.



**Figure 9:** Date vs. S concentration at site LC.



**Figure 10:** Date vs. Fe concentration at site LB.

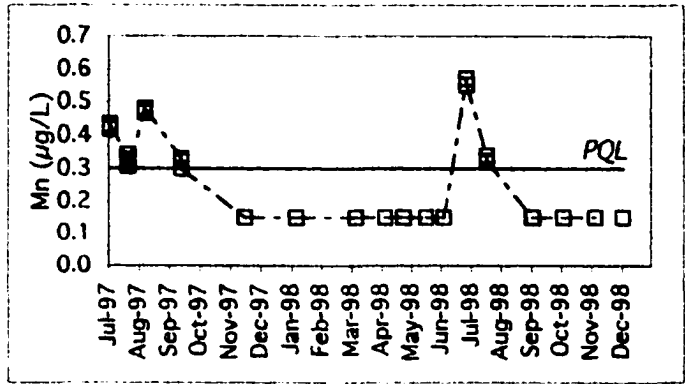


Figure 11: Date vs. Mn concentration at site LC

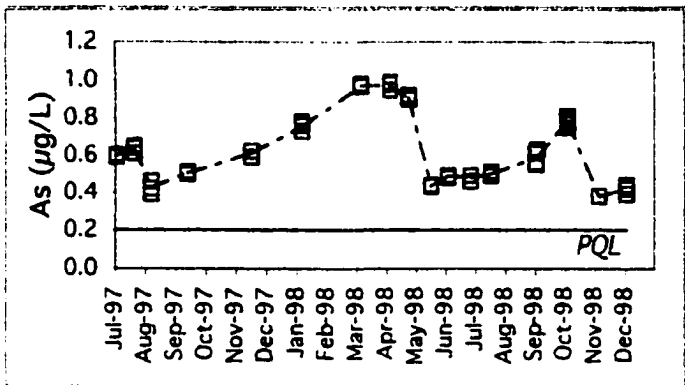


Figure 12: Date vs. As concentration at site LC

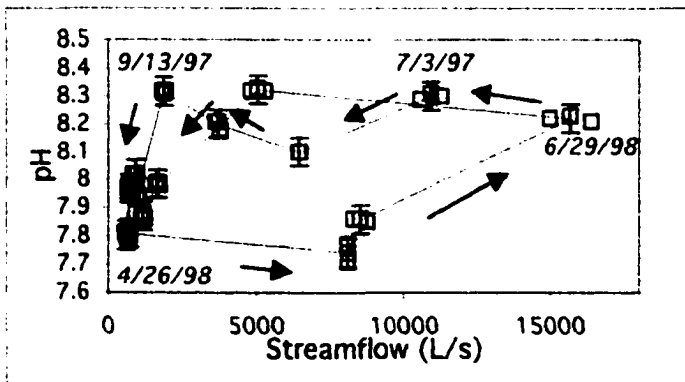


Figure 13: Streamflow vs pH at site LC

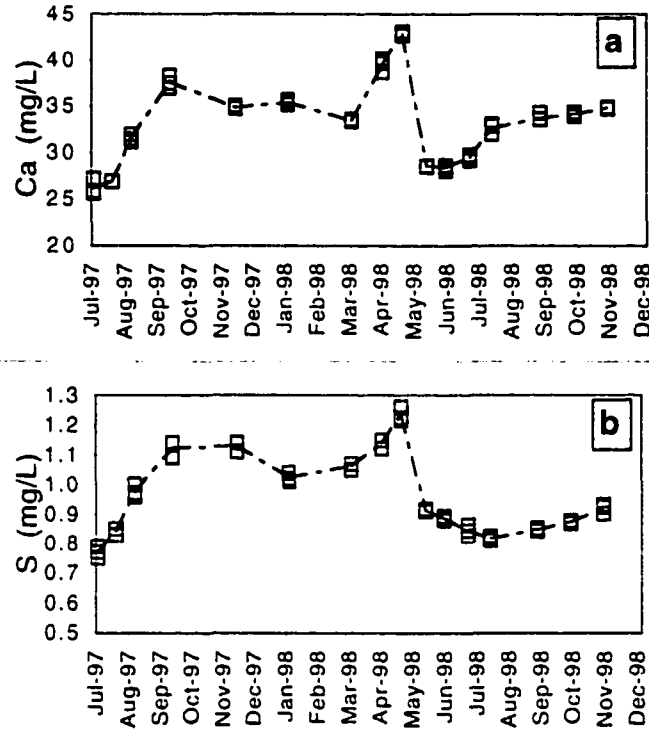


Figure 14: Date vs. (a) Ca, and (b) S at site LB. Compare timing of peaks with streamflow in Figure 3c.

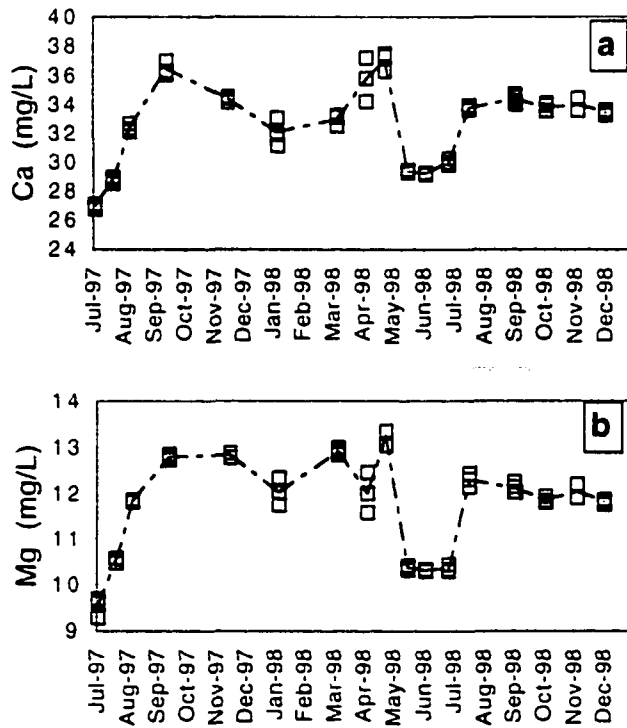
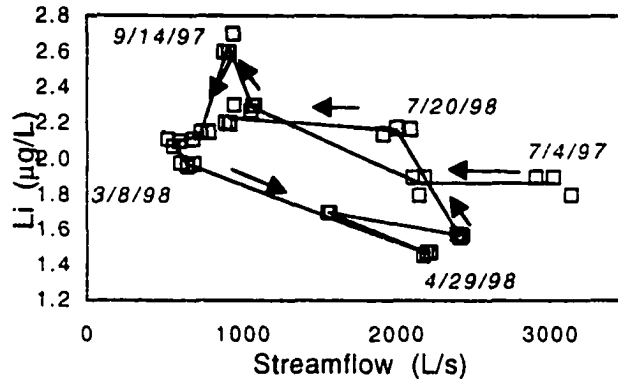
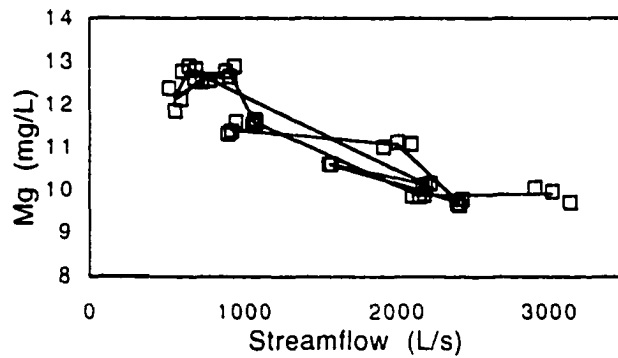


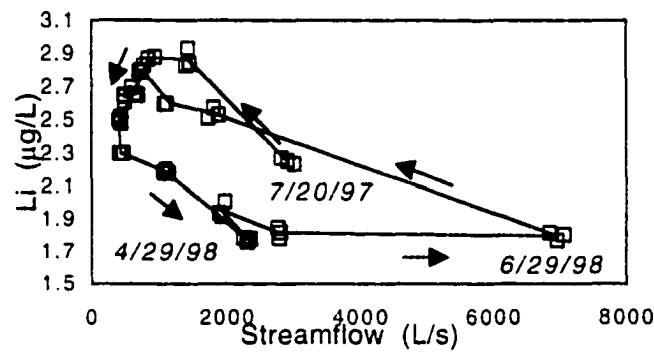
Figure 15: Date versus (a) Ca and (b) Mg at site LC. Compare timing of early runoff concentration peaks with streamflow peaks in Figure 3d.



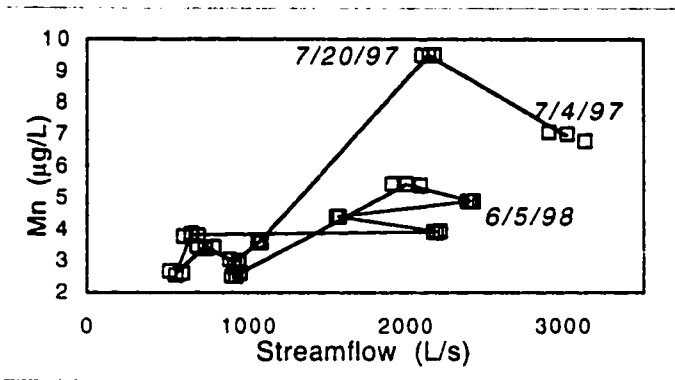
**Figure 16:** Streamflow vs. Li concentration at site BH. Similar patterns for Ba, Ca, and Si.



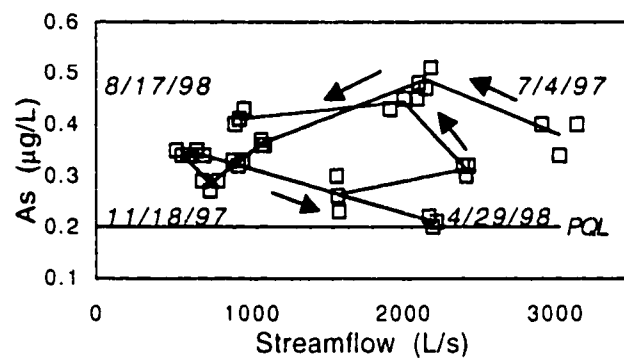
**Figure 17:** Streamflow vs. Mg concentration at site BH. Similar pattern for K.



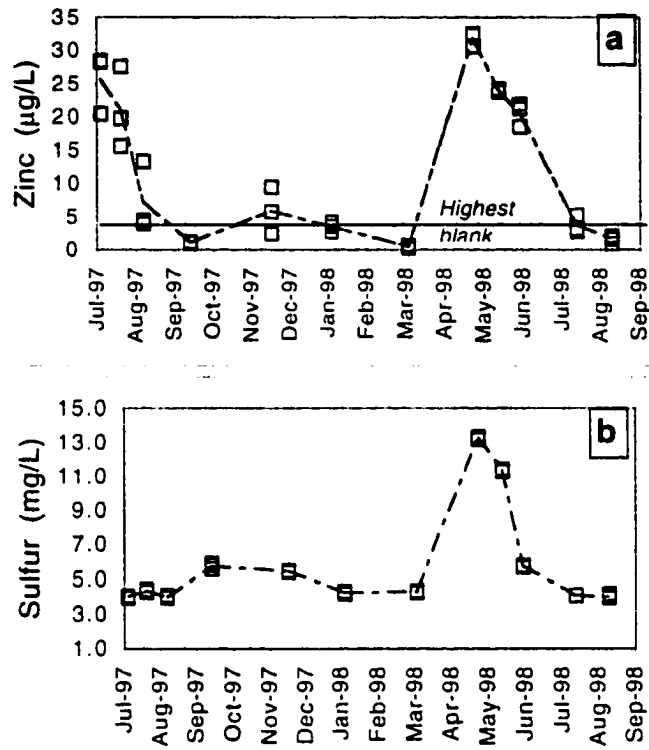
**Figure 18:** Streamflow vs. Li concentration at BC. Similar patterns for Ba, K, Si, and Sr.



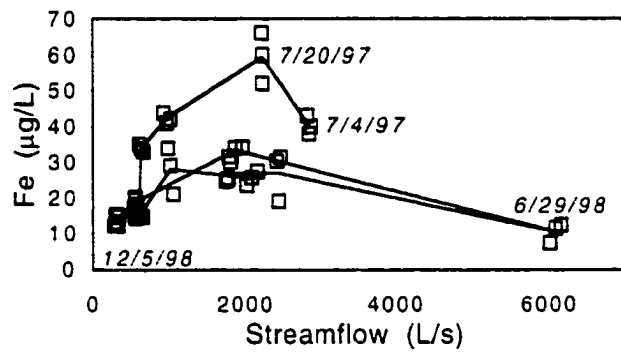
**Figure 19:** Streamflow vs. Mn concentration at site BH. Similar pattern for Fe.



**Figure 20:** Streamflow vs. As at site BH.



**Figure 21:** Date vs. (a) Zn concentration, and (b) S concentration at site BH. Compare with Figure 4a for timing of peaks.



**Figure 22:** Streamflow vs. Fe concentration at site BB.



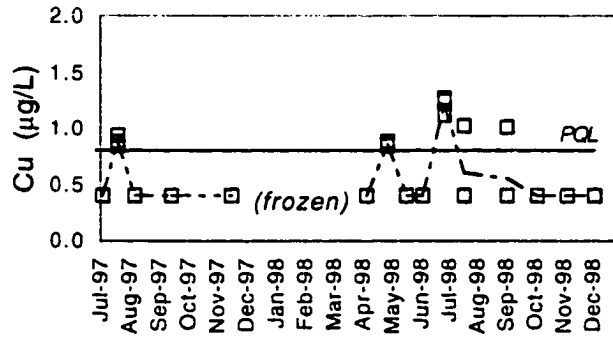


Figure 23: Date vs. Cu concentration at site BB.

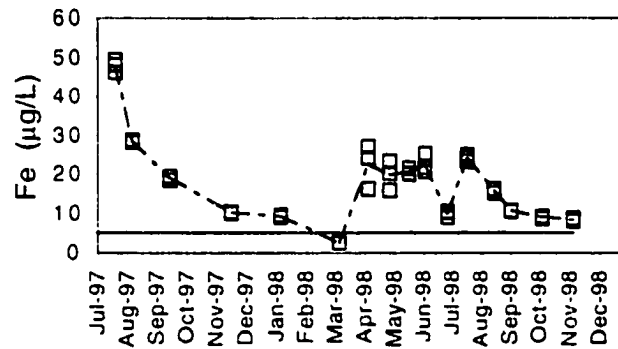


Figure 24: Date vs. Fe concentration at site BC.

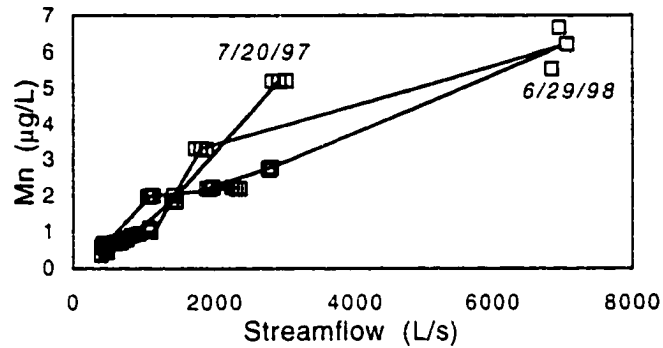
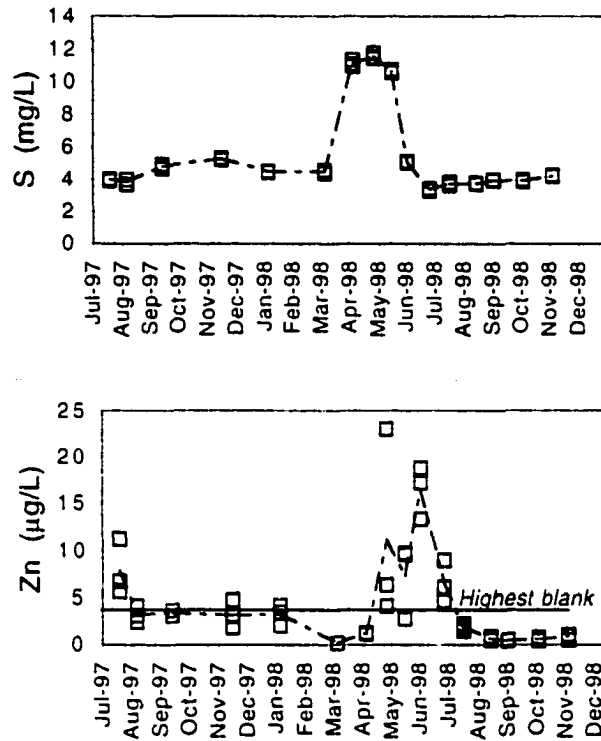
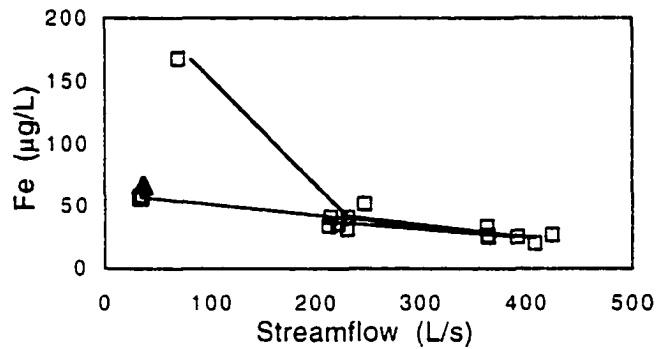


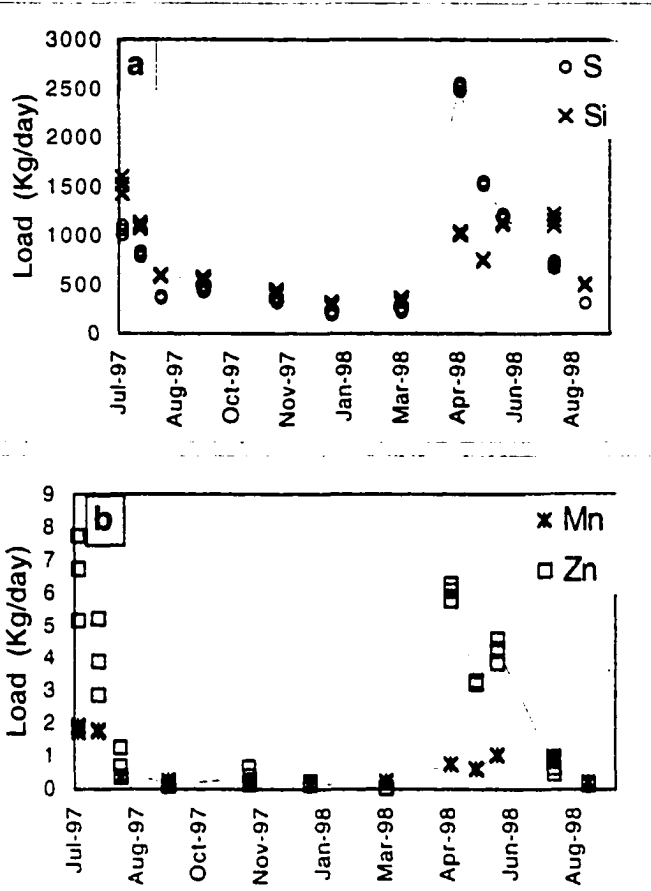
Figure 25: Streamflow vs. Mn concentrations at site BC.



**Figure 26:** Date vs. (a) S and (b) Zn concentrations at site BC. Compare with Figure 4c to note timing of peaks.



**Figure 27:** Streamflow vs. Fe concentrations at site HC.



**Figure 28:** Date vs. (a) S and Si loads and (b) Zn and Mn loads at site BH. Notice the earlier drops in the Zn and S peaks compared with the Mn and Si peaks and with the streamflow peaks in Figure 4a. Si and Mn were chosen as comparisons because their loads were similar in scale to those of S and Zn.

**All data for water samples collected in the Upper Blackfoot Basin: July 1997-December 1998**  
 All elements BPCl for: Al (<0.5 µg/L), Cu (<0.5 µg/L), Co (<0.5 µg/L), Ni (<2 µg/L), Pb (<6 µg/L), Ti (<2 µg/L), and V (<2 µg/L).  
 PQLs vary for some elements because they changed over the course of the analysis.

NAME	SAMPLE DATE	SIFHEAM	SIFHEAM	FLOW (cfs)	FLOW (L/s)	pH	DO (units)	Conductivity (µmS/cm)	Temp (Cels)	Water Air Temp (Cels)	Inorganic Carbon (mg/L)	Alk (mg/L)	Sulfate As (µg/L)	CaCO3 (mg/L)	Ba (µg/L)	Ca (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	K (µg/L)	Li (µg/L)	Mg (µg/L)	Mn (µg/L)	Na (µg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)		
																													Flow	Flow
<b>Copper Creek</b>																														
C-1	7/31/97	161	4559	8.4	9.8	0.18	10.1	20.9	19.9	NA	1.85	0.6	164	21.7	<1	<0.3	5	0.2	0.8	7.9	0.5	0.5	0.60	2.6	34	<0.2				
C-2	7/31/97	163	4616	8.4	9.8	0.18	10.1	20.9	19.9	NA	1.81	0.6	171	22.55	<1	<0.3	5	0.2	0.8	8.1	0.6	0.5	0.63	2.7	35	<0.2				
C-3	7/31/97			8.4	9.8	0.18	10.1	20.9	20.0	NA	1.85	0.6	163	21.8	<1	<0.3	5	0.2	0.8	7.9	0.8	0.6	0.61	2.6	34	0.9				
C-1	7/20/97	108	3058	8.3	9.7	0.19	9.0	14.3	23.9	NA	2.05	0.6	193	23.07	<1	0.4	6	0.3	0.9	8.6	0.5	0.6	0.69	2.9	39	<0.2				
C-2	7/20/97	117	3313	8.3	9.7	0.19	9.0	14.3	24.2	NA	2.34	0.7	191	23.15	<1	0.3	6	0.3	1.0	8.6	0.5	0.6	0.67	2.9	39	<0.2				
C-3	7/20/97	113	3200	8.3	9.7	0.19	9.0	14.3	24.0	NA	2.01	0.7	191	23.1	<1	0.3	6	0.3	0.9	8.5	0.5	0.5	0.66	2.9	39	<0.2				
C-1	8/7/97	51	1444	8.3	11.5	0.22	8.1	19.1	27.0	NA	2.34	0.5	245	29.65	<1	<0.3	7	0.3	1.3	11.2	0.4	0.4	0.70	3.2	19	1.2				
C-2	8/7/97	52	1472	8.3	11.5	0.22	8.1	19.1	27.0	NA	2.43	0.5	266	30.33	<1	<0.3	7	0.3	1.3	11.6	0.4	0.8	0.67	3.2	51	<0.2				
C-3	8/7/97			8.3	11.5	0.22	8.1	19.1	27.8	NA	2.46	0.4	256	31.28	<1	<0.3	7	0.3	1.3	11.8	0.5	0.7	0.67	3.2	52	<0.2				
C-1	9/13/97	23	651	8.3	10.5	NA	6.6	NA	29.9	NA	2.77	0.5	270	32.4	<1	<0.3	7	0.4	1.4	11.9	0.3	1.4	1.01	3.8	49	<0.2				
C-2	9/13/97	25	708	8.3	10.6	NA	6.6	NA	29.7	NA	2.88	0.5	269	32.57	<1	<0.3	7	0.4	1.5	12.2	0.3	1.2	0.98	3.8	51	<0.2				
C-3	9/13/97			8.3	10.5	NA	6.6	NA	29.5	NA	2.57	0.5	267	32.8	<1	<0.3	7	0.4	1.4	12.2	0.3	1.5	1.00	3.7	51	<0.2				
C-1	1/6/98	14	386	8.1	NA	0.24	0.1	4.7	27.3	NA	3	0.5	260	30.45	1	<0.3	6	0.4	1.4	12.2	<0.3	1.0	0.96	3.9	49	0.2				
C-2	1/6/98	16	453	8.1	NA	0.24	0.1	4.7	26.7	NA	3.1	0.5	258	30.48	1	<0.3	6	0.4	1.4	12.2	<0.3	1.0	0.94	3.9	49	0.7				
C-3	1/6/98			8.1	NA	0.24	0.1	4.7	26.7	NA	3	0.5	255	29.55	1	<0.3	6	0.4	1.4	12.0	<0.3	1.0	0.96	3.9	48	1.7				
C-1	4/7/98	13.86	393	8.26	NA	0.21	2.7	6.0	27.8	NA	NA	0.5	257	30.9	<1	<0.8	5	0.4	1.4	10.9	<0.3	1.6	1.04	4.1	45	<0.3				
C-2	4/7/98	14.58	413	8.23	NA	0.21	2.8	28.0	NA	NA	0.5	250	30.2	<1	<0.8	5	0.4	1.3	10.4	<0.3	1.5	1.01	4.0	44	1.4					
C-3	4/7/98			8.26	NA	0.21	2.8	27.8	NA	NA	0.6	237	28.6	<1	<0.8	5	0.4	1.3	10.4	<0.3	1.5	0.95	3.8	41	<0.3					
C-1	4/26/98	28.22	790	8.10	NA	0.21	6.2	15.2	26.2	NA	NA	0.5	217	26.7	<1	<0.8	5	0.3	1.1	9.6	<0.3	1.3	0.87	3.5	38	<0.3				
C-2	4/26/98	28.75	800	8.08	NA	0.21	6.2	15.2	26.2	NA	NA	0.5	214	25.7	<1	<0.8	5	0.3	1.1	9.2	<0.3	1.4	0.86	3.5	38	<0.3				
C-3	4/26/98			8.08	NA	0.21	6.2	15.2	26.2	NA	NA	0.6	213	26.5	<1	<0.8	5	0.3	1.1	9.5	<0.3	1.5	0.88	3.4	39	<0.3				
C-1	5/18/98	105.59	2990	7.97	11.1	0.18	4.8	2.5	22.0	NA	NA	0.5	193	24.6	<1	<0.8	5	0.2	0.8	8.7	<0.3	1.2	0.83	2.7	35	<0.3				
C-2	5/18/98	103.32	2928	8.00	11.3	0.18	4.8	2.5	21.9	NA	NA	0.5	194	24.6	<1	<0.8	5	0.2	0.8	8.8	<0.3	1.1	0.82	2.7	36	<0.3				
C-3	5/18/98			7.98	11.2	0.18	4.8	2.5	21.8	NA	NA	0.5	190	24.5	<1	<0.8	5	0.2	0.8	8.7	<0.3	1.1	0.81	2.6	36	<0.3				
C-1	6/6/98	103.0	2917	7.98	NA	0.18	7.3	19.6	NA	9.6	NA	0.2	188	24.4	<1	<0.8	5	0.2	0.7	8.6	<0.3	1.1	0.77	2.6	35	<0.3				
C-2	6/6/98	108.67	3078	8.00	NA	0.18	7.3	19.6	NA	9.0	NA	0.6	185	24.0	<1	<0.8	5	0.2	0.7	8.5	<0.3	1.0	0.75	2.5	34	<0.3				
C-3	6/6/98			7.99	NA	0.18	7.3	19.6	NA	9.0	NA	0.5	185	24.4	<1	<0.8	5	0.2	0.7	8.6	<0.3	1.0	0.77	2.6	36	<0.3				
C-1	7/20/98	62.75	1777	8.39	9.3	0.21	7.9	20.3	NA	11.0	NA	0.5	234	28.1	<1	<0.8	5	0.3	1.1	10.3	<0.3	1.4	0.70	3.4	50	<0.3				
C-2	7/20/98	60.07	1701	8.40	9.6	0.21	7.9	20.2	NA	10.6	NA	0.5	232	28.2	<1	<0.8	5	0.3	1.1	10.4	<0.3	1.4	0.70	3.4	50	<0.3				
C-3	7/20/98			8.40		0.21	8.0	20.2	NA	10.9	NA	0.6	230	28.0	<1	<0.8	5	0.3	1.0	10.5	<0.3	1.5	0.67	3.3	49	<0.3				
<b>Landers Fork site LA</b>																														
LA-1	7/31/97	114	3228	8.5	9.2	0.22	11.1	11.0	24.2	NA	2.47	0.6	131	27.33	<1	<0.3	6	0.4	2.1	10.0	0.3	0.6	0.87	2.7	36	0.5				
LA-2	7/31/97	116	3285	8.5	9.2	0.22	11.1	11.0	24.3	NA	2.49	0.6	131	27.69	<1	<0.3	6	0.4	2.1	10.1	0.3	0.6	0.86	2.7	36	<0.2				
LA-3	7/31/97			8.5	9.2	0.22	11.1	11.0	24.3	NA	2.46	0.6	127	26.68	<1	<0.3	5	0.4	2.1	9.8	0.3	0.5	0.83	2.6	35	0.4				
LA-1	7/20/97	84	2370	8.3	8.8	0.22	12.8	16.7	28.8	NA	2.84	0.4	144	27.79	<1	<0.3	6	0.4	2.3	10.5	0.4	0.7	0.93	2.7	39	<0.2				
LA-2	7/20/97	85	2407	8.3	8.8	0.22	12.8	16.7	28.8	NA	2.88	0.4	143	27.94	<1	<0.3	6	0.4	2.4	10.5	0.4	0.6	0.90	2.7	39	<0.2				
LA-3	7/20/97			8.3	8.8	0.22	12.8	16.7	28.9	NA	2.74	0.6	142	27.65	<1	<0.3	6	0.4	2.4	10.5	0.4	0.8	0.92	2.7	39	<0.2				
LA-1	8/7/97	38	1076	8.6	10.1	0.26	13.5	23.8	31.8	NA	3.11	0.4	161	31.75	<1	<0.3	6	0.4	2.7	11.9	<0.3	0.9	1.11	3.0	45	<0.2				
LA-2	8/7/97	40	1133	8.6	10.1	0.26	13.5	23.8	31.8	NA	3.1	0.4	162	32.42	<1	<0.3	6	0.4	2.7	12.1	<0.3	0.9	1.11	3.1	46	<0.2				
LA-3	8/7/97			8.6	10.1	0.26	13.5	23.8	31.7	NA	3.23	0.4	166	32.54	<1	0.7	7	0.4	2.7	12.2	<0.3	0.8	1.08	3.0	46	0.2				

SAMPLE NAME	SAMPLE DATE	SITE#	AI FLOW (cfs)	SIRE#	AI FLOW (l/s)	pH	DO (units)	Conductivity (µmS/cm)	Water Temp (Celsius)	Air Temp (Celsius)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO <sub>3</sub> )	Sulfate	Ba	Ct	Cr	Cu	Fe	K	Li	Mg	Mn	Ta	S	Si	Sr	Zn		
LA-1	9/13/97	16	453	82	9.3	NA	115	NA	35.1	NA	3.43	0.3	194	39.77	<1	<0.3	7	0.5	3.3	14.4	<0.3	1.2	1.32	3.3	3.3	55	<0.2		
LA-2	9/13/97	16	453	82	9.4	NA	115	NA	34.6	NA	3.5	0.4	192	39.54	<1	<0.3	7	0.5	3.3	14.4	<0.3	1.6	1.35	3.3	3.3	54	<0.2		
LA-3	9/13/97	16	453	82	9.4	NA	115	NA	35.2	NA	3.4	0.3	192	39.75	<1	<0.3	7	0.5	3.3	14.4	<0.3	1.4	1.31	3.3	3.3	55	<0.2		
LA-1	4/26/98	32.6H	925	8.14	15.5	0.21	6.6	17.4	26.4	NA	NA	0.4	129	27.2	<1	<0.8	5	0.4	1.7	9.2	0.6	1.1	0.90	2.3	3.5	<0.3			
LA-2	4/26/98	30.51	864	8.16	16.5	0.20	6.6	16.5	26.8	NA	NA	0.4	126	26.7	<1	<0.8	5	0.4	1.7	9.1	0.6	1.1	0.86	2.2	3.5	<0.3			
LA-3	4/26/98	8.14								NA	NA	0.4	126	26.7	<1	<0.8	5	0.4	1.7	9.2	0.7	1.1	0.92	2.3	3.5	<0.3			
LA-1	5/18/98	149.14	4224	8.04	10.2	0.20	7.0	5.0	25.7	NA	NA	0.3	112	27.5	<1	<0.8	5	0.3	1.7	9.8	<0.3	1.0	0.90	2.2	3.1	<0.3			
LA-2	5/18/98	148.71	4211	8.04	10.2	0.21			24.6	NA	NA	0.4	112	27.3	<1	<0.8	5	0.3	1.6	9.7	<0.3	1.0	0.90	2.2	3.1	<0.3			
LA-3	5/18/98			8.05	10.1	0.21			25.4	NA	NA	0.4	112	27.2	<1	<0.8	5	0.3	1.6	9.7	<0.3	1.0	0.90	2.2	3.1	<0.3			
LA-1	6/6/98	144.8H	4103	8.08	NA	0.21	8.9	20.8	NA	108	NA	0.4	120	29.2	<1	<0.8	5	0.3	1.8	10.3	<0.3	1.2	0.93	2.3	3.4	<0.3			
LA-2	6/6/98	139.77	3958	8.09	NA	0.21			NA	108	NA	0.4	119	28.9	<1	<0.8	5	0.3	1.8	10.3	<0.3	1.1	0.92	2.3	3.3	<0.3			
LA-3	6/6/98			8.09	NA	0.21			NA	106	NA	0.4	120	29.0	<1	<0.8	5	0.3	1.8	10.3	<0.3	1.0	0.92	2.3	3.3	<0.3			
LA-1	7/20/98	64.49	1826	8.52	8.5	0.25	11.9	22.8	NA	124	NA	0.4	150	34.1	1	<0.8	5	0.4	2.5	12.7	<0.3	1.5	0.86	3.0	4.8	<0.3			
LA-2	7/20/98			8.52	8.5	0.25	11.9	22.7	NA	127	NA	0.4	152	34.7	<1	<0.8	5	0.4	2.6	12.9	<0.3	1.5	0.86	3.0	4.9	<0.3			
LA-3	7/20/98			8.51	8.5	0.25	11.6	22.7	NA	129	NA	0.4	153	34.7	<1	<0.8	5	0.4	2.6	12.9	<0.3	1.5	0.86	3.1	4.9	<0.3			
Lenders Path site - LB																													
LB-1	7/3/97	303	8580	8.4	9.20	0.21	NA	NA	23.4	NA	2.26	0.6	160	25.67	<1	<0.3	6	0.3	1.5	9.3	0.4	0.6	0.75	2.8	3.7	<0.2			
LB-2	7/3/97	332	9401	8.4	9.20	0.21	NA	NA	23.7	NA	2.28	0.5	160	25.81	<1	<0.3	5	0.3	1.5	9.3	0.4	0.7	0.77	2.8	3.7	<0.2			
LB-3	7/3/97			8.4	9.2	0.21	NA	NA	24.2	NA	2.37	0.6	170	27.13	<1	<0.3	6	0.4	1.6	9.7	0.4	0.5	0.79	2.9	3.8	0.5			
LB-1	7/20/97	191	5409	7.9	9.0	0.22	10.0	12.9	28.4	NA	2.59	0.6	181	26.92	<1	<0.3	6	0.4	1.7	10.0	0.4	0.7	0.83	3.0	4.1	<0.2			
LB-2	7/20/97	196	5607	7.9	9.0	0.22	10.0	12.9	28.4	NA	2.5	0.6	184	26.92	<1	<0.3	6	0.4	1.7	10.0	0.4	0.7	0.85	3.0	4.1	<0.2			
LB-3	7/20/97			7.9	9.0	0.22	10.0	12.9	28.4	NA	2.77	0.6	183	26.9	<1	<0.3	6	0.4	1.7	10.0	0.4	0.8	0.85	3.0	4.1	<0.2			
LB-1	8/7/97	95	2690	8.2	10.3	0.24	11.5	27.5	30.9	NA	2.83	0.4	216	31.19	<1	<0.3	7	0.4	2.1	11.5	0.4	0.8	0.97	3.3	4.8	<0.2			
LB-2	8/7/97	102	2888	8.2	10.3	0.24	11.5	27.5	31.2	NA	2.86	0.4	216	31.91	<1	<0.3	7	0.4	2.1	11.7	0.4	0.8	0.96	3.4	4.7	0.3			
LB-3	8/7/97			8.2	10.3	0.24	11.5	27.5	31.3	NA	2.82	0.4	219	31.44	<1	<0.3	7	0.4	2.1	11.6	0.4	0.9	1.00	3.4	4.8	1.6			
LB-1	9/13/97	38	1076	8.3	9.4	NA	10.3	NA	34.3	NA	2.85	0.4	258	37.44	<1	<0.3	7	0.5	2.5	13.1	0.3	1.6	1.14	3.8	5.3	<0.2			
LB-2	9/13/97	39	1104	8.3	9.4	NA	10.3	NA	34.1	NA	2.96	0.3	266	36.94	<1	<0.3	6	0.5	2.5	13.1	0.3	1.6	1.14	3.8	5.5	<0.2			
LB-3	9/13/97			8.3	9.4	NA	10.3	NA	34.3	NA	2.93	0.4	259	38.22	<1	<0.3	7	0.5	2.5	13.3	0.3	1.3	1.09	3.8	5.4	<0.2			
LB-1	11/16/97	11	311	7.6	NA	0.27	2.1	7.5	35.9	NA	3.06	0.2	249	35	1	<0.3	6	0.5	2.2	13.1	<0.3	1.1	1.14	3.6	5.3	0.5			
LB-2	11/16/97	12	340	7.7	NA	0.27	2.1	7.5	36.9	NA	2.99	0.3	248	34.8	1	<0.3	6	0.5	2.2	13.0	<0.3	1.1	1.14	3.6	5.3	1.0			
LB-3	11/16/97			7.6	NA	0.27	2.1	7.5	35.6	NA	2.96	0.3	247	34.72	1	<0.3	6	0.5	2.2	13.0	<0.3	0.9	1.11	3.6	5.3	<0.2			
LB-1	1/6/98	5	142	7.6	15.0	0.27	3.1	0.2	34.2	NA	3.1	0.3	245	35.3	1	<0.3	6	0.6	2.3	13.1	<0.3	1.0	1.01	3.6	5.3	1.0			
LB-2	1/6/98	6	170	7.6		0.27	3.1	0.2	35.0	NA	3.2	0.3	239	35.65	1	<0.3	6	0.6	2.3	13.1	<0.3	1.0	1.02	3.6	5.2	1.7			
LB-3	1/6/98			7.6		0.28	3.1	0.2	33.8	NA	3.2	0.3	240	35.14	1	<0.3	6	0.6	2.3	13.0	<0.3	1.0	1.04	3.6	5.2	2.4			
LB-1	3/8/98	1	287.67	NA	NA		4.0	-1.3	33.68	NA	NA	0.3	234	33.56	<1	<0.3	5	0.6	2.4	12.9	<0.3	1.8	1.05	3.7	5.1	<0.2			
LB-2	3/8/98	2	57.764	NA	NA		3.9	-1.3	34.67	NA	NA	0.3	232	33.4	<1	<0.3	5	0.6	2.3	12.8	<0.3	1.7	1.07	3.7	5.1	<0.2			
LB-3	3/8/98	15	42.765	NA	NA		4.0	-1.2	34.47	NA	NA	0.3	234	33.3	<1	<0.3	5	0.6	2.4	12.8	<0.3	1.6	1.07	3.7	5.1	<0.2			
LB-1	4/7/98	1.18	33	7.78	11.0	0.27	5.3	7.4	34.4	NA	NA	0.3	238	38.6	<1	<0.8	5	0.6	2.6	13.1	<0.3	1.5	1.12	3.7	5.0	<0.3			
LB-2	4/7/98	1.69	48	7.79	11.0	0.26	5.4		35.1	NA	NA	0.3	245	39.7	<1	<0.8	5	0.6	2.6	13.2	<0.3	1.5	1.15	3.8	5.1	0.4			
LB-3	4/7/98			7.78	11.0	0.27	5.3		34.9	NA	NA	0.3	245	40.1	<1	<0.8	5	0.6	2.6	13.3	<0.3	1.6	1.15	3.7	5.1	2.1			
LB-1	4/26/98	3.63	103	7.72	15.0	0.28	7.8	16.9	36.4	NA	NA	0.3	264	42.9	<1	<0.8	5	0.6	2.7	14.2	<0.3	1.6	1.23	3.9	5.6	<0.3			
LB-2	4/26/98	3.6	102	7.70	15.5	0.28			36.2	NA	NA	0.3	263	42.7	<1	<0.8	5	0.6	2.6	14.1	<0.3	1.6	1.22	3.8	5.5	<0.3			
LB-3	4/26/98			7.72		0.28			36.5	NA	NA	0.2	269	43.1	<1	<0.8	5	0.6	2.6	13.8	<0.3	1.5	1.26	3.9	5.5	<0.3			

SAMPLE NAME	SAMPLE DATE	STREAM FLOW (cfs)	STREAM FLOW (l/s)	pH	DO (mg/L)	Conductivity (µmS/cm)	Water Temp (C)	Air Temp (C)	Inorganic Carbon (mg/L)	Total Alk (µmol CaCO <sub>3</sub> )	Sulfate (µg/L)	Ba (µg/L)	Ca (mg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	K (µg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Na (mg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)		
LB-1	5/19/98	218	6174	7.72	12.0	0.21	2.5	1.5	24.9	NA	0.4	151	28.4	1	<0.8	<5	0.3	1.4	10.1	<0.3	<0.3	0.91	2.5	36	<0.3		
LB-2	5/19/98	219	6202	7.75	12.1	0.21	2.5	1.5	25.1	NA	0.4	153	28.5	<1	<0.8	<5	0.3	1.5	10.0	<0.3	<0.3	0.91	2.5	36	<0.3		
LB-3	5/19/98			7.72	11.9	0.21			25.5	NA	0.4	151	28.5	<1	<0.8	<5	0.3	1.5	10.0	<0.3	<0.3	0.92	2.5	36	<0.3		
LB-1	6/6/98	252	7137	7.99	13.0	0.21	6.3	15.1	NA	112	0.4	153	28.1	<1	<0.8	<5	0.3	1.5	9.9	<0.3	<0.3	0.89	2.5	36	<0.3		
LB-2	6/6/98	256	7250	8.00	13.2	0.21			NA	110	0.4	152	28.4	<1	<0.8	<5	0.3	1.6	10.0	<0.3	<0.3	0.88	2.5	36	<0.3		
LB-3	6/6/98			7.98	13.2	0.21			NA	116	0.4	155	28.6	<1	<0.8	<5	0.3	1.6	10.0	<0.3	<0.3	0.89	2.6	36	<0.3		
LB-1	6/29/98	413	11696	7.96	12.1	0.20	7.9	17.0	NA	107	0.4	148	29.2	<1	<0.8	<5	0.3	1.5	10.2	0.5	1.3	0.83	2.7	36	<0.3		
LB-2	6/29/98	420	11894	7.98	11.9	0.20	8.0	17.0	NA	110	0.4	150	29.5	<1	<0.8	<5	0.4	1.5	10.2	0.4	1.6	0.86	2.9	37	<0.3		
LB-3	6/29/98			7.98	12.0	0.20	8.1	17.1	NA	106	0.4	151	29.7	<1	<0.8	<5	0.3	1.6	10.3	0.5	1.2	0.84	2.7	37	<0.3		
LB-1	7/20/98	129	3653	8.32	8.1	0.25	12.9	23.9	NA	121	0.4	212	32.9	<1	<0.8	<5	0.4	2.1	12.1	<0.3	<0.3	1.07	3.4	51	<0.3		
LB-2	7/20/98	133	3767	8.35	8.2	0.25	12.9	24.0	NA	124	0.4	211	33.0	<1	<0.8	<5	0.4	2.0	12.0	<0.3	<0.3	1.05	3.4	51	<0.3		
LB-3	7/20/98			8.35	8.2	0.25	13.0	24.0	NA	124	0.4	213	32.0	<1	<0.8	<5	0.4	1.9	11.8	<0.3	<0.3	1.01	3.4	50	<0.3		
LB-1	9/4/98	25.91	734	7.86	9.1	0.26	11.5	23.9	33.7	125	0.4	239	33.6	<1	<0.8	<5	0.5	2.2	11.8	<0.3	<0.3	0.84	4.0	53	<0.3		
LB-2	9/4/98	24.41	691	7.88	9.0	0.27	11.6	23.8	33.9	128	0.4	241	34.2	<1	<0.8	<5	0.5	2.3	12.0	<0.3	<0.3	0.85	4.0	54	<0.3		
LB-3	9/4/98			7.86	9.0	0.27	11.5	23.7	34.1	128	0.4	241	33.6	<1	<0.8	<5	0.5	2.2	11.9	<0.3	<0.3	0.85	4.0	54	<0.3		
LB-1	10/6/98	17.44	494	7.66	8.6	0.26	9.1	12.5	34.2	135	0.5	234	33.9	<1	<0.8	<5	0.5	2.4	12.0	<0.3	<0.3	0.87	3.9	53	0.5		
LB-2	10/6/98			7.68	8.6	0.26	9.0		34.2	140	0.5	236	34.3	<1	<0.8	<5	0.5	2.3	12.1	<0.3	<0.3	0.87	3.9	54	<0.3		
LB-3	10/6/98			7.67	8.7	0.26			34.5	133	0.5	236	34.0	<1	<0.8	<5	0.5	2.3	12.0	<0.3	<0.3	0.88	3.9	53	<0.3		
LB-1	11/7/98	4.58	130	7.92	11.1	0.27	4.0	5.1	NA	132	0.2	240	34.9	<1	<0.8	<5	0.5	2.4	12.4	<0.3	<0.3	0.90	4.0	55	<0.3		
LB-2	11/7/98			7.91	11.1	0.27	4.0		NA	133	0.2	247	34.8	<1	<0.8	<5	0.6	2.5	12.5	<0.3	<0.3	0.92	4.1	56	<0.3		
LB-3	11/7/98			7.91	11.0	0.27			NA	133	0.2	248	34.9	<1	<0.8	<5	0.6	2.4	12.5	<0.3	<0.3	0.93	4.2	57	<0.3		
<b>LB Series</b>																											
LBSEEP	1/6/98			NA	NA	NA	NA	NA	34.8	NA	3.34	0.4	214	34.6	1	<0.3	6	0.4	2.0	13.0	<0.3	0.9	1.07	3.4	50	1.8	
LBSEEP1	4/7/98			7.44	6.7	0.26	5.0	8.0	35.8	NA	0.3	215	33.4	<1	<0.8	<5	0.5	2.3	11.6	<0.3	<0.3	1.8	103	3.4	43	<0.3	
LBSEEP2	4/7/98			7.47	6.9	0.27	5.1	8.1	35.8	NA	0.3	226	25.2	<1	<0.8	<5	0.4	1.7	6.5	<0.3	<0.3	1.0	107	3.5	34	1.4	
LBSEEP3	4/7/98			7.45	7.2	0.27	5.0	8.0	35.6	NA	0.3	240	38.0	<1	<0.8	<5	0.6	2.7	12.9	<0.3	<0.3	1.7	115	3.8	50	1.1	
LBSEEP1	4/26/98			7.69	14.0	0.28	4.6	NA	36.4	NA	0.3	253	41.6	<1	<0.8	<5	0.7	2.8	13.9	<0.3	<0.3	1.8	121	4.0	55	<0.3	
LBSEEP2	4/26/98			7.67		0.28			35.7	NA	0.3	251	41.0	<1	<0.8	<5	0.6	2.7	13.8	<0.3	<0.3	1.6	110	3.9	53	<0.3	
LBSEEP3	4/26/98			7.67		0.28			36.1	NA	0.3	252	40.8	<1	<0.8	<5	0.6	2.8	13.8	<0.3	<0.3	1.7	118	4.0	53	<0.3	
<b>Lenders Fork Site LC</b>																											
LC-1	7/3/97	398	11270	8.3	9.8	0.21	6.9	NA	23.9	NA	2.28	0.6	173	27.01	<1	<0.3	6	0.37	1.7	9.6	0.4	0.6	0.82	3.0	39	0.8	
LC-2	7/3/97	373	10562	8.3	9.8	0.21	6.9	NA	23.9	NA	2.31	0.6	173	27.05	<1	<0.3	6	0.36	1.8	9.7	0.4	0.6	0.81	3.0	39	0.5	
LC-3	7/3/97			8.3	9.8	0.21	6.9	NA	24.0	NA	2.3	0.6	168	26.76	<1	<0.3	6	0.34	1.6	9.3	0.4	0.5	0.74	2.8	38	0.2	
LC-1	7/21/97	227	6428	8.1	NA	0.23	7.4	11.5	30.0	NA	2.83	0.6	198	28.52	<1	<0.3	7	0.4	1.9	10.5	0.3	0.8	0.90	3.2	44	1.0	
LC-2	7/21/97	225	6371	8.1	NA	0.23	7.4	11.5	30.1	NA	2.73	0.7	200	28.96	<1	<0.3	7	0.4	1.9	10.6	0.3	0.7	0.89	3.2	44	<0.2	
LC-3	7/21/97	227	6428	8.1	NA	0.23	7.4	11.5	30.0	NA	2.78	0.6	200	28.76	<1	<0.3	6	0.4	1.9	10.6	0.3	0.8	0.90	3.2	44	<0.2	
LC-1	8/7/97	128	3675	8.2	10.1	0.25	12.3	24.4	32.0	NA	3.06	0.4	236	32.29	<1	<0.3	7	0.5	2.2	11.9	0.5	0.8	1.00	3.6	50	<0.2	
LC-2	8/7/97	133	3766	8.2	10.1	0.25	12.3	24.4	31.9	NA	2.93	0.4	235	32.14	<1	<0.3	7	0.5	2.3	11.8	0.5	0.8	1.01	3.6	50	1.1	
LC-3	8/7/97			8.2	10.1	0.25	12.3	24.4	31.7	NA	2.98	0.4	240	32.67	<1	<0.3	8	0.5	2.3	11.8	0.5	0.9	1.03	3.6	51	4.6	
LC-1	9/13/97	64	1812	8.3	9.4	NA	9.8	NA	34.2	NA	3.09	0.5	295	36.3	<1	<0.3	5	0.6	2.6	12.8	0.3	1.3	1.55	4.2	58	0.2	
LC-2	9/13/97	68	1926	8.3	9.5	NA	9.8	NA	34.9	NA	3.15	0.5	299	36.05	<1	<0.3	5	0.6	2.6	12.8	0.3	1.0	1.55	4.1	58	<0.2	
LC-3	9/13/97			8.3	9.4	NA	9.8	NA	34.6	NA	3.14	0.5	291	36.99	<1	<0.3	6	0.6	2.6	12.7	0.3	1.4	1.38	4.2	56	<0.2	
LC-1	11/16/97	33	934	7.64	12.5	1.027	6.0	0.4	34.6	NA	3.03	0.6	269	34.51	1	<0.3	6	0.5	2.3	12.9	<0.3	1.0	1.12	4.2	57	<0.2	

SAMPLE NAME	SAMPLE DATE	STREAM FLOW (cfs)	STREAM FLOW (ft/s)	STREAM pH	D.O. (mg/L)	Conductivity (µmS/cm)	Water Temp (Celsius)	Air Temp (Celsius)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO3)	Sulfate As (µg/L)	Ba (µg/L)	Cu (µg/L)	Zn (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Na (mg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)		
																									7.98	7.94
LC-2	11/16/97	36	1019	7.98	7.94	0.27	6.0	0.4	34.4	NA	3	0.04	0.6	265	34.43	<0.3	6	0.5	2.3	12.9	<0.3	1.0	1.09	4.1	56	<0.2
LC-3	11/16/97																									
LC-1	1/6/98	26	736	8.0	15.19	0.27	4.0	0.6	33.0	NA	3.4	0.8	243	31.16	<0.3	6	0.5	2.2	11.7	<0.3	1.0	1.11	4.0	52	<0.3	
LC-2	1/6/98	26	736	8.0	8.0	0.26	4.0	0.6	33.3	NA	3.3	0.7	250	31.97	<0.3	6	0.5	2.2	12.0	<0.3	1.0	1.14	4.1	53	<0.2	
LC-3	1/6/98					0.27	4.0	0.6	32.5	NA	3.4	0.8	260	33.08	<0.3	6	0.5	2.2	12.3	<0.3	1.0	1.10	4.2	55	<0.2	
LC-1	3/8/98	20	586	NA	NA	NA	NA	NA	33.54	NA	NA	1.268	32.55	<0.3	5	0.6	2.2	12.9	<0.3	2.0	1.19	3.7	51	<0.2		
LC-2	3/8/98	24	680	NA	NA	NA	NA	NA	34.53	NA	NA	1.268	33.2	<0.3	5	0.6	2.2	12.8	<0.3	1.6	1.15	3.7	51	<0.2		
LC-3	3/8/98	22	623	NA	NA	NA	NA	NA	33.78	NA	NA	1.269	33.2	<0.3	5	0.6	2.2	12.8	<0.3	1.9	1.17	3.7	51	<0.2		
LC-1	4/7/98	24.07	682	7.97	9.9	0.25	6.3	8.2	33.6	NA	NA	1.0	262	37.2	<0.8	5	0.6	2.4	12.5	<0.3	1.6	1.15	4.0	55	<0.3	
LC-2	4/7/98	24.75	701	7.95	9.9	0.25	6.3		33.9	NA	NA	1.0	253	35.8	<0.8	5	0.5	2.3	12.0	<0.3	1.6	1.11	3.9	53	<0.3	
LC-3	4/7/98					0.25	6.2		33.7	NA	NA	1.0	254	34.2	<0.8	5	0.5	2.1	11.6	<0.3	1.5	1.10	3.9	50	<0.3	
LC-1	4/26/98	25.39	719	7.80	17.0	0.27	7.6	15.8	33.7	NA	NA	0.9	275	36.3	<0.8	5	0.5	2.3	13.0	<0.3	1.6	1.22	4.0	54	<0.3	
LC-2	4/26/98	24.5	694	7.80	18.0	0.27			33.8	NA	NA	0.9	278	37.5	<0.8	5	0.6	2.4	13.4	<0.3	1.6	1.24	4.0	55	<0.3	
LC-3	4/26/98					0.27			34.5	NA	NA	0.9	279	37.4	<0.8	5	0.5	2.4	13.4	<0.3	1.6	1.23	4.0	55	<0.3	
LC-1	5/19/98	286.08	8102	7.74	10.5	0.22	3.2	7.0	26.0	NA	NA	0.4	169	29.4	<0.8	5	0.4	1.6	10.4	<0.3	1.1	0.95	2.7	38	<0.3	
LC-2	5/19/98	284.82	8066	7.77	10.5	0.22			26.2	NA	NA	0.4	169	29.3	<0.8	5	0.3	1.6	10.4	<0.3	1.2	0.94	2.7	38	<0.3	
LC-3	5/19/98					0.22			26.0	NA	NA	0.4	167	29.2	<0.8	5	0.3	1.6	10.3	<0.3	1.1	0.94	2.7	38	<0.3	
LC-1	6/6/98	292.28	8277	7.86	11.8	0.22	5.2	8.0	NA	116	NA	0.5	168	29.3	<0.8	5	0.3	1.6	10.3	<0.3	1.1	0.91	2.7	38	<0.3	
LC-2	6/6/98	308.52	8737	7.85	11.7	0.22			NA	112	NA	0.5	168	29.3	<0.8	5	0.3	1.6	10.3	<0.3	1.1	0.90	2.7	38	<0.3	
LC-3	6/6/98					0.22			NA	114	NA	0.5	169	29.1	<0.8	5	0.3	1.6	10.3	<0.3	1.1	0.91	2.7	38	<0.3	
LC-1	6/29/98	554	15689	8.23	10.8	0.21	11.8	27.1	NA	108	NA	0.5	166	29.8	<0.8	5	0.4	1.6	10.3	0.6	1.3	0.88	2.8	38	<0.3	
LC-2	6/29/98			8.21	10.8	0.21	11.9	27.0	NA	107	NA	0.5	163	30.0	<0.8	5	0.4	1.6	10.4	0.6	1.3	0.87	2.8	38	<0.3	
LC-3	6/29/98			8.22	10.9	0.21	11.9	27.1	NA	104	NA	0.5	162	30.3	<0.8	5	0.4	1.6	10.3	0.6	1.4	0.87	2.9	39	<0.3	
LC-1	7/20/98	177.69	5032	8.33	8.5	0.25	13.9	26.7	NA	122	NA	0.5	230	33.9	<0.8	5	0.4	2.2	12.4	0.3	1.7	0.84	3.6	54	<0.3	
LC-2	7/20/98			8.32	8.5	0.25	13.8	26.7	NA	118	NA	0.5	229	33.6	<0.8	5	0.4	2.2	12.3	0.3	1.5	0.82	3.6	53	<0.3	
LC-3	7/20/98			8.32	8.5	0.25	13.8	26.8	NA	122	NA	0.5	231	33.8	<0.8	5	0.5	2.2	12.1	0.3	1.4	0.84	3.6	54	<0.3	
LC-1	9/4/98	60.36	1709	7.98	9.1	0.27	11.1	22.5	34.1	131	NA	0.6	271	34.5	<0.8	5	0.6	2.4	12.1	<0.3	0.9	0.92	4.4	59	<0.3	
LC-2	9/4/98	57.15	1618	7.98	9.1	0.27	11.2	22.7	34.4	126	NA	0.6	262	34.7	<0.8	5	0.6	2.5	12.2	<0.3	0.8	0.88	4.4	58	<0.3	
LC-3	9/4/98			7.99	9.1	0.27	11.2	22.7	34.5	132	NA	0.6	271	34.2	<0.8	5	0.6	2.3	12.0	<0.3	0.8	0.90	4.4	59	<0.3	
LC-1	10/6/98	41.74	1182	7.88	8.9	0.26	9.4	11.8	33.9	123	3.0	0.8	258	33.6	<0.8	5	0.5	2.4	11.8	<0.3	0.8	0.88	4.3	57	<0.3	
LC-2	10/6/98			7.86	8.8	0.26	9.4		33.8	128	3.0	0.8	253	33.5	<0.8	5	0.5	2.4	11.8	<0.3	0.8	0.87	4.3	56	<0.3	
LC-3	10/6/98			7.87	8.8	0.26	9.4		33.5	124	3.0	0.8	257	34.1	<0.8	5	0.5	2.4	11.9	<0.3	0.8	0.88	4.3	57	<0.3	
LC-1	11/7/98	32.07	908	8.02	11.6	0.27	4.2	0.7	NA	131	NA	0.4	263	34.4	<0.8	5	0.5	2.4	12.2	<0.3	0.8	0.90	4.5	59	<0.3	
LC-2	11/7/98			8.02	11.6	0.27			NA	132	NA	0.4	255	33.6	<0.8	5	0.5	2.4	11.9	<0.3	0.7	0.87	4.4	58	<0.3	
LC-3	11/7/98			8.02	11.6	0.27			NA	132	NA	0.4	257	33.3	<0.8	5	0.5	2.3	11.8	<0.3	0.9	0.88	4.5	58	<0.3	
LC-1	12/5/98	27.01	765	NA	NA	0.28	4.0	NA	33.1	135	NA	0.4	260	33.6	<0.8	5	0.5	2.3	11.9	<0.3	0.8	0.89	4.5	59	<0.3	
LC-2	12/5/98			NA	NA	0.27			33.6	137	NA	0.4	263	33.5	<0.8	5	0.5	2.4	11.8	<0.3	0.8	0.90	4.5	59	<0.3	
LC-3	12/5/98			NA	NA	0.27			33.9	139	NA	0.4	257	33.3	<0.8	5	0.5	2.3	11.8	<0.3	0.9	0.88	4.5	58	<0.3	
LC-SEEP-1	11/16/97			7.43	8.0	0.29	6.6	0.4	37.9	NA	3.27	0.9	311	37.19	<0.3	7	0.6	2.8	13.6	<0.3	1.4	1.25	5.1	65	0.3	
LC-SEEP-2	11/16/97			7.40	9.0	0.29	6.6	0.4	38.4	NA	3.25	0.9	310	37.16	<0.3	7	0.6	2.8	13.6	<0.3	1.4	1.24	5.1	65	6.0	
LC-SEEP-1	1/6/98			7.40	13	0.29	5.3	0.6	35.6	NA	3.60	0.9	282	35.44	<0.3	6	0.6	2.7	12.9	<0.3	1.1	1.15	4.8	62	1.7	
LC-SEEP-2	1/6/98			7.38	14	0.29	5.3	0.6	38.1	NA	3.60	0.9	281	35.44	<0.3	6	0.6	2.7	12.9	<0.3	1.1	1.14	4.8	61	1.6	

SAMPLE NAME	SAMPLE DATE	SITENAME	STREAM FLOW (cfs)	STREAM FLOW (L/s)	pH	DO (units)	DO (mg/L)	Conductivity (µS/cm)	Water Temp (°C)	Air Temp (°C)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO <sub>3</sub> )	Sulfate As <sub>2</sub> (µg/L)	Ba	Cd	Cu	Fe	K	Li	Mg	Mn	NH <sub>4</sub>	S	Si	Si	Zn	
LCSEEP1	3/8/98				7.44	6.7	0.26	4.4	8.0	37.0	NA	NA	0.9	281	35.1	<0.8	<5	0.6	2.6	13.4	<0.3	1.0	2.18	4.7	63	<0.2	
LCSEEP2	3/8/98				7.47	6.9	0.27	4.4	8.1	37.0	NA	NA	0.9	281	35.4	<0.8	<5	0.6	2.6	13.4	<0.3	1.0	2.13	4.6	62	<0.2	
LCSEEP3	3/8/98				7.47	6.9	0.27	4.4	8.1	36.7	NA	NA	1.0	281	35.13	<0.8	<5	0.6	2.6	13.4	<0.3	1.0	2.15	4.6	63	<0.2	
LCSEEP-1	4/7/98				7.49	6.0	0.27	3.8			36.5	NA	0.9	289	42.2	<0.8	<5	0.6	2.8	13.8	<0.3	1.8	1.21	4.6	64	2.7	
LCSEEP-2	4/7/98				7.49	5.8	0.27	3.9			36.2	NA	0.9	289	42.3	<0.8	<5	0.6	2.7	13.7	<0.3	1.8	1.23	4.6	65	0.5	
LCSEEP-3	4/7/98				7.50	5.9	0.27	4.0			36.4	NA	0.9														
LCSEEP-1	4/26/98				7.79	NA	0.29	3.9			37.0	NA	0.9	287	38.5	<0.8	<5	0.6	2.7	13.7	<0.3	2.3	1.29	4.5	60	0.5	
LCSEEP-2	4/26/98				7.75	NA	0.27	3.6			36.9	NA	1.0	289	40.3	<0.8	<5	0.6	2.7	13.9	<0.3	2.0	1.27	4.5	62	<0.3	
LCSEEP-3	4/26/98				7.79	NA	0.29	3.5			36.5	NA	0.9	287	39.6	<0.8	<5	0.6	2.8	14.0	<0.3	1.9	1.25	4.4	61	<0.3	
LCSEEP-1	10/6/98				7.39	6.2	0.29	7.6			38.9	139	3.1	1.1	307	39.3	<0.8	<5	0.6	2.9	13.1	<0.3	1.0	0.93	5.5	69	<0.3
LCSEEP-2	10/6/98				7.40	6.2	0.29	7.6			38.9	143	3.2	1.1	307	39.3	<0.8	<5	0.7	2.9	13.1	<0.3	0.9	0.94	5.5	68	<0.3
LCSEEP-3	10/6/98				7.40	6.2	0.30	7.6			39.0	138	3.1	1.1	310	39.6	<0.8	<5	0.6	2.9	13.2	<0.3	0.9	0.94	5.6	70	<0.3
LCSEEP-1	11/7/98				7.48	8.3	0.30	5.7			NA	145	NA	0.5	308	37.5	<0.8	<5	0.7	2.9	13.0	<0.3	1.0	0.95	5.7	69	1.0
LCSEEP-2	11/7/98				7.48	8.7	0.30	5.8			NA		NA														
LCSEEP-3	11/7/98				7.48	8.3	0.30	5.7			NA		NA														
LCSEEP-1	12/5/98				7.12	NA	0.28	6.3			37.4	130	NA	0.5	292	36.3	<0.8	<5	0.6	2.8	12.5	<0.3	0.9	0.93	5.4	67	<0.3
LCSEEP-2	12/5/98				7.13	NA					NA		NA														
LCSEEP-3	12/5/98				7.13	NA					NA		NA														
<b>Landsburg Fork, Site "LD"</b>																											
LD-1	7/20/97		228	6400	8.4	9.3	0.22	10.8	23.0	29.2	NA	2.92	0.6	195	28.51	<0.3	6	0.4	1.8	10.3	0.6	0.8	0.88	3.2	43	<0.2	
LD-2	7/20/97		228	6513	8.4	9.3	0.22	10.8	23.0	30.1	NA	2.55	0.6	196	27.82	<0.3	6	0.4	1.8	10.3	0.6	0.6	0.87	3.2	43	<0.2	
LD-3	7/20/97		228	6456	8.4	9.3	0.22	10.8	23.0	30.0	NA	2.64	0.6	197	27.56	<0.3	6	0.4	1.8	10.2	0.6	0.7	0.89	3.2	43	<0.2	
LD-1	8/7/97		112	3172	8.5	10.1	0.26	13.9	28.6	32.3	NA	3	0.5	236	33.31	<0.3	7	0.5	2.2	11.9	0.5	0.8	0.96	3.6	50	0.4	
LD-2	8/7/97		116	3285	8.5	10.1	0.26	13.9	28.6	32.2	NA	3	0.5	234	32.81	<0.3	7	0.5	2.2	11.8	0.5	0.9	0.98	3.5	49	0.5	
LD-3	8/7/97				8.5	10.1	0.26	13.9	28.6	31.5	NA	2.9	0.5	234	32.75	<0.3	7	0.5	2.2	11.8	0.5	0.8	0.95	3.5	50	1.3	
LD-1	9/14/97		54	1529	8.3	NA	NA	NA	9.8	NA	34.4	NA	3.01	0.5	300	36.33	<0.3	5	0.6	2.8	12.9	0.3	1.0	1.55	4.2	58	<0.2
LD-2	9/14/97		49	1388	8.3	NA	NA	NA	9.8	NA	34.0	NA	3.01	0.5	290	37.88	<0.3	6	0.6	2.5	12.8	0.3	1.3	1.37	4.2	58	<0.2
LD-3	9/14/97				8.3	NA	NA	NA	9.8	NA	33.7	NA	3.09	0.5	297	36.46	<0.3	5	0.6	2.7	12.9	0.3	1.0	1.53	4.2	58	<0.2
LD-1	11/16/97		30	850	8.0	NA	0.27	5.5	1.0	34.8	NA	3.01	0.7	266	34.25	<0.3	6	0.5	2.3	12.8	<0.3	0.9	1.09	4.1	56	<0.2	
LD-2	11/16/97		28	783	8.0	NA	0.28	5.5	1.0	34.5	NA	3.01	0.7	263	34.33	<0.3	6	0.5	2.3	12.8	<0.3	1.2	1.09	4.1	56	<0.2	
LD-3	11/16/97		32	906	8.0	NA	0.27	5.5	1.0	34.7	NA	2.98	0.6	287	33.75	<0.3	6	0.5	2.3	12.7	<0.3	1.0	1.10	4.1	56	<0.2	
LD-1	1/6/98		25	708	8.1	NA	0.27	NA	NA	NA	33.6	NA	3.4	0.7	262	32.1	<0.3	6	0.5	2.2	12.0	<0.3	1.0	1.13	4.1	55	0.2
LD-2	1/6/98		23	651	8.1	NA	0.27	NA	NA	NA	34.0	NA	3.4	0.8	260	32.11	<0.3	6	0.5	2.2	12.0	<0.3	1.0	1.12	4.1	55	0.3
LD-3	1/6/98		27	765	8.1	NA	0.27	NA	NA	NA	33.0	NA	3.3	0.7	261	32.83	<0.3	6	0.5	2.3	12.3	<0.3	1.2	1.10	4.1	56	<0.2
LD-1	3/8/98		11	311	NA	NA	NA	NA	NA	NA	33.58	NA	NA	1.265	33.1	<0.3	<5	0.8	2.3	12.9	<0.3	1.5	1.17	3.7	51	<0.2	
LD-2	3/8/98		15	425	NA	NA	NA	NA	NA	NA	34.03	NA	NA	0.9288	32.9	<0.3	<5	0.8	2.3	12.8	<0.3	1.6	1.15	3.7	51	<0.2	
LD-3	3/8/98		13	368	NA	NA	NA	NA	NA	NA	33.35	NA	NA	0.9282	33.4	<0.3	<5	0.8	2.2	12.8	<0.3	2.0	1.10	3.7	51	<0.2	
LD-1	4/7/98		16.34	463	8.10	9.8	0.25	8.3	9.7	32.5	NA	NA	1.0	256	33.4	<0.8	<5	0.5	2.1	11.3	<0.3	1.5	1.11	3.9	50	<0.3	
LD-2	4/7/98		17.85	506	8.08	9.8	0.25	8.4			33.1	NA	NA	0.9	246	33.4	<0.8	<5	0.5	2.1	11.3	<0.3	1.5	1.08	3.8	50	<0.3
LD-3	4/7/98				8.10	9.7	0.25	8.3			33.2	NA	NA	0.9	251	34.0	<0.8	<5	0.5	2.2	11.5	<0.3	1.5	1.10	3.8	51	<0.3
LD-1	7/20/98		134.49	3409	8.38	8.3	0.25	15.1	29.1	NA	122	NA	0.5	258	33.5	<0.8	<5	0.4	2.1	12.2	0.3	1.8	0.85	3.6	54	<0.3	
LD-2	7/20/98		135.03	3624	8.39	8.3	0.25	15.1	29.1	NA	117	NA	0.5	229	33.7	<0.8	<5	0.5	2.2	12.3	0.3	1.9	0.84	3.8	54	<0.3	
LD-3	7/20/98				8.39	8.3	0.25	15.2	29.0	NA	119	NA	0.5	227	33.4	<0.8	<5	0.4	2.1	12.2	0.3	1.6	0.82	3.6	53	<0.3	



SAMPLE NAME	SAMPLE DATE	STREAM FLOW (cfs)	STREAM FLOW (l/s)	PH	D.O. (mg/L)	Conductivity (mS/cm)	Water Temp (Cel)	Air Temp (Cel)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO3)	Sulfate (µg/L)	Ba (µg/L)	Ca (mg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	K (µg/L)	Li (µg/L)	Mg (µg/L)	Mn (µg/L)	Na (mg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)		
LD-1	8/17/98	72.08	2041	8.31	9.7	0.26	12.5	23.9	NA	150	2.9	0.5	237	32.8	<1	<0.8	<5	0.5	2.2	11.5	<0.3	1.0	0.86	3.9	5.4	<0.3	
LD-2	8/17/98			8.31	9.7	0.26	12.6	24.0	NA	145	2.9	0.6	244	33.1	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.8	0.84	3.9	5.5	<0.3	
LD-3	8/17/98			8.32	9.7	0.27	12.5	23.9	NA	120	2.9	0.6	246	33.6	<1	<0.8	<5	0.5	2.2	11.6	<0.3	1.0	0.89	3.7	5.6	<0.3	
LD-4	8/17/98								NA	130	2.9	0.5	247	33.5	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.9	0.88	3.7	5.8	<0.3	
LD-5	8/17/98								NA	130	2.9	0.5	245	33.3	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.9	0.88	3.7	5.5	<0.3	
LD-6	8/17/98								NA	135	2.9	0.5	243	33.8	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.9	0.87	3.7	5.5	<0.3	
LD-7	8/17/98								NA	130	2.9	0.5	247	33.1	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.7	0.87	3.9	5.7	<0.3	
LD-8	8/17/98								NA	125	2.9	0.5	251	33.5	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.8	0.86	4.0	5.6	<0.3	
LD-9	8/17/98								NA	135	2.9	0.5	245	33.7	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.9	0.88	3.7	5.5	<0.3	
LD-10	8/17/98								NA	125	2.9		242	33.7	<1	<0.8	<5	0.5	2.2	11.7	<0.3	0.7	0.85	3.7	5.5	<0.3	
<b>Blackfoot River, site -BA-</b>																											
BA-1	7/4/97	94	2652	8.21	8.7	0.2	13.1	23	20.35		10.82	0.4	201	22.31	<1	0.8	4.0	0.6	1.8	9.62	7.4	1.7	3.95	5.62	7.6	25.3	
BA-2	7/4/97	99	2803	8.21	8.7	0.2	13.1	23	20.29		10.85	0.4	200	22.62	<1	0.9	4.3	0.6	1.8	9.72	7.5	1.8	3.97	5.66	7.7	27.7	
BA-3	7/4/97			8.21	8.7	0.2	13.1	23	20.52		10.82	0.4	195	22.19	<1	0.8	4.4	0.6	1.8	9.64	7.3	1.7	3.87	5.58	7.5	29	
BA-1	7/20/97	74	2095	7.62	8.7	0.2	11.4	11.7	22.78		10.78	0.3	202	21.11	<1	1.0	5.8	0.8	1.9	9.74	9.7	2.0	4.28	5.85	8.4	29.4	
BA-2	7/20/97	77	2180	7.62	8.7	0.2	11.4	11.7	22.75		10.73	0.3	203	21.38	<1	0.9	5.6	0.8	1.9	9.81	9.8	1.8	4.27	5.89	8.5	29.7	
BA-3	7/20/97	76	2152	7.62	8.7	0.2	11.4	11.7	22.76		10.76	0.3	201	20.97	<1	0.9	5.7	0.8	1.8	9.66	9.6	1.8	4.2	5.8	8.4	30.4	
BA-1	8/8/97	41	1161	8.17	(NA)	0.24	10.1	11.5	26.29		10.61	0.3	231	25.83	1	0.7	4.2	0.8	2.3	11.6	5.0	2.2	3.95	6.33	9.7	11.1	
BA-2	8/8/97	41	1161	8.17	(NA)	0.24	10.1	11.5	26.16		10.54	0.3	229	25.53	1	0.7	4.2	0.7	2.3	11.5	4.9	2.2	4.03	6.36	9.8	8.2	
BA-3	8/8/97	41	1161	8.17	(NA)	0.24	10.1	11.5	26.49		10.66	0.3	231	25.36	1	0.6	4.0	0.7	2.2	11.5	4.8	2.2	3.93	6.29	9.6	8.8	
BA-1	9/13/97	27	765	8.3	9.7	(NA)	13.3	(NA)	29.1		14.6	0.4	279	28.5	<1	0.6	3.2	0.9	2.6	12.6	4.2	2.8	6.08	7	11.6	1.3	
BA-2	9/13/97	28	793	8.3	9.8	(NA)	13.3	(NA)	28.0		14.7	0.3	274	29.35	<1	0.3	3.4	0.9	2.7	12.9	4.3	2.7	5.79	7.02	11.8	2.5	
BA-3	9/13/97			8.3	9.7	(NA)	13.3	(NA)	28.7		14.7	0.3	275	29.33	<1	0.4	3.3	0.9	2.6	12.8	4.2	2.7	5.91	7.02	11.6	1.2	
<b>Blackfoot River, site -BH-</b>																											
BH-1	7/4/97	103	2917	8.2	9.1	0.20	12.2	18.3	20.2		10.83	0.4	207	23.66	<1	0.8	4.4	0.6	1.9	10.0	7.1	1.7	4.06	5.87	8.0	28.4	
BH-2	7/4/97	111	3143	8.2	9.1	0.20	12.2	18.3	20.2		10.79	0.4	207	23.66	<1	0.9	4.4	0.6	1.8	9.70	6.8	1.8	3.98	5.66	7.8	20.4	
BH-3	7/4/97			8.2	9.1	0.20	12.2	18.3	20.2		10.8	0.3	208	23.66	<1	0.8	4.2	0.6	1.9	9.95	7.0	1.6	4.06	5.84	8.0	28.2	
BH-1	7/20/97	74	2095	7.9	8.8	0.20	11.7	15.0	22.8		10.77	0.5	204	21.45	<1	1.0	6.7	0.8	1.9	9.88	9.5	1.9	4.42	5.95	8.6	19.7	
BH-2	7/20/97	80	2265	7.9	8.8	0.20	11.7	15.0	22.8		10.82	0.5	202	21.39	<1	1.0	6.9	0.8	1.9	9.85	9.5	1.7	4.31	5.88	8.5	27.5	
BH-3	7/20/97			7.9	8.8	0.20	11.7	15.0	22.8		10.87	0.5	201	21.42	<1	1.0	6.4	0.8	1.8	9.85	9.5	1.8	4.32	5.88	8.5	15.6	
BH-1	8/8/97	38	1078	8.3	(NA)	0.24	10.9	15.3	26.2		10.51	0.4	237	25.82	1	0.6	4.0	0.7	2.3	11.5	3.6	2.2	4.09	6.39	9.9	4.4	
BH-2	8/8/97	38	1076	8.3	(NA)	0.24	10.9	15.3	26.0		10.48	0.4	234	25.71	1	0.6	4.0	0.7	2.3	11.6	3.6	2.2	4	6.35	9.8	13.3	
BH-3	8/8/97			8.3	(NA)	0.24	10.9	15.3	26.1		10.48	0.4	233	26.02	1	0.6	4.2	0.7	2.3	11.6	3.6	2.2	3.98	6.36	9.9	3.9	
BH-1	9/13/97	31	878	8.3	10.2	(NA)	13.8	(NA)	28.5		14.54	0.3	275	29.38	<1	0.5	3.0	0.9	2.7	12.9	3.0	2.9	5.9	7.04	11.6	1	
BH-2	9/13/97	33	934	8.2	10.3	(NA)	13.8	(NA)	28.7		14.5	0.3	271	29.13	<1	0.4	3.1	0.9	2.6	12.8	3.0	2.8	5.81	6.96	11.5	1.1	
BH-3	9/13/97			8.3	10.1	(NA)	13.8	(NA)	26.9		14.57	0.3	263	28.38	<1	0.5	3.1	0.9	2.6	12.7	2.8	3.0	5.6	6.93	10.7	1.1	
BH-1	11/18/97	24	680	8.0	12.8	0.25	(NA)	1.4	27.6		15.19	0.3	229	26.82	1	0.3	1.6	0.8	2.1	12.6	3.4	2.3	5.43	6.55	10.6	9.5	
BH-2	11/18/97	28	793	8.0	12.7	0.25	(NA)	1.4	27.3		15.23	0.3	230	27.1	0	0.3	1.6	0.8	2.2	12.6	3.434	2.4	5.46	6.57	10.6	5.7	
BH-3	11/18/97	26	736	8.0	12.5	0.25	(NA)	1.4	27.3		15.34	0.3	230	26.91	1	0.3	1.6	0.8	2.1	12.6	3.5	2.4	5.49	6.59	10.6	2.4	
BH-1	1/6/98	18	510	8.1	18.0	11.024	0.0	1.7	27.3		14.1	0.3	210	25.4	1	<0.3	1.2	0.8	2.1	11.9	2.5	2.2	4.24	6.12	10.7	3.5	
BH-2	1/6/98	22	623	8.1	18.0	11.024	0.0	1.7	26.7		14.1	0.3	217	26.12	2	<0.3	1.1	0.8	2.1	12.1	2.6	2.2	4.31	6.23	11.0	4.1	
BH-3	1/6/98	20	566	8.1	18.0	11.024	0.0	1.7	26.7		14.1	0.4	222	26.66	1	<0.3	1.2	0.8	2.1	12.4	2.7	2.3	4.21	6.23	11.3	2.7	
BH-1	3/8/98	21	595	8.06	NA	NA	0	-3.2	27.76	NA	NA	0.4	215	26.36	<1	<0.3	8	0.9	2.0	12.9	3.9	2.1	8.07	6.08	11.4	(BPO)	
BH-2	3/8/98	25	708	8.08	NA	NA	0.1	-3.3	28.17	NA	NA	0.3	211	26.12	<1	<0.3	8	0.9	2.0	12.8	3.8	2.1	7.98	6.02	11.4	0.5	

SAMPLE NAME	SAMPLE DATE	STREAM FLOW		pH	DO	Con- ductivity (mS/cm)	Water Temp (C)	Air Temp (C)	Inorganic Carbon (mg/L)	Total Alk (mg/L)	Sulfate As (μg/L)	Fe	Cu	Ca	Mg	Li	K	Mn	Na	S	Sr	Zn				
		(cfs)	(l/s)																							
BH3	3/8/98	23	651	8.08	NA	NA	0	-3.3	27.37	NA	NA	0.3	21	26.34	<1	<0.3	8	0.8	2.0	12.8	3.8	2.2	7.9	5.99	114	0.6
BH1	4/29/98	78.62	2227	7.80	NA	0.19	5.6	14.4	18.9	NA	NA	0.2	144	21.3	<1	<0.8	32	0.7	1.5	10.2	3.9	1.9	13.2	5.3	74	32.6
BH2	4/29/98	78.87	2177	7.80	NA	0.19	5.6	14.4	17.2	NA	NA	0.2	144	21.0	<1	<0.8	34	0.7	1.5	10.1	3.9	1.9	13.3	5.4	73	32.5
BH3	4/29/98	77.9	2177	7.79	NA	0.19	5.6	14.4	18.2	NA	NA	0.2	144	21.0	<1	<0.8	39	0.7	1.5	10.1	3.9	1.9	13.3	5.4	73	30.6
BH1	5/19/98	55.75	1579	7.86	11.7	0.21	7.6	18.2	20.2	NA	NA	0.2	174	21.8	<1	<0.8	34	0.7	1.7	10.6	4.4	1.9	11.4	5.5	77	24.0
BH2	5/19/98	55.17	1562	7.88	11.7	0.21	7.6	18.2	20.1	NA	NA	0.2	173	21.8	<1	<0.8	33	0.7	1.7	10.6	4.4	1.9	11.3	5.5	76	24.1
BH3	5/19/98	7.87	11.8	7.87	11.8	0.21	7.6	18.2	20.2	NA	NA	0.3	173	21.6	<1	<0.8	32	0.7	1.7	10.6	4.4	1.9	11.4	5.5	75	23.7
BH1	6/5/98	84.7	2399	7.90	11.8	0.19	11.7	14.7	NA	86	NA	0.3	163	21.3	<1	<0.8	31	0.6	1.6	9.67	4.9	2.3	5.77	5.4	71	21.8
BH2	6/5/98	85.9H	2435	7.92	12.0	0.19	11.7	14.7	NA	84	NA	0.3	163	21.6	<1	<0.8	38	0.6	1.6	9.77	4.9	2.3	5.71	5.4	72	18.5
BH3	6/5/98	7.90	11.9	7.90	11.9	0.19	11.7	14.7	NA	64	NA	0.3	165	21.6	<1	<0.8	38	0.6	1.6	9.64	4.9	2.2	5.79	5.4	73	21.2
BH1	7/20/98	70.89	2008	8.32	7.8	0.21	18.0	22.7	NA	94	NA	0.5	229	25.3	<1	<0.8	35	0.8	2.2	11.1	5.4	2.7	4.09	6.7	106	5.2
BH2	7/20/98	8.33	7.8	8.33	7.8	0.21	18.0	22.8	NA	91	NA	0.5	226	25.0	<1	1.1	3.5	0.8	2.2	11.1	5.4	2.7	4.09	6.7	105	3.1
BH3	7/20/98	8.33	7.8	8.33	7.8	0.21	17.9	22.8	NA	93	NA	0.4	225	24.7	<1	<0.8	34	0.8	2.1	11.0	5.4	2.7	4.07	6.7	103	2.7
BH1	8/17/98	33.65	953	8.16	9.4	0.24	11.9	18.0	NA	100	13.3	0.4	240	26.8	<1	0.8	2.3	0.9	2.3	11.6	2.6	2.1	4.15	6.7	114	0.9
BH2	8/17/98	31.7	898	8.20	9.4	0.24	11.9	18.1	NA	105	13.4	0.4	228	26.2	<1	<0.8	21	0.8	2.2	11.3	2.5	1.9	4.00	6.3	110	2.0
BH3	8/17/98	8.18	9.4	8.18	9.4	0.24	11.8	18.1	NA	100	13.4	0.4	223	26.4	<1	<0.8	22	0.8	2.2	11.4	2.5	1.9	3.97	6.5	108	2.0
<b>Blackfoot River, site -BB-</b>																										
BB1	7/4/97	100	2832	8.3	8.4	0.20	14.5	19.3	20.1	10.45	0.6	190	21.8	<1	0.7	4.0	0.6	2	9.36	5.8	1.8	3.68	5.9	94	13.5	
BB2	7/4/97	102	2888	8.3	8.4	0.20	14.5	19.3	20.0	10.5	0.6	190	21.71	<1	0.7	4.3	0.6	2.1	9.31	5.9	1.8	3.4	5.8	94	22	
BB3	7/4/97			8.3	8.4	0.20	14.5	19.3	20.1	10.48	0.6	178	20.86	<1	0.7	3.8	0.6	2.1	9.34	5.7	1.9	3.6	5.7	88	11.2	
BB1	7/20/97	79	2237	8.0	8.9	0.20	12.1	18.9	22.6	10.68	0.5	194	20.85	<1	0.9	6.6	0.8	2.1	9.43	8.1	2.0	4.08	6.1	104	18.9	
BB2	7/20/97	79	2237	8.0	8.9	0.20	12.1	18.9	22.6	10.62	0.5	190	20.6	<1	0.9	6.0	0.7	2.1	9.35	7.5	2.1	4.01	6.0	102	15.1	
BB3	7/20/97			8.0	8.9	0.20	12.1	18.9	23.6	10.57	0.5	191	20.61	<1	0.8	5.2	0.8	2.1	9.38	7.5	2.0	4.04	6.0	103	16.3	
BB1	8/7/97	33	934	8.25	9.8	0.23	16.7	15.1	25.33	10.13	0.4	226	24.94	1	0.5	4.2	0.8	2.8	10.8	13.6	2.4	3.74	6.6	132	4.7	
BB2	8/7/97	36	1019	8.25	9.8	0.23	16.7	15.1	25.28	10.06	0.4	229	25.04	1	0.6	4.4	0.8	2.6	10.9	2.6	2.3	3.82	6.6	128	4.1	
BB3	8/7/97			8.25	9.8	0.23	16.7	15.1	25.39	10.21	0.4	220	24.1	1	0.6	4.1	0.8	2.6	10.8	2.8	2.2	3.68	6.5	122	5.4	
BB1	9/13/97	22	623	8.1	9.8	(NA)	13.6	(NA)	27.9	14.04	0.4	254	29.72	<1	0.4	3.3	0.9	2.7	12.0	1.6	3.0	4.97	7.1	127	1.1	
BB2	9/13/97	23	651	8.1	10.0	(NA)	13.6	(NA)	27.4	14.11	0.4	258	29.64	<1	0.3	3.5	0.9	2.7	12.1	1.7	2.7	5.07	7.2	128	1.8	
BB3	9/13/97			8.1	9.8	(NA)	13.6	(NA)	27.5	14.03	0.4	253	29.35	<1	0.5	3.4	0.9	2.8	12.1	1.7	3.0	4.98	7.2	127	1	
BB1	11/16/97	19	538	8.1	13.5	0.26	0.1	2.3	29.0	15.65	0.4	233	28.07	1	0.4	1.5	0.9	2.4	13.1	3.6	2.7	5.67	7.0	126	6	
BB2	11/16/97	23	651	8.1		0.26	0.1	2.3	29.5	15.72	0.3	232	28.05	1	0.3	1.5	0.9	2.4	13.1	3.5	2.6	5.59	7.0	126	3.8	
BB3	11/16/97	21	595	8.1		0.26	0.1	2.3	28.5	15.85	0.3	228	28.52	1	0.3	1.4	0.9	2.4	13.2	3.5	2.8	5.48	7.0	126	2	
BB1	4/7/98	37.65	1066	8.10	10.7	0.21	7.1	8.1	22.0	NA	NA	0.2	168	25.0	<1	<0.8	21	0.9	2.1	11.1	4.4	2.3	11.4	5.9	125	1.5
BB2	4/7/98	34.91	989	8.12	10.7	0.21	7.2	22.6	22.6	NA	NA	0.3	170	24.7	<1	<0.8	34	0.9	2.1	11.2	4.4	2.5	11.7	6.0	126	1.7
BB3	4/7/98			8.12	10.6	0.21	7.1	21.8	21.8	NA	NA	0.3	172	24.8	<1	<0.8	29	0.9	2.0	11.1	4.4	2.3	11.7	6.0	125	2.4
BB1	4/29/98	71.81	2034	7.93	NA	0.18	6.8	15.4	18.2	NA	NA	0.2	135	20.3	<1	0.9	2.3	0.7	1.7	9.42	3.1	2.2	11.9	5.5	97	15.6
BB2	4/29/98	76.66	2171	7.93	NA	0.19	7.5	(NA)	17.5	NA	NA	0.2	135	20.2	<1	0.9	2.7	0.7	1.7	9.39	3.2	2.0	11.9	5.5	96	18.9
BB3	4/29/98			7.92	NA	0.18			17.7	NA	NA	0.2	135	20.0	<1	0.9	2.6	0.7	1.7	9.32	3.2	2.0	12.0	5.5	95	18.9
BB1	5/19/98	64.27	1820	7.97	11.3	0.19	8.6	18.2	18.7	NA	NA	0.3	162	20.2	<1	<0.8	30	0.7	1.8	9.70	3.4	2.2	10.3	5.8	95	15.0
BB2	5/19/98	62.08	1758	7.96	11.4	0.19	8.6	18.2	18.6	NA	NA	0.3	159	20.1	<1	<0.8	25	0.7	1.8	9.50	3.3	2.1	10.4	5.8	96	13.9
BB3	5/19/98			7.96	11.4	0.19			18.5	NA	NA	0.3	158	19.8	<1	<0.8	25	0.7	1.8	9.40	3.3	1.9	10.4	5.8	94	14.1
BB1	6/5/98	85.66	2426	7.88	12.1	0.18	11.9	18.2	NA	82	NA	0.3	150	19.8	<1	<0.8	30	0.6	1.7	8.80	3.9	2.5	5.08	5.7	90	11.0
BB2	6/5/98	87.41	2475	7.89	12.1	0.18			NA	78	NA	0.3	153	19.9	<1	<0.8	31	0.6	1.7	8.77	3.9	2.6	5.20	5.7	91	11.1

SAMPLE NAME	SAMPLE DATE	SITESHAM FLOW (cfs)	SITESHAM FLOW (l/s)	STREAM pH	D.O. (units)	Conductivity (mS/cm)	Water Temp (C)	Air Temp (C)	Inorganic Carbon (mg/l)	Total Alk (mg/l)	Sulfate As (ug/L)	Bh (ug/L)	Ca (mg/L)	Cr (ug/L)	Cu (ug/L)	Fe (ug/L)	K (ug/L)	Li (ug/L)	Mg (mg/L)	Mn (ug/L)	Na (mg/L)	S (mg/L)	Si (mg/L)	Sr (ug/L)	Zn (ug/L)		
BB 3	6/5/98			7.89	12.2	0.18			NA	80	NA	0.4	153	20.3	<1	<0.8	19	0.6	1.7	8.80	3.9	2.6	5.24	5.8	93	8.5	
BB 1	6/29/98	217.99	6173	7.80	10.1	0.16	15.0	25.1	NA	77	NA	0.4	157	19.3	<1	1.3	12	0.6	1.7	8.13	5.9	3.0	3.26	5.6	84	10.3	
BB 2	6/29/98	212.78	6026	7.75	10.1	0.16	15.0	25.2	NA	77	NA	0.4	159	19.6	<1	1.1	7	0.6	1.7	8.13	6.0	2.9	3.26	5.8	96	7.9	
BB 3	6/29/98			7.77	10.2	0.16	15.0	25.1	NA	73	NA	0.4	156	19.3	1	1.3	11	0.6	1.7	8.14	5.8	3.3	3.27	5.7	84	5.7	
BB 1	7/20/98	66.66	1888	8.34	6.9	0.21	16.8	23.9	NA	89	NA	0.5	212	23.6	<1	<0.8	34	0.7	2.4	10.4	4.6	3.3	3.54	7.0	129	2.1	
BB 2	7/20/98			8.34	6.9	0.20	16.9	24.1	NA	82	NA	0.5	216	23.9	<1	<0.8	34	0.8	2.4	10.4	4.6	3.1	3.60	7.1	133	2.5	
BB 3	7/20/98			8.35	6.9	0.21	16.7	24.1	NA	85	NA	0.5	214	24.0	1	1.0	32	0.8	2.5	10.5	4.6	3.2	3.50	7.0	134	2.8	
BB 1	9/4/98	18.83	533	7.89	8.5	0.24	10.2	15.9	28.1	105	NA	0.3	229	27.3	<1	<0.8	17	0.9	2.8	11.5	1.3	2.2	3.48	7.3	147	1.4	
BB 2	9/4/98	20.3	575	7.86	8.5	0.24	10.2	15.9	28.0	103	NA	0.3	228	27.1	<1	1.0	18	0.9	2.7	11.5	1.3	3.4	3.74	7.1	144	0.8	
BB 3	9/4/98			7.88	8.5	0.24	10.3	15.7	27.8	107	NA	0.4	243	27.7	<1	<0.8	20	1.0	2.8	11.8	1.5	2.3	3.82	7.4	150	0.8	
BB 1	10/6/98	20.87	591	7.78	9.2	0.23	7.0	10.5	27.6	104	12.5	0.4	227	27.6	<1	<0.8	15	0.9	2.7	11.7	1.5	2.3	3.86	7.1	146	0.5	
BB 2	10/6/98			7.77	9.2	0.22	7.2	10.5	27.5	102	12.5	0.5	222	27.0	<1	<0.8	15	0.8	2.6	11.5	1.5	2.2	3.82	7.0	142	0.5	
BB 3	10/6/98			7.78	9.3	0.22	7.0	10.4	27.5	107	12.5	0.5	223	27.1	<1	<0.8	15	0.8	2.6	11.5	1.6	2.2	3.84	7.1	142	0.7	
BB 1	11/7/98	11.27	319	8.35	13.7	0.25	3.0	2.5	NA	108	NA	0.2	221	27.2	<1	<0.8	15	0.8	2.6	11.9	1.3	2.3	4.12	7.3	148	0.5	
BB 2	11/7/98			8.35	13.7	0.25	3.0		NA	102	NA	0.2	217	27.3	<1	<0.8	15	0.8	2.5	11.8	1.4	2.3	4.07	7.2	145	0.5	
BB 3	11/7/98			8.37	13.7	0.25	3.0		NA	109	NA		226	27.5	<1	<0.8	15	0.9	2.6	12.0	1.4	2.4	4.20	7.4	151	0.6	
BB 1	12/5/98	10.7	303	8.17	NA	0.24	0.0		28.0	111	NA	0.1	223	28.1	<1	<0.8	13	0.8	2.6	12.1	2.0	2.4	4.55	7.3	147	5.4	
BB 2	12/5/98			8.17	NA	0.25			27.4	110	NA	0.1	214	26.9	<1	<0.8	12	0.8	2.4	11.6	1.9	2.3	4.37	7.0	139	5.1	
BB 3	12/5/98			8.18	NA	0.26			27.5	104	NA	0.2	221	28.1	<1	<0.8	12	0.8	2.5	12.1	2.0	2.5	4.55	7.3	146	2.8	
<b>Blackfoot River Site - BC</b>																											
BC 1	7/20/97	100	2832	7.9	8.5	0.21	12.6	19.3	23.8		10.52	0.5	192	21.46	<1	0.8	48	0.8	2.3	9.65	5.2	2.2	3.92	6.1	106	5.7	
BC 2	7/20/97	107	3030	7.9	8.5	0.21	12.6	19.3	23.7		10.62	0.5	194	21.08	<1	0.8	46	0.8	2.2	9.55	5.2	2.0	3.99	6.0	106	11.2	
BC 3	7/20/97			7.9	8.5	0.21	12.6	19.3	23.6		10.74	0.5	193	21.23	<1	0.8	49	0.8	2.2	9.62	5.2	2.2	4.00	6.1	106	6.7	
BC 1	8/7/97	50	1416	8.1	9.2	0.23	14.8	16.1	26.2		10.11	0.4	233	26.23	1	0.4	28	0.8	2.8	11.2	1.8	2.5	3.93	6.7	133	2.4	
BC 2	8/7/97	52	1472	8.1	9.2	0.23	14.8	16.1	26.1		10.03	0.4	230	25.58	1	0.4	28	0.8	2.8	11.1	1.8	2.4	3.93	6.6	131	4.1	
BC 3	8/7/97			8.1	9.2	0.23	14.8	16.1	25.6		10.04	0.4	248	27.77	1	0.6	29	0.9	2.9	11.9	2.0	2.4	3.65	6.6	141	3.1	
BC 1	9/14/97	29	821	7.9	NA	NA	9.0	NA	27.6		13.57	0.4	253	29.65	<1	0.3	19	0.9	2.9	12.1	0.9	2.8	4.9	7.2	129	3.1	
BC 2	9/14/97	33	934	7.9	NA	NA	9.0	NA	28.9		13.5	0.3	245	29.87	<1	<0.3	18	0.8	2.9	12.0	0.9	2.7	4.86	7.0	127	3.6	
BC 3	9/14/97	29	821	7.9	NA	NA	9.0	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
BC 1	11/16/97	15	425	7.8	13.5	0.25	0.4	3.1	28.8		14.28	0.3	226	27.24	1	0.6	10	0.8	2.5	12.4	0.7	2.7	5.2	6.8	134	1.8	
BC 2	11/16/97	15	425	7.8	13.5	0.25	0.4	3.1	28.2		14.32	0.3	227	27.09	1	<0.3	10	0.8	2.5	12.3	0.7	2.8	5.27	6.7	134	3	
BC 3	11/16/97			7.8	13.5	0.25	0.4	3.1	27.9		14.24	0.3	228	27.3	1	<0.3	10	0.8	2.5	12.4	0.7	2.5	5.21	6.8	134	4.7	
BC 1	1/6/98	14	396	7.8	16.0	0.25	1.6	2.7	27.5		15	0.4	222	27.23	1	<0.3	9	0.8	2.5	12.1	0.4	2.5	4.46	6.4	137	3.4	
BC 2	1/6/98	14	398	7.8	16.0	0.25	1.6	2.7	27.6		15.1	0.4	220	27.16	1	<0.3	9	0.8	2.5	12.1	0.4	2.8	4.45	6.4	137	2	
BC 3	1/6/98			7.8	16.0	0.25	1.6	2.7	27.3		15.2	0.3	220	27.46	1	<0.3	9	0.8	2.5	12.1	0.4	2.6	4.40	6.4	137	4.2	
BC 1	3/8/98	13	368	7.85	NA	NA	0.4	-2.2	27.87	NA	NA	0.3	208	26.33	<1	<0.3	-5	0.8	2.3	12.3	0.6	2.4	8.10	6.0	140	0.2	
BC 2	3/8/98	17	481	7.83	NA	NA	0.4	-2.3	27.47	NA	NA	0.3	215	26.49	<1	<0.3	-5	0.8	2.3	12.6	0.6	2.3	8.36	6.2	141	(BPOL)	
BC 3	3/8/98	15	425	7.87	NA	NA	0.3	-2.2	27.6	NA	NA	0.3	209	26.15	<1	<0.3	-5	0.8	2.3	12.3	0.6	2.3	8.15	6.0	138	(BPOL)	
BC 1	4/7/98	40.33	1142	8.10	10.8	0.21	6.9	8.0	22.9	NA	NA	0.3	186	26.1	1	<0.8	27	0.9	2.2	11.5	2.0	2.3	11.3	6.1	130	1.2	
BC 2	4/7/98	37.27	1055	8.08	10.8	0.21	6.9		23.0	NA	NA	0.3	175	25.6	<1	<0.8	16	0.8	2.2	11.3	2.0	2.5	11.0	5.9	125	1.2	
BC 3	4/7/98			8.09	10.8	0.21	6.9		22.9	NA	NA	0.3	175	25.9	<1	<0.8	24	0.9	2.2	11.4	2.0	2.2	11.1	5.9	130	1.1	

SAMPLE NAME	SAMPLE DATE	STREAM LOCATION	STRAIN	STREAM FLOW (cfs)	STREAM FLOW (l/s)	DO (mg/L)	Conductivity (µmS/cm)	Water Temp (C)	Air Temp (C)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO3)	Sulfate As <sub>2</sub> (µg/L)	Pb (µg/L)	Cd (µg/L)	Cu (µg/L)	Fu (µg/L)	K (mg/L)	Li (mg/L)	Mg (mg/L)	Mn (µg/L)	NH <sub>4</sub> (mg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)		
BC1	4/20/98	70.95	2264	7.93	14.5	0.19	8.0	17.0	18.7	NA	NA	0.2	14.6	21.4	<1	<0.8	23	0.7	1.8	9.7	2.2	2.0	11.8	5.6	103	23.1	
BC2	4/29/98	83.7	2370	7.94	15.5	0.19				18.6	NA	0.3	14.2	21.2	<1	<0.8	16	0.7	1.8	9.5	2.2	2.1	11.5	5.5	100	6.3	
BC3	4/29/98			7.92		0.19			18.3	NA	NA	0.3	14.2	21.4	<1	0.9	20	0.7	1.8	9.7	2.2	2.2	11.5	5.6	101	4.1	
BC1	5/19/98	70.03	1983	7.91	11.6	0.20	10.0	22.6	19.7	NA	NA	0.3	16.7	21.1	<1	<0.8	21	0.7	2.0	9.9	2.2	2.3	10.7	5.8	100	2.7	
BC2	5/19/98	68.92	1895	7.90	11.5	0.20			19.5	NA	NA	0.3	16.5	20.7	<1	<0.8	20	0.7	1.9	9.8	2.2	2.1	10.7	5.8	98	9.6	
BC3	5/19/98			7.92	11.6	0.20			19.6	NA	NA	0.3	16.3	20.4	<1	<0.8	20	0.7	1.9	9.7	2.2	2.0	10.6	5.7	96	9.7	
BC1	6/5/98	98.01	2176	7.80	10.8	0.19	11.0	10.6	NA	96	NA	0.3	16.2	21.5	<1	<0.8	21	0.6	1.8	9.3	2.8	2.6	5.08	5.7	97	13.4	
BC2	6/5/98	99.42	2816	7.79	10.6	0.19			NA	82	NA	0.3	15.9	20.9	<1	<0.8	25	0.6	1.8	9.1	2.8	2.5	5.03	5.7	94	18.8	
BC3	6/5/98			7.82	10.8	0.19			NA	82	NA	0.3	15.9	20.9	<1	<0.8	21	0.6	1.8	9.1	2.7	2.6	5.01	5.7	93	17.2	
BC1	6/29/98	242.31	6862	7.78	10.5	0.17	13.9	26.1	NA	74	NA	0.3	15.8	20.5	<1	1.5	10	0.6	1.8	8.5	5.5	4.0	3.39	6.4	90	6.1	
BC2	6/29/98	249.7	7072	7.75	10.5	0.17	14.0	26.2	NA	85	NA	0.3	15.9	20.2	1.0	9	0.6	1.8	8.4	6.2	3.0	3.33	5.7	86	9.0		
BC3	6/29/98			7.77	10.6	0.17	14.0	26.1	NA	75	NA	0.3	16.5	19.8	<1	1.0	10	0.6	1.8	8.3	6.7	2.5	3.28	5.8	87	4.6	
BC1	7/20/98	64.02	1813	8.25	7.9	0.21	1.77	30.4	NA	93	NA	0.5	21.8	25.1	<1	<0.8	24	0.8	2.6	10.9	3.3	3.4	3.79	7.0	137	1.8	
BC2	7/20/98			8.28	7.9	0.21	1.77	30.4	NA	89	NA	0.4	21.8	24.8	<1	<0.8	23	0.8	2.5	10.7	3.3	3.3	3.64	7.0	137	1.4	
BC3	7/20/98			8.21	7.9	0.21	1.77	30.5	NA	90	NA	0.5	21.8	24.8	<1	<0.8	25	0.8	2.5	10.6	3.3	3.2	3.68	7.0	137	2.2	
BC1	8/17/98	37.61	1065	8.26	9.7	0.23	12.3	22.0	NA	95	12.6	0.4	21.4	26.3	<1	<0.8	16	0.8	2.6	10.8	1.0	2.4	3.72	6.8	141	0.5	
BC2	8/17/98	39.04	1106	8.26	9.7	0.23	12.3	22.1	NA	110	12.8	0.4	21.1	26.1	<1	<0.8	16	0.8	2.6	10.8	1.0	2.4	3.70	6.8	140	0.5	
BC3	8/17/98			8.28	9.7	0.24	12.4	22.1	NA	105	12.8	0.4	21.1	25.9	<1	<0.8	15	0.8	2.6	10.8	1.0	2.3	3.70	6.8	139	0.5	
BC1	9/4/98	26.93	763	7.76	9.1	0.24	10.6	23.5	27.6	100	NA	0.4	22.9	27.3	<1	<0.8	11	0.9	2.8	11.4	0.8	2.3	3.85	7.2	148	0.4	
BC2	9/4/98	24.64	698	7.77	9.1	0.24	10.6	23.6	27.5	103	NA	0.4	23.0	27.0	<1	<0.8	11	0.9	2.8	11.3	0.8	2.3	3.92	7.2	147	0.4	
BC3	9/4/98			7.78	9.1	0.24	10.7	23.7	27.5	103	NA	0.4	22.6	27.1	<1	<0.8	10	0.9	2.8	11.3	0.8	2.2	3.89	7.2	147	0.5	
BC1	10/6/98	22.2	629	7.73	9.2	0.23	6.8	11.8	27.4	104	12.8	0.4	21.6	27.0	<1	<0.8	9	0.8	2.7	11.2	0.7	2.1	3.87	6.9	141	0.4	
BC2	10/6/98			7.72	9.2	0.23	6.8			103	12.8	0.5	22.1	27.1	<1	<0.8	9	0.8	2.7	11.4	0.7	2.1	3.94	7.0	143	0.7	
BC3	10/6/98			7.73	9.2	0.23	6.8		27.6	99	12.7	0.5	22.2	27.1	<1	<0.8	9	0.8	2.7	11.4	0.7	2.1	3.92	7.0	143	0.7	
BC1	11/7/98	16.6	470	8.02	12.8	0.25	4.2	1.0	NA	108	NA	0.2	22.1	27.6	<1	<0.8	8	0.8	2.6	11.8	0.4	2.3	4.19	7.3	148	0.5	
BC2	11/7/98	16.97	481	8.02	12.8	0.25	4.2		NA	103	NA	0.2	22.1	27.4	<1	<0.8	8	0.8	2.6	11.7	0.5	2.3	4.19	7.3	148	1.0	
BC3	11/7/98			8.02	12.8	0.25	4.0		NA	103	NA	0.2	22.4	27.4	<1	<0.8	9	0.8	2.6	11.7	0.5	2.4	4.22	7.3	149	0.9	
Blanchford River, site "BD"																											
BD1	7/3/97	399	11298	8.4	9.0	0.21	NA	NA	24.0	NA	3.76	0.6	18.1	26.46	<1	0.4	10	0.4	1.7	9.45	1.0	0.8	1.25	3.4	49	4	
BD2	7/3/97	469	13281	8.4	9.0	0.21	NA	NA	23.5	NA	5.12	0.6	18.5	26.36	<1	0.4	14	0.5	1.8	9.67	1.1	1.1	1.71	3.9	59	5.2	
BD3	7/3/97	434	12230	8.4	9.0	0.21	NA	NA	23.3	NA	5.51	0.6	17.2	23.89	<1	0.4	15	0.5	1.7	9.06	1.8	1.2	1.76	3.8	57	3.8	
BD1	7/20/97	319	9033	8.3	8.7	0.22	13.6	23.7	27.8	NA	5.54	0.6	18.9	25.5	<1	0.3	17	0.5	2.0	9.99	1.7	1.0	1.64	3.8	58	0.6	
BD2	7/20/97	325	9203	8.3	8.7	0.22	13.6	23.7	27.5	NA	5.82	0.6	19.2	25.55	<1	0.4	19	0.5	2.0	10.1	2.0	1.0	1.83	4.1	63	1.5	
BD3	7/20/97			8.3	8.7	0.22	13.6	23.7	27.2	NA	6.3	0.6	19.0	25.11	<1	0.4	20	0.5	2.1	10.0	2.1	1.0	1.94	4.2	66	1.6	
BD1	8/7/97	151	4276	8.3	NA	0.25	12.1	16.7	29.7	NA	5.62	0.4	22.1	29	<1	0.3	12	0.6	2.4	11.3	0.9	1.3	1.79	4.3	72	0.5	
BD2	8/7/97			8.3	NA	0.25	12.1	16.7	30.2	NA	5.63	0.4	21.9	29.89	<1	0.3	12	0.6	2.4	11.5	0.9	1.3	1.68	4.3	70	1.3	
BD3	8/7/97			8.3	NA	0.25	12.1	16.7	29.9	NA	5.31	0.4	23.3	30.57	<1	0.4	12	0.6	2.4	11.5	0.9	1.2	1.73	4.3	72	0.5	
BD1	9/14/97	78	2209	8.2	11.2	NA	7.5	NA	33.6	NA	6.85	0.4	27.3	34.35	<1	<0.3	12	0.7	2.6	12.4	0.4	1.9	2.56	5.2	80	0.3	
BD2	9/14/97	81	2294	8.2	11.2	NA	7.5	NA	33.4	NA	6.34	0.4	27.2	34.49	<1	<0.3	11	0.6	2.6	12.4	0.4	2.0	2.41	5.1	77	0.2	
BD3	9/14/97			8.2	11.4	NA	7.5	NA	33.1	NA	6.13	0.4	27.2	35.23	<1	<0.3	11	0.6	2.6	12.5	0.4	1.7	2.24	5.0	75	0.3	
Hogum Creek, site "HC"																											
HC1	11/18/97	1	28	7.5	NA	0.18	0.0	1.4	23.3	NA	7.99	0.3	14.6	21.92	1	<0.3	68	0.8	4.4	7.71	20.6	5.5	2.75	8.7	433	2.3	
HC2	11/18/97	1	28	7.5	NA	0.17	0.0	1.4	23.1	NA	8.07	0.2	14.8	22.01	1	<0.3	65	0.8	4.4	7.72	20.6	5.6	2.77	8.7	438	2.6	
HC3	11/18/97	1	28	7.6	NA	0.18	0.0	1.4	23.2	NA	8.06	0.3	14.6	22.19	1	<0.3	68	0.8	4.4	7.77	20.7	5.5	2.72	8.7	435	2.3	

SAMPLE NAME	SAMPLE DATE	STREAM FLOW (cfs)	STREAM FLOW (l/s)	PH	D.O. (units)	Conductivity (mS/cm)	Water Temp (Cels)	Air Temp (Cels)	Inorganic Carbon (mg/L)	Total Alk (mg/L CaCO3)	Sulfate (µg/L)	Ba (µg/L)	Ca (mg/L)	Cr (µg/L)	Cu (µg/L)	Fu (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Na (mg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)	
HC-1	1/6/98	1	28	7.6	12.0	0.20	0.0	0.9	28.8	10.1	0.2	140	2202	1	0.3	56	0.8	4.6	7.67	16.4	5.3	2.91	8.0	436	1.4	
HC-2	1/6/98	1	28	7.6	0.20	0.20	0.0	0.9	29.0	10.1	0.3	141	2192	1	<0.3	56	0.8	4.4	7.62	16.4	5.3	2.96	8.0	438	0.9	
HC-3	1/6/98			7.6		0.20	0.0	-0.9	29.8	10.1	0.3	140	2173	1	<0.3	58	0.8	4.5	7.55	16.3	5.4	2.93	8.0	434	2.7	
HC-1	4/29/98	1283	363	7.40	NA	0.11	3.3	11.4	13.9	NA	0.5	85	12.6	<1	<0.8	33	0.7	3.0	4.15	3.8	4.4	2.90	7.2	267	<0.3	
HC-2	4/29/98	1288	365	7.41	NA	0.11			13.2	NA	0.5	82	12.4	<1	<0.8	25	0.7	3.0	4.09	3.6	4.8	2.95	7.2	261	<0.3	
HC-3	4/29/98			7.39	NA	0.11			13.8	NA	0.5	82	12.5	<1	<0.8	26	0.7	3.0	4.14	3.6	4.8	2.96	7.2	265	<0.3	
HC-1	5/19/98	7.51	213	7.35	11.6	0.10	4.5	16.1	10.7	NA	0.5	78	10.2	<1	<0.8	34	0.7	2.8	3.59	4.0	4.3	2.56	8.0	226	<0.3	
HC-2	5/19/98	8.16	231	7.36	11.6	0.10			11.0	NA	0.5	80	10.2	<1	<0.8	40	0.7	2.8	3.60	4.2	4.1	2.49	8.1	226	<0.3	
HC-3	5/19/98			7.35	11.7	0.10			10.8	NA	0.5	80	10.0	<1	<0.8	35	0.7	2.8	3.57	4.3	4.1	2.53	8.1	222	<0.3	
HC-1	6/5/98	13.84	392	7.38	11.9	0.10	7.5	15.6	NA	5.4	0.6	82	9.9	<1	<0.8	25	0.6	2.8	3.43	3.2	4.2	1.11	8.0	222	<0.3	
HC-2	6/5/98	15.01	425	7.41	11.8	0.10			NA	5.0	0.6	87	10.1	<1	<0.8	27	0.6	2.8	3.45	3.3	3.8	1.12	8.1	227	<0.3	
HC-3	6/5/98			7.40	11.8	0.09			NA	5.4	0.6	85	10.0	<1	<0.8	20	0.6	2.7	3.41	3.2	4.0	1.11	8.0	226	<0.3	
HC-1	7/20/98	8.15	231	8.04	7.7	0.13	15.9	23.3	NA	6.1	0.8	120	15.0	<1	<0.8	31	0.8	3.7	4.96	5.8	6.1	1.23	9.8	334	<0.3	
HC-2	7/20/98			8.06	7.7	0.13	15.9	23.3	NA	6.1	0.8	119	14.6	<1	<0.8	52	0.8	3.6	4.82	6.1	5.2	1.11	9.3	327	<0.3	
HC-3	7/20/98			8.04	7.7	0.13	15.9	23.3	NA	6.0	0.8	121	15.2	<1	<0.8	41	0.8	3.8	5.01	6.1	5.9	1.23	9.8	338	<0.3	
HC-1	8/17/98	2.44	69	7.79	8.7	0.17	11.9	14.9	NA	8.0	4.9	1.1	138	18.9	<1	<0.8	168	0.9	4.4	6.2	10.9	4.6	1.38	9.6	416	<0.3
HC-2	8/17/98	2.44	69	7.81	8.7	0.17	12.0	14.8	NA																	
HC-3	8/17/98	3.09	88	7.80	8.7	0.17	12.0	14.7	NA																	

## **Chapter 3:** **Geochemical dispersion trains of solute and bed sediment trace elements in the Blackfoot River, Montana**

### **I. Abstract**

The Blackfoot River (Montana) and its major tributaries were sampled from the headwaters of the basin to near its confluence with the Clark Fork River over the course of 5 days in August, 1998. Streamflow was measured, fine-grained (<63  $\mu\text{m}$ ) streambed sediment was collected, and the dissolved (<0.2  $\mu\text{m}$ ) phase of the surface water was sampled using clean techniques. Water and sediment collected from near the historic Upper Blackfoot Mining Complex contained the highest concentrations of trace metals in the basin, despite the onset of remediation efforts in 1993. Many solute trace metals were at their highest several kilometers downstream from the mining district, where the river flows through an unremediated marsh system that has collected mine wastes in the past. Downstream of the headwaters area, water and bed sediment metal concentrations declined sharply. Comparison of sediment samples with those collected in August, 1989 and August, 1995 do not show evidence of basin-scale long term changes. The area of the proposed McDonald Gold Project near the confluence of the Landers Fork with the Blackfoot River was not contributing anomalous concentrations of naturally-occurring dissolved metals into the basin.

### **II. Introduction:**

One of the current research priorities of the Mineral Resources Program of the United States Geological Survey (USGS) is to evaluate geochemical baselines in watersheds where mineral deposits erode naturally or are exposed by mining and mineral processing. Baseline characterization research is important for understanding how to differentiate between natural and human influences on the geochemistry of surface waters, soils, and sediments. Globally, there is essentially no pre-disturbance data on the solute geochemistry of rivers in watersheds that have been mined. In order to set realistic remediation targets in contaminated areas and to better quantify potential environmental impacts of proposed mining projects, it is necessary to characterize the geochemical distribution of trace elements in both mining impacted and unimpacted rivers.

The 215 km long Blackfoot River in western Montana is a tributary to the Clark Fork River, which in turn flows into the Columbia River (Fig. 1). It was chosen as a case study for the USGS's investigations on geochemical baselines because it contains both historic and proposed mines. The Upper Blackfoot Mining Complex is located in the headwaters of the basin, and the area has been undergoing remediation since 1993. The proposed mine (the McDonald Gold Project) is located approximately 25 km downstream from the headwaters near the confluence of the Blackfoot River with the Landers Fork. In the research presented here, we characterize the spatial distribution of the aqueous and bed sediment geochemistry in the Blackfoot River and many of its tributaries over a single, short (5 day) time period and make some comparisons with previous data.

The primary goal of the current study was to examine the downstream dispersion of mining-related contaminants in the water and bed sediments of the Blackfoot River from the historical mining area in the headwaters. Although bed sediment dispersion trains have been typically used for prospecting purposes and for impact characterization of mining (Hawkes, 1976; Helgen and Moore, 1996), dispersion trains in the water column are not commonly evaluated in relation to bed sediment trains, even though they are subject to human and aquatic health standards. Detecting levels of trace metals in water samples is typically more difficult than for bed sediments, due to their lower concentrations and their shorter dispersion train lengths. Within each type of dispersion train, it is of geochemical interest to observe how tributaries affect the mainstem concentrations and to identify which elements are more mobile than others downstream from the source of contamination.

A second goal of the project was to compare the abundance and distribution on selected chemical elements in bed sediment in the basin to that determined in 1989 and 1995 by Moore and other (1991) and Menten (1997), respectively. The 1989 sampling event occurred prior to the start of the remediation projects in the headwaters region in 1993. In 1995, Menges (1997) found few changes in the trace metal concentrations in the bed sediments in the basin other than in the immediate area of the remediation site. We wanted

to determine if there had been further changes in the geochemistry of bed sediments in the three years since the sampling represented in the Menges (1997) study.

The third purpose of this study is to bring the unmined McDonald Gold ore body area into the geochemical context of the Blackfoot River watershed. This necessitates testing whether or not there is a measurable input of trace metals from the mineralized yet unmined area to the waters and sediments of the Landers Fork and Blackfoot River in the vicinity of the deposit. Based on research on the dispersion trains in water draining unmined yet mineralized areas, naturally elevated concentrations rarely extend more than a few hundred meters from the source (Hoffman and Fletcher, 1972; Runnells and others, 1992; Schmitt and others, 1993; Leybourne and others, 1998). In bed sediments, natural dispersion trains typically do not extend for longer than 20 km from the mineral source (Helgen and Moore, 1996).

Although Moore and others (1991) also examined the bed sediment and solute dispersion trains in the Blackfoot River watershed, their research took place prior to the remediation work in the headwaters. Additionally they did not use “clean” sampling protocols for surface water. In the past decade, several investigations have demonstrated that standard water quality sampling methods have likely caused some degree of contamination to samples taken from both unpolluted and polluted watersheds (Windom and others, 1991; Benoit, 1994; Taylor and Shiller, 1995). The new clean methods to collect, process, and analyze trace element samples currently are replacing the problematic older methods (Horowitz and others, 1994; Hurley and others, 1996; Balough and others, 1998). With the increasing number of watersheds being impacted by mining and other human activities, it is important to build a database of accurate surface water geochemistry measurements in order to adequately monitor and regulate water quality into the future. As a result, an additional and final purpose to this project is to add to the growing database of water quality measurements which are as accurate and reliable as currently possible.



### **III. Site description and history**

Mining from 1865 to 1953 in the Upper Blackfoot Mining Complex in the headwaters of the Blackfoot River has been linked to water and bed sediment contamination and declines in benthic organisms and fish populations (Spence, 1975; Moore and others, 1991, Menges, 1997). These impacts are not limited to the headwaters, but continue for tens of kilometers downstream. The district is a collection of numerous mines and prospects scattered within the drainages of small tributaries which come together to form the Blackfoot River. The earliest operations consisted of gold placer mining, but later operations led to the building of an on-site smelter, and after the 1920s, activities were expanded to vein mining of Pb, Ag, Au, and Cu (Spence, 1975). Ore and waste rock contain sulfide minerals such as pyrite ( $\text{FeS}_2$ ), galena ( $\text{PbS}$ ), and sphalerite ( $\text{ZnS}$ ), tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), chalcopyrite ( $\text{CuFeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), as well as quartz ( $\text{SiO}_2$ ) and rhodochrosite ( $\text{MnCO}_3$ ) (Pardee and Schrader, 1933). The tailings, waste rock, and acid mine drainage from adits have been the primary sources of contamination to the Blackfoot. A particularly damaging event occurred in 1975, when a tailings dam broke and released approximately 100,000 tons of pyritic mine tailings into the river (Spence, 1975). The collection of mines in the area have been undergoing remediation since 1993 by ASARCO and ARCO. The remediation activities have focussed on plugging adits, excavating, liming, and revegetating waste rock and tailings, and treating acid mine drainage by channeling it into an oxidation pond and a wetland treatment system.

Elsewhere in the basin, little mining has taken place other than some relatively small-scale operations in the Nevada, Elk, and Union Creek basins. Portions of the watershed are used extensively for grazing, irrigation, and logging, but there are no major urban areas or industries. Several of the major tributaries of the Blackfoot River (Landers Fork, Northfork, and Monture Creek) originate in wilderness areas, supplying high quality water and sediment to the mainstem. The Blackfoot River is a Class I trout stream and is

classified by Montana's water quality standards as B-1, indicating it can support all beneficial uses such as drinking water, recreation, and fisheries (MDHES, 1994).

Current mining interests in the watershed are focussed on the McDonald Gold Deposit, near the confluence of the Landers Fork and the Blackfoot River. The proposed mine targets a gold and silver-bearing ore body hosted almost entirely in an lithic-rich rhyolite tuff concealed at the surface by glacial till and alluvium (Schafer and Associates, 1994). The proposed mine would be an open-pit operation with cyanide heap leaching and waste rock disposal situated along the floodplains of the streams. Other studies in the area have shown that the ground water and surface water of the Landers Fork and Blackfoot River are closely connected hydrologically (Nagorski and others, 1998; Nagorski and others, 2001). Notably, sections of both rivers receive perennial inputs of groundwater where they flow adjacent to the ore deposit. Therefore, a major concern is that mining would affect the physical dynamics and geochemical conditions in the adjacent rivers.

#### **IV. Methods**

##### *1. Sampling design:*

We sampled at fourteen sites along the Blackfoot River (BFR) and fourteen tributaries from August 16 to August 20, 1998 (Fig. 1). We selected sites along the BFR so that the mainstem was sampled above and below the major tributaries. This design resulted in more closely spaced sampling intervals in the upper portion of the basin. We did not sample many of the numerous small headwater tributaries, many of which have been impacted by mining. The most upstream site sampled was below most of the remediated area at the headwaters of the Blackfoot River, which is below the confluence of many of the mining-impacted tributaries. Three more tributaries (Shave Gulch, Paymaster Gulch and Swamp Gulch) not sampled for this project join the Blackfoot between the first and second sampling sites. Paymaster Gulch and Swamp Gulch were subject to remediation treatments in the early 1990s. These and other tributaries not included in this study were

omitted because we estimated them to have relatively insignificant flow contributions to the mainstem.

We sampled all the selected tributaries as close to their confluence to the BFR as possible; generally, this was within 1 km of the confluence. For one tributary, Meadow Creek, this resulted in sampling the creek at a location where it flows through the metals-contaminated marsh system. As a result, Meadow Creek was not included in calculations of average tributary concentrations, which were used as estimates of baseline concentrations in the watershed.

We began sampling at the headwaters and progressed downstream, except that we did not sample two sites near the headwaters until the fifth day. Also on the final sampling day, we resampled an upper basin site to check for any changes in river chemistry compared to Day 1 (no measurable changes were found). Considering that the average measured water velocity was 0.5 m/s, the estimated travel time downstream from the headwaters to the confluence (215 km) with the Clark Fork River was 5.2 days. Therefore, we roughly followed a parcel of water as it traveled down the basin. During the study period, weather conditions varied from sunny to partly cloudy, with only trace amounts of precipitation in the watershed (WRCDC, 1999).

## *2. Streamflow measurement:*

We measured streamflow following standard USGS protocol, with the exception that for a few of the small headwater streams that were <2 m in width, we used only 6 instead of the recommended minimum of 10 sampling stations per transect (Rantz and others, 1982). The streamflow measured on the Northfork for this project compared well with the streamflow reported by the real-time USGS gauge data ( $6.23 \pm 0.08$  cubic meters per second ( $\text{m}^3/\text{s}$ ) vs.  $6.40 \pm 0.31$   $\text{m}^3/\text{s}$ , respectively) (USGS, 1999). We determined our measurement precision by measuring discharge at some sites multiple times. Our measurement error decreased with higher streamflows. Accordingly, we assigned sites

with  $<0.28 \text{ m}^3/\text{s}$  an error of  $\pm 0.003 \text{ m}^3/\text{s}$ ,  $0.28\text{-}1.84 \text{ m}^3/\text{s}$  an error of  $\pm 0.11 \text{ m}^3/\text{s}$ , and  $>1.84 \text{ m}^3/\text{s}$  an error of  $\pm 0.17 \text{ m}^3/\text{s}$ . These errors represent the maximum measurement discrepancies obtained by the multiple measurements.

### 3. *Water sampling:*

At each site, we measured pH, dissolved oxygen, temperature, and conductivity in situ, using an Orion model 230A meter with a Ross electrode for pH; an Orion model 820 meter for dissolved oxygen; a Hach Conductivity/TDS meter for conductivity; and a Barnant 100 Thermocouple Thermometer Model No. 600-2820 (JKT) for temperature.

At all sites, we collected the water samples by depth and width integration as best as possible. At 12 of the sites, we collected a single water sample; at 13 of the sites we collected 4 samples; and at 3 sites we collected 10 samples. The purpose of collecting multiple samples per site was to define the spatial variability along the sampling transect. Four samples per site were deemed adequate for this estimation, based on previous studies in the upper part of the basin (Nagorski and others, 1998). However, at the 3 sites where we collected 10 samples, we did so to test whether 4 samples could adequately capture variability in differently-sized river sections. Results show insignificant improvement in the within-site variability estimate with the use of 10 versus 4 samples. Error bars on the data from sites with multiple samples represent the standard deviation of the mean concentration of the multiple samples. Error bars at sites with single samples were derived from the average percent relative standard deviation at all sites with multiple samples.

We collected, processed, and filtered samples using clean techniques. These measures included the exclusive use of materials that had undergone extensive acid-washing (2 hours in 50% HCl followed by 24 hours in 1% trace metal grade  $\text{HNO}_3$ , with a minimum of 3 rinses with Milli-Q deionized water before and after each acid treatment), double-bagging of sample bottles, and filtering of samples under a class 100 laminar flow hood wearing clean nitrile gloves. In the field, two people were required to obtain the

water samples, and both wore nitrile gloves that were changed between each site. One person was designated as “dirty hands” and the other as “clean hands.” The former handled the outside bag, whereas only the latter could open the inner bag and take out the sample bottle. The clean hands person opened the sample bottle moments before sampling, emptied out the Milli-Q water which was stored in it, and rinsed the bottle and cap with river water. The sample was then taken by filling the 1-liter LDPE Nalgene sample bottle to capacity. We were careful to always sample upstream of where we had physically disturbed the site by wading and to sample upstream of bridges. We then returned the sample bottle to its double bags and stored it on ice for transport to the laboratory (University of Montana’s Murdock Environmental Biogeochemistry Laboratory).

At the laboratory, we filtered the samples under the laminar flow hood within 12 hours of collection. We used Gelman Sciences Serum Acrodisc GF filters (each with a borosilicate glass fiber prefilter layer over a 0.2 $\mu$ m polyethersulfone membrane) and discarded the first 50 mL of filtrate in order to reduce the effective pore size of the filter and to rinse the filtration materials (Taylor and Shiller, 1995). Next, we filtered 60 mL of sample into pre-cleaned but non-acid washed amber glass bottles for anion and carbon analysis. We then filtered another 125 mL into ultra-clean LDPE bottles for cation and arsenic analysis. We acidified each of these samples with approximately 200  $\mu$ L (to bring the pH to <2) of ultrapure, double distilled from quartz, Optima (Fisher Scientific) HCl. We stored the sample bottles in sealed plastic bags until analysis.

#### *4. Bed sediment sampling:*

Following collection of the water samples, we took streambed sediment samples at each site. At half of the sites, we collected 4 samples, and at the other half, we collected 1 sample. At the single-sample sites, we integrated the sample over the same sized area that would have been divided into four sections had the site been selected for multiple samples. Error bars were determined the same way as described for water samples, in which the

mean variability found at sites with multiple samples was applied to sites with single samples.

We sampled the sediment by scooping the top 1-2 centimeters of fine-grained bed sediment with a plastic spoon. Sediment availability varied among sites, and hence the area from which sediment was integrated per sample varied from approximately 30-100 meters of streambank length. We strove to collect an equal amount of sample from each channel bank and sieved the sediment with ambient stream water through a 63 $\mu$ m mesh plastic screen set in a plastic funnel casing. After collecting the sieved sediment-water slurries in 250 mL acid washed polypropylene bottles, we stored them on ice for transport to the laboratory.

Upon returning to the laboratory at the end of the field day, we centrifuged the samples at 2000 rpm for 15 minutes, decanted the water, and dried the sediments at 70°C for one day. Next, we crushed each dried sample to a fine powder in the sample bottle with an acid-washed glass rod. We used a microwave aqua-regia digest procedure to prepare the samples for analysis. This method entailed adding 0.5 ml of Milli-Q water, 1.25 ml trace metal grade HNO<sub>3</sub>, and 3.75 ml trace metal grade HCl to 0.5 g of sediment sample, microwaving the mixture for 6 minutes on high power (ca. 570 watts), and adding Milli-Q water to bring the cooled solution to 50 grams. We centrifuged the completed digests for 5 minutes at 2500 rpm and transferred the clarified solutions to acid-washed polyethylene bottles for chemical analysis.

##### *5. Laboratory analysis:*

We analyzed the trace element and major ion concentrations in the water using a Thermo Jarrel-Ash ICAPES (IRIS) with ultrasonic nebulization (Cetac, U-5000AT+) according to EPA Method 200.15 (Martin and others, 1994). We used the ICAPES with cyclone nebulization according to EPA Method 200.7 (EPA, 1991) for the analysis of sediment digests.

We measured anions on a Dionex Ion Chromatograph (IC) within 48 hours of sample collection according to EPA Method 300.0 (Pfaff, 1993). We acidified remaining sample in the amber bottles with reagent-grade HCl to pH<2 and used it for determination of organic carbon using a Shimadzu Carbon Analyzer according to Standard Method 505A (Franson, 1985) 46 days after sample collection. We determined alkalinity by titration with sulfuric acid to pH 4.5 within 1 day of sample collection.

Following Standard Method 303A, we measured total arsenic using atomic absorption spectroscopy with hydride generation (HGAAS) (Franson, 1985). However, we modified the arsenic reduction method to follow a method developed at our laboratory (Mickey, written communication, 1997). This method calls for the addition of KI and HCl to all standards and samples to achieve final concentrations of 2% KI and 1 M HCl. We made the additions at least 2 hours prior to analysis to allow for complete reduction of oxidized arsenic species. We ran solutions of 0.35% sodium borohydride (stabilized with 0.5% NaOH and 6N HCl) together with the samples through the hydride generator.

#### *6. Quality assurance/ quality control:*

We conducted all laboratory analysis under a strict quality control program. At the start of each day's analysis, we calibrated all instruments and checked and corrected (if needed) the calibration at intervals of approximately every 10 samples. The detection limits used, called the Practical Quantifiable Limits (PQL), were defined as the concentrations at which elements could be reproduced within a variability range of approximately 30%.

For water samples, the mean difference between duplicate runs of samples on all instruments was less than 8.5%. Spike recoveries for all analytes measured above detection were between 92-115%. On the ICAPES, USGS water standards T-143 and T-145 run with water sample analysis fell within the reported acceptable range for all elements except for Ba in T-143 and T-145 and Sr in T-145, which were slightly low. External standards run on the HGAAS (USGS T-143 and T-113) and IC (QC SPEX) also fell

within the reported ranges. Accuracy was checked on the HGAAS, Shimadzu, and the IC by running in-house standards, and the mean differences between the standards and the measured concentrations were less than 10%. Lab blanks were below the detection limits on all instruments. Field blanks were mostly below detection, with the exception that Ca (0.02 mg/L), Mg (0.01 mg/L), and Na (0.23 mg/L) were detected in most of the blanks. These levels are low enough not to interfere with concentrations in environmental samples.

During ICAPES analysis of the sediment digests, the mean percent difference between duplicate runs of samples was less than 10%. Mean percent recoveries for spikes of all analytes were between 89-105%. As with the water samples, USGS standards T-143 and T-145 were analyzed using ICAPES during sediment analysis. All elements fell within the reported range, with the exception of mean Ca in T-143, which was 2% higher than the reported acceptable limit. All lab blanks were below detection limits, as were digest blanks, with the exception of trace amounts of Ca, Cr, Fe, Mg, Na, Si, and Ti. These contaminants were also not high enough to interfere with the concentrations in the environmental samples.

#### 7. Dissolved load calculations

Loads were calculated by multiplying the discharge ( $\text{m}^3/\text{s}$ ) at each site with the concentration ( $\text{mg/L}$  or  $\mu\text{g/L}$ ) of the solute of interest. The propagated error associated with each load calculation was found using the formula:

$$\text{Load error} = \sqrt{B^2 \Delta A^2 + A^2 \Delta B^2}, \quad (\text{Taylor, 1982})$$

where

B = discharge;

$\Delta B$  = discharge error;

A = concentration of solute;

$\Delta A$  = concentration error (within-site variability)

Loads could not be quantified at sites where solute concentrations were below the specific element's PQL.



## 8. Average tributary concentrations

The chemical concentrations in the water and bed sediments of the mainstem were compared with the average concentrations in the water and bed sediments of the Blackfoot River tributaries. However, Meadow Creek was not included in the calculations of average tributary concentrations because it was sampled where it flows through the contaminated marshes near the headwaters. Many tributaries had some metal concentrations below the PQL. In these cases, we assigned a value of one-half the PQL to the undetectable concentration and calculated the averages using these assigned values.

## **V. Results**

### *1. Water chemistry:*

#### *a. Mainstem*

Dissolved ( $<0.2 \mu\text{m}$ ) Al, Cd, Co, Cu, Mn, Ni, S,  $\text{SO}_4^{2-}$  and Zn peaked in the headwaters area, below the historic mining district, and then declined sharply downstream as cleaner tributaries joined the mainstem (Table 1). Mainstem Al, Cd, Co, Cu, Fe, Mn, and Ni concentrations dropped to average tributary concentrations or fell below detection at distances of 9-19 km from the most upstream site (Fig. 2a). Zinc and  $\text{SO}_4^{2-}$  were more mobile, remaining elevated above average tributary concentrations for 25 km and 37 km, respectively (Fig. 2b,c). Zinc may have been elevated over the average tributary levels for even longer distances, but this cannot be determined due to its drop below its PQL at 25 km downstream from the headwaters. Samples from the uppermost 3 kms of the mainstem had concentrations of Al, Co, Cu, Mn, Ni, S, and  $\text{SO}_4^{2-}$  that were at least 3 times greater than the mean tributary concentrations. Manganese and Zn were enriched by at least 2 orders of magnitude (exact enrichment factors cannot be calculated due to the undetectable levels lower in the basin).

Aluminum, Co, Cu, Mn, Ni, S,  $\text{SO}_4^{2-}$  and Zn were at their highest levels not at the site closest to the mining district, but at the second site, 2.5 km downstream from the first (Fig. 2a, b, c). This second site is located in the contaminated marsh system and downstream of the input of Pass Creek, Paymaster Creek, and Swamp Gulch. Conductivity, Fe, K, Li, Na, and Si were also higher at the second site, and pH was lower (7.3 compared to 7.7) (Figure 2d).

Other elements did not follow the pattern of declining downstream from a peak at the uppermost couple of sites. For example, Fe did not peak until river km 203.3 (BFR-above Alice Creek), where the BFR emerges from the second of three marshes downstream from the mining district (Figure 2e). Arsenic was below detection ( $<0.2 \mu\text{g/L}$ ) at the uppermost site, but its concentration gradually increased to its peak of  $2.3 \mu\text{g/L}$  at river km 108.5, below the confluence with Nevada Creek, which had the highest As concentration in the basin samples (Figure 2f). Calcium concentrations almost doubled between the headwaters and river km 153 (Figure 2g). Mainstem Ba, K, Li, Mg, Na, Si, and Sr concentrations fluctuated little downstream, even though tributary concentrations of these elements varied far more widely.

#### *b. Tributaries*

Most tributaries were below detection levels for dissolved Al, Cd, Co, Cu, Mn, Ni, and Zn (Table 1). Tributaries with exceptionally high concentrations (relative to the mainstem) of measured solutes include: Hogum Creek, with the highest Fe and Sr detected in all the samples; Meadow and Elk Creeks, which were the only tributaries with detectable Al ( $>5 \mu\text{g/L}$ ); and Nevada Creek, with the highest dissolved organic carbon, As, K, Li, Na, and Si of all basin-wide samples. Meadow Creek, sampled where it flows through the contaminated marshes, had the highest tributary concentrations of Cd, Co, Cu, Mn, Ni, S, and Zn, and it was very similar chemically to the Blackfoot River sites immediately above and below their confluence.

In the Landers Fork, concentrations of Cd, Co, Cu, Fe, Mn, Ni, and Zn were all below detection. It was the only site in the basin with Mn at levels below detection ( $<0.3 \mu\text{g/L}$ ) and was one of only three sites with Fe below detection ( $<5 \mu\text{g/L}$ ). Most of the detectable solutes (sulfate, As, K, Li, Na, S, Si, and Sr) were lower than the mean tributary concentrations, while alkalinity, Ba, Ca, and Mg were higher than the mean. All of these detectable elements fell within one standard deviation of the mean concentrations in the watershed tributaries, indicating that the Landers Fork was not geochemically anomalous in the basin.

*c. Reactive solutes:*

Reactivity of the solutes in the Blackfoot was evaluated by examining whether a drop in solute concentration occurred between two mainstem sites after accounting for tributary contributions and measurement errors. A loss in solute concentrations along losing or steady-streamflow reaches (determined by the streamflow measurements) was assumed to be a product of solutes transferring to the solid phase. Results of this evaluation indicated that  $\text{SO}_4^{2-}$ , Fe, Mn, S, and Zn were dropping out of solution along several reaches of the river. Iron, Mn, and Zn were reactive between river kms 210.0 and 209.8 (above and below Meadow Creek); between kms 203.3 and 193.2 (BFR-above Alice Creek to BFR-above Hogum Creek); and between kms 193.2 and 187.7 (BFR-above Hogum Creek to BFR-above Landers Fork). Iron and Mn also were reactive along the reach above and below Nevada Creek's input (river kms 117.6 to 108.5). Sulfate (and S) were reactive between river kms 203.3 and 193.2. Additionally, alkalinity (as  $\text{mg/L CaCO}_3$ ) and Ba were found to be reactive between the uppermost site (river km 212.5) and the second site (river km 210.0).

Gaining reaches were more difficult to evaluate for reactivity, because a decrease in concentration may have occurred due to dilution by the gained water or by chemical reactions. Hence, for the most part, reactivity could not be determined along gaining

reaches because groundwater entering the reach was not sampled. However, if the concentration at the downstream site was still lower than predicted assuming the extreme case that the gained water had zero dissolved elements, then we could determine that solutes were coming out of solution along the stretch of the river. According to this evaluation, Cd, Cu, Mn and Zn were reactive along the gaining reach between river km 209.8 and km 203.3, and Fe and Mn were reactive along the gaining reach between river kms 108.5 and 74.4.

*d. Evaluation of the tributary load contributions to the BFR:*

There was generally a positive, approximately linear relationship between the solute loads of alkalinity, As,  $\text{SO}_4^{2-}$ , Ba, Ca, K, Li, Mg, Na, Si, and Sr in tributaries of the BFR and the tributary sizes (expressed as discharge) (Figure 3a). Manganese loads had no clear pattern, indicating that its load contributions from tributaries could not be predicted from discharge (Figure 3b). Because no more than two tributaries contained above detection limit levels of Al, Cd, Co, Cr, Cu, Ni, and Zn, no conclusions could be made about the relationship between loads of those metals with tributary sizes. Considering the detectable elements, the Landers Fork was not an unusually large source of solute loads, because its solute loads fall in line with most other tributaries (Fig. 3a and 3c). Because the amount by which it increased the mainstem load of detectable trace metals is not unusually high for its size, a geochemical signal of the McDonald ore body in the area was not discernable in the solute phase. Outliers in the data included Hogum Creek, with high loads of Fe; Clearwater River with low loads of most solutes, especially Fe; and Nevada Creek with anomalously large loads of As,  $\text{SO}_4^{2-}$ , K, Li, Mn, Na, Si, and Sr (Figure 3c).

## 2. *Bed sediment*

### a. *Mainstem*

A sharp downstream decline in the mainstem sediment concentrations is seen for Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, Si, V, and Zn (Fig. 4a, b). Bed sediment collected immediately below the mining district (river km 212.5) contained the highest concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, and Zn of all the mainstem and tributary samples. These elements were elevated over average tributary concentrations by up to 3 orders of magnitude. The furthest downstream site in the basin, at river km 6.0, contained the lowest concentrations of Al, As, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn in the mainstem.

Arsenic, Co, Cu, Fe, Pb, V, and Zn reached average tributary concentrations at river km 117.6, almost 100 km downstream from the mines. Aluminum, Ba, Be, Cd, Mn, Ni, S, reached average tributary concentrations by river km 186.6 (below input of the Landers Fork), about 30 km downstream of the headwaters (Fig. 4c, d).

Yet not all elements were at a maximum in the headwaters. In fact, the sample taken below the Mike Horse Mine contained the lowest concentrations of Be, Li, Na, P, and Ti in the Blackfoot mainstem and the lowest Ba in all the basin samples. Barium, Ca, Cr, K, Li, Mg, Na, P, Sr, and Ti do not show clear downstream spatial trends below the mine (Figure 4e). Calcium and Mg are at their lowest between river kms 210.0 and 186.6 (Figure 4f). Chromium, K, P, Sr, and Ti exhibit relatively little fluctuation; their maximum concentrations in the mainstem are no more than twice their minimum concentrations.

### b. *Tributaries*

Downstream from the headwaters mining complex, the influence of tributaries with atypical concentrations of some elements is seen on the mainstem. For example, Sr concentrations increase below the input of Hogum Creek (river km 187.7) and Nevada Creek (river km 108.5), which have anomalously high Sr levels. A 2 to 4-fold increase in

Mg and Ca in the BFR mainstem occurs below the confluence with the Landers Fork (river km 186.6), which contained the highest Mg and Ca concentrations of the tributaries sampled (Figure 4f).

Meadow Creek, which joins the Blackfoot several kms downstream from the Mike Horse Mine in the marsh area, contained the highest Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, Si, and Zn of all tributaries sampled. As noted earlier, Meadow Creek was sampled in the marshy area and only 10 m upstream of its confluence with the Blackfoot, and as a result, its high concentrations of solute and sediment metals may be due to influence of the mining- contaminated marsh itself. Monture Creek had the lowest concentrations of Al, As, Cr, Cu, Fe, K, Mg, Na, Ni, Si, Ti, V, and Zn of all the basin samples. No other site contained as many elements which were at minimum basin concentrations. The Hardscrabble Creek sample had the highest Ba and the lowest Co and Li of the tributaries. Hogum Creek contained the highest Be of the tributaries and the highest Cr, P, and Sr of all the basin samples. Arrastra Creek had the highest V and B (together with Elk Creek), the lowest Mn of all the tributaries, and the highest Li concentrations of all the sites in the basin. The highest Na concentration was found in the Nevada Creek sample, and the sample from Elk Creek had the highest K of both mainstem and tributary samples. The Clearwater River, Monture Creek, and Elk Creek were the only sites with As concentrations below detection (<6.5 ppm).

The Landers Fork was anomalous in that it had the highest Mg concentrations of all the tributaries, the highest Ca of all the basin-wide samples, the lowest Ba of all tributaries, and the lowest S concentrations found in all of the basin-wide samples. Still, elemental concentrations in the sediments from the Landers Fork fell within one standard deviation of the mean concentrations of the basin tributaries, with the exception that its Ca and Mg concentrations were higher and its P and S concentrations were lower than the mean  $\pm 1$  standard deviation. This result implies that a geochemical signal of the McDonald ore body was not found in the streambed sediments either.

### *c. Comparisons with 1989 and 1995 bed sediment data*

In August 1989, Moore and others (1991) collected bed sediment samples at many of the same sites sampled in this study. In August, 1995, Menges (1997) revisited many of those sites for bed sediment collection, and she digested and analyzed both the 1989 and 1995 samples using the same method used in this study. Hence, direct comparisons among the sets of data can be made.

Generally, the downstream trends of metal concentrations are the same for each of the datasets. In all of them, there is a steep downstream decline in such elements as Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn, which are typically at least one order of magnitude higher in the headwaters than in most of the mainstem (Fig. 5). Although there are some site-specific changes, a basin-wide systematic decline in metal concentrations through time is not apparent.

## **VI. Discussion**

### *1. Water chemistry:*

Much of the sharp decline in the solute trace element concentrations may be explained by simple dilution by cleaner tributaries. Yet not all elements exhibited the same proportional declines in trace elements at each stage downstream. The longer distance (from the mining complex) over which above-average tributary concentrations of Zn and  $\text{SO}_4^{2-}$  concentrations persisted compared to other solutes can be explained by their higher degree of conservative behavior. Although the load data indicate that both  $\text{SO}_4^{2-}$  and Zn were reactive in the upper basin, they were less reactive than elements such as Al, Cu, and Fe. Zinc is generally believed to be more mobile than other trace metals in aqueous systems. Its sorption onto amorphous Fe oxyhydroxides is reportedly favored at higher pH levels than for many other trace metals, (Benjamin and Leckie, 1981; Filipek and others,

1987; Rampe and Runnells, 1989). Therefore, it would be expected to remain in the dissolved phase for a greater distance downstream from an acidic source than would the more reactive metals. Other researchers have identified  $\text{SO}_4^{2-}$  as a nearly or fully conservative ion in surface water as well (e.g. Bencala and others, 1987; Kimball and others, 1994; Schemel and others, 2000).

The reactivity of many of the trace metals and sulfate in the upper basin is expected in oxygenated, near-neutral pH surface waters. Presumably the metals are being lost from the water column by microbially-mediated precipitation and sorption reactions involving the formation of Fe and Mn oxides and the co-precipitation of other trace metals, metal sulfate formation, and scavenging by organic matter in the river. Such processes have been documented in many other streams impacted by mining contamination (e.g. Rampe and Runnells, 1989; McKnight and Bencala, 1990; Schemel and others, 2000). Additionally, our results are largely consistent with the geochemical patterns observed by Moore and others (1991) in their Blackfoot River water samples.

The increase in concentrations of several dissolved metals and sulfate and the drop in pH at the second mainstem site, a couple of kilometers below the mining district, are likely still due to the impacts from the mining. This sampling site (at river km 210.0) is in a marsh area, the first part of a system of three marshes that extend from river km 211.6 to 196.6. The marshes have collected wastes from the past mine operations, including those released during the tailings dam break in 1975 (Spence, 1975; Moore and others, 1991.) The site is also downstream of Paymaster Creek and Swamp Gulch, which are small, mining-impacted tributaries which were not sampled in this study. Although these creeks have undergone remediation, it is possible that they still supplied the metals and acidity measured in the samples at river km 210.0.

The mining-contaminated marshes might have been the source for the higher metals at the second site due to geochemical processes in the fine-grained organic-rich marsh sediments. Geochemical partitioning within saturated sediments is strongly controlled by



pH and reduction-oxidation reactions, and other studies have suggested that marshes, wetlands, hyporheic sediments, and reservoir sediments can therefore influence the geochemistry of receiving waters (Shotyk, 1988, Moore, 1994; Shiller, 1997; Nagorski and Moore, 1999). In reduced zones, many metals are favored to reside in the solute phase over the particulate phase, largely due to the instability of Fe- and Mn- oxides and hydroxides, which in turn can release co-precipitated metals when dissolved (Stumm and Morgan, 1996). Although no groundwater was sampled in this study, it is reasonable to speculate that it had higher metal concentration than did the oxygenated overlying surface waters. Hence, the increase in filterable metals in the surface water may be a result of hydrologic flushing of the more highly concentrated marsh ground water into the stream channel.

## *2. Bed sediment*

The high concentrations of metals in the bed sediments at the uppermost sites indicate that the headwater mining district is still the major source of contaminants to the sediments of the Blackfoot River. The relatively low-metal sediment concentrations in upper-basin tributaries explain the sharp downstream decline in metal concentrations in the upper basin. Because Pass Creek, Alice Creek, Hardscrabble Creek, and the Landers Fork contain many-fold lower concentrations of elements such as As, Cd, Cu, Fe, Mn, Ni, Pb, S, and Zn, the mixing of their sediments with those in the mainstem lead to the observed declines in metal concentrations. (Table 2 and Fig. 5).

In her 1995 samples, Menges (1997) calculated that the bed sediment concentrations of Al, As, Cd, Fe, Mn, Ni, and Pb reached average tributary levels or fell below detection at 25 km from the headwaters, and that Cu and Zn reached average tributary concentrations at 80 and 140 km from the headwaters, respectively. Results from this project are somewhat different, with As, Fe, and Pb persisting over average tributary values for longer distances, up to 97 km downstream from the mining district. However,

these discrepancies are most likely merely a product of differences in the amount and type of data used to calculate the average tributary values in the two studies. Our study included a larger number of tributaries than did the study by Menges (1997). Although both projects compared mainstem concentrations to average concentrations in uncontaminated tributaries, the use of additional data in our calculation lowered the levels for the sediment concentrations. Importantly, Monture Creek was not sampled by Menges (1997), while we found this tributary to contain the lowest basin-wide concentrations of Al, As, Cr, Cu, Fe, K, Mg, Na, Ni, Si, Ti, V, and Zn. The lack of differences in the mainstem bed sediment concentrations in 1989, 1995, and 1998 further support this explanation for differences in attainment of average tributary levels as being a difference in the data used in the average tributary calculations rather than true changes in the sediment concentrations and distributions over time. These results underscore the importance of having large sample sizes, using consistent sampling designs, and employing consistent sample preparation and analytical protocols in long-term observational studies.

### *3. Differences between trends in water and sediment dispersion trains:*

Although in general the metal concentrations in both the water and bed sediment were highest in the headwaters region, their patterns did not correspond exactly. While the bed sediment metal concentrations exhibited predictable dispersion curves according to sediment dilution models (Hawkes, 1976; Helgen and Moore, 1996), the solute trends were more complicated. Their pattern irregularities were likely due to their higher sensitivity to tributary contributions, in-stream chemical reactions, ground water inputs, and other physical and chemical factors in the watershed.

An example of the differences in sediment and water patterns is the As distributions. Although the lowest solute As concentrations in the basin were in the headwaters, sediment concentrations of As were highest there, indicating strong partitioning into the solid phase for As or major differences in As sources (Fig. 2d and 4a).

Additionally, solute Fe was relatively low at the headwater sites and peaked at river km 203, while sediment Fe was highest at the top of the basin and declined by over an order of magnitude downstream (Fig. 2c and 4b.) Comparison of sediment with solute distributions of other metals also show that many solute peaks were offset by one or two sites downstream of the mines. This trend may indicate that some solutes near the remediated mining district were being precipitated out of the water column, but the downstream marshes or unsampled tributaries resupplied the solute phase with some trace elements.

## **VII. Summary and Conclusions**

Bed sediment and water quality analysis of samples taken from the Blackfoot River and its major tributaries show a downstream decline in trace metal concentrations from the general vicinity of the historic Upper Blackfoot Mining Complex. Most solute contaminants extended for 20 km downstream of the mining complex, while elevated metal concentrations in sediments extended for up to 100 km below the headwaters. Sediment metal concentrations follow patterns predicted by simple dilution models (Helgen and Moore, 1996), while solute trends were more complicated. Solute  $\text{SO}_4^{2-}$ , Cd, Cu, Fe, Mn, and Zn were identified as behaving non-conservatively along portions of the river, mostly in the headwaters area.

Comparison of the trends in water and sediment dispersion trains reveal that many solute peaks occurred one or two sites further downstream from the headwaters than the sediment samples, which showed peak concentrations mostly at the furthest upstream site. This indicates that solute concentrations near the remediated mining district might have been partially transferred to the solid phase, but the contaminated marshes or unsampled tributaries resupplied the dissolved phase with some trace metals.

The Landers Fork had no anomalously high solute concentrations or loads, at least for the detectable elements, and only a few anomalously high sediment concentrations despite its proximity to an unmined ore body. No basin-wide changes in sediment concentrations of metals were found compared to those collected in 1989 and 1995 despite the onset of remediation work in the headwaters in 1993. Aluminum, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn were still at least one order of magnitude higher in the headwaters than in most of the mainstem.

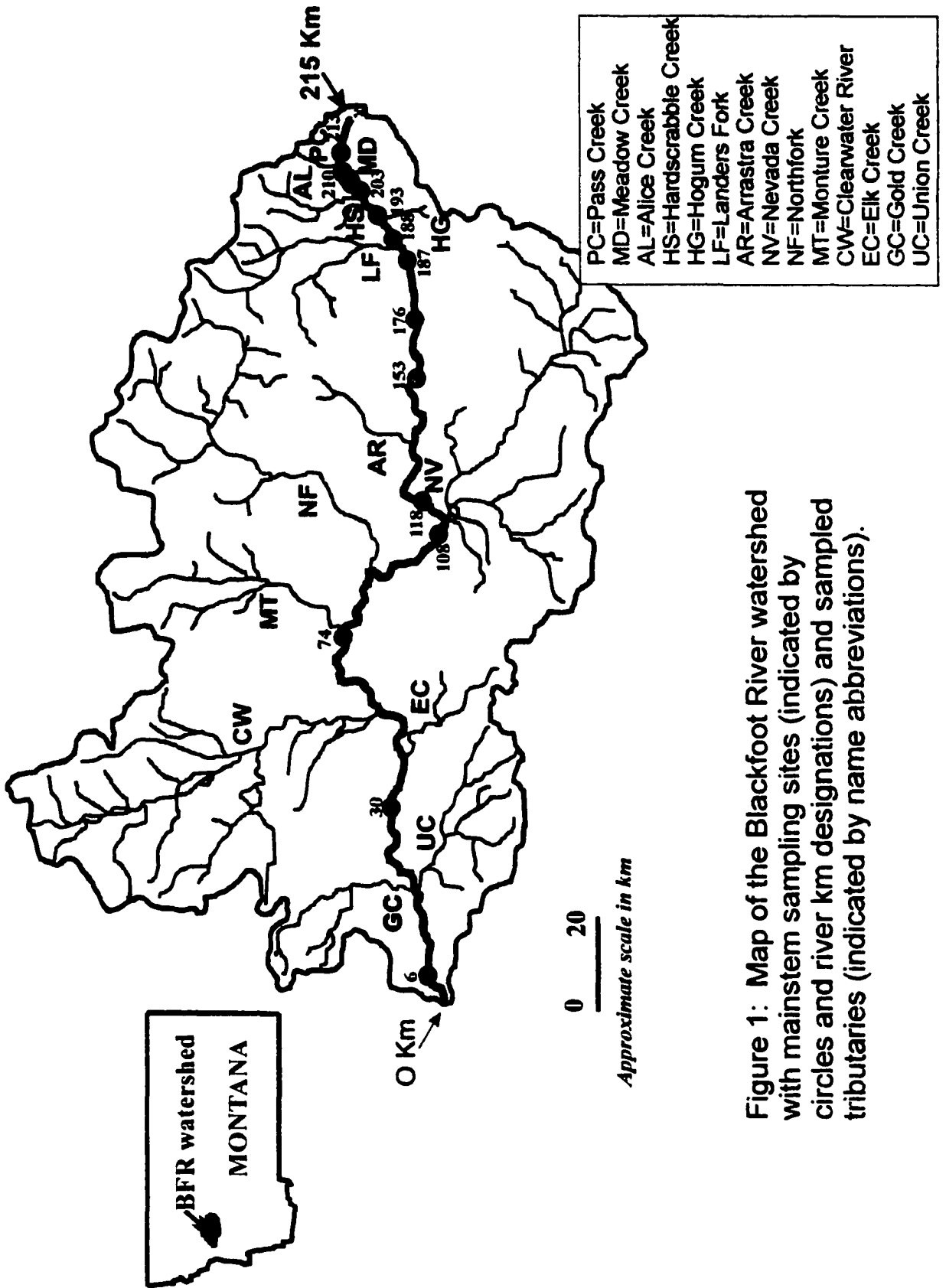
Table 1. Mean concentrations of filtered (<0.2µm) water samples.

River Km	Q (m <sup>3</sup> /s)	pH (units)	D.O. (mg/L)	Alk. (mg/L)	Sulfate (mg/L)	Org. C (mg/L)	As (µg/L)	Al (µg/L)	Ba (µg/L)	Ca (mg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Na (mg/L)	Ni (µg/L)	S (mg/L)	Si (mg/L)	Sr (µg/L)	Zn (µg/L)	
<b>PQL</b>																									
<b>BLACKFOOT MAINSTEM</b>																									
212.5	0.10	7.69	8.12	86	48.2	<1	0.2	5	1	0.01	0.5	0.5	0.8	5	0.10	0.5	0.01	0.3	0.15	2	0.02	0.02	2	0.2	
BF bel. Mike Horse Mine							0.2	<5	143	25.14	2.6	<0.5	3.6	5	0.6	1.3	14.42	157.4	2.39	<2	14.25	3.66	73	535.3	
BF ab. Meadow	0.16	7.27	8.73	46	88.8	1.0	<0.2	10	103	26.85	2.1	0.9	4.0	27	0.9	2.1	14.05	244.8	4.13	3	25.95	6.79	76	762.1	
209.8	0.21	7.51	8.71	51	87.4	1.0	<0.2	10	103	26.00	1.8	0.7	3.9	20	0.9	2.0	13.47	209.5	3.68	2	24.33	6.63	73	681.2	
BF bel. Meadow							0.2	<5	198	25.53	0.6	<0.5	0.9	37	0.7	1.3	12.56	81.8	1.95	<2	13.13	5.96	74	84.2	
BF ab. Alice Cr.	0.44	7.86	8.50	78	44.3	1.4	0.2	<5	228	26.47	<0.5	<0.5	<0.8	21	0.8	2.2	11.40	2.5	2.00	<2	4.02	6.50	110	1.6	
BF ab. Hogum	0.93	8.18	9.43	104	13.3	1.2	0.4	<5	213	26.04	<0.5	<0.5	<0.8	16	0.8	2.6	10.80	1.0	2.29	<2	3.72	6.79	140	0.6	
BF ab. Landers Fork	1.09	8.27	9.71	104	12.8	1.3	0.4	<5	232	30.72	<0.5	<0.5	<0.8	7	0.6	2.4	11.38	0.5	1.36	<2	1.95	4.97	89	<0.2	
BF bel. Landers Fork	3.09	8.25	9.83	131	6.6	<1	0.5	<5	232	35.51	<0.5	<0.5	<0.8	<5	0.6	2.4	11.49	1.2	1.16	<2	1.97	4.97	91	<0.2	
BF at Lincoln	1.53	8.11	7.78	120	6.6	<1	0.5	<5	228	42.84	<0.5	<0.5	<0.8	11	0.8	3.4	12.32	3.3	1.68	<2	1.76	5.79	110	<0.2	
BF ab. Nevada	5.87	8.31	9.61	170	5.7	<1	1.1	<5	224	41.45	<0.5	<0.5	<0.8	18	0.9	3.5	12.58	7.6	1.77	<2	1.67	6.16	110	<0.2	
BF ab. Nevada	6.78	8.38	9.98	144	5.5	<1	1.5	<5	203	41.01	<0.5	<0.5	<0.8	14	1.3	4.9	12.21	8.6	3.89	<2	2.73	7.19	142	<0.2	
BF bel. Nevada	7.43	8.46	9.75	143	9.3	1.9	2.3	<5	209	33.27	<0.5	<0.5	<0.8	6	0.9	3.6	12.46	1.6	2.48	<2	1.91	4.53	99	<0.2	
BF bel. Monture Cr.	17.77	8.35	9.96	130	6.6	1.4	1.3	<5	199	30.56	<0.5	<0.5	<0.8	6	0.9	3.9	11.80	1.5	2.61	<2	1.74	4.37	90	<0.2	
BF at Whitaker Bridge	25.60	8.74	11.27	121	6.0	1.6	1.2	<5	198	31.47	<0.5	<0.5	<0.8	5	0.9	3.9	11.82	1.6	2.70	<2	1.73	4.16	89	<0.2	
BF at Marco	20.59	8.77	10.25	123	6.0	1.7	1.1	<5																	
<b>TRIBUTARIES</b>																									
210.8	0.01	7.90	8.50	80	4.3	<1	0.9	<5	215	18.52	<0.5	<0.5	<0.8	5	0.4	0.8	7.35	3.2	2.01	<2	1.28	5.14	55	0.4	
Pass Creek							0.1	6	98	25.99	1.9	0.6	3.7	18	0.9	2.0	13.51	191.7	3.82	2	24.56	6.51	74	670.9	
Meadow Cr.	0.05	7.53	8.24	45	85.6	1.0	0.1	<5	281	27.36	0.5	<0.5	<0.8	19	0.7	2.3	11.18	2.3	1.63	<2	0.84	5.41	73	<0.2	
Alice Creek	0.43	8.17	8.42	110	2.8	1.3	0.4	<5	385	39.26	<0.5	<0.5	<0.8	32	1.7	6.4	14.59	1.6	3.26	<2	0.49	9.82	130	<0.2	
Hardscrabble Cr.	195.6	0.03	8.40	8.52	155	1.6	4.1	1.0	138	18.93	<0.5	<0.5	<0.8	168	0.9	4.4	6.19	10.9	4.57	<2	1.38	9.64	416	<0.2	
Hogum Creek	192.4	0.08	7.80	8.68	80	4.9	2.5	<5	245	33.43	<0.5	<0.5	<0.8	<5	0.5	2.2	11.69	<0.3	0.87	<2	0.87	3.79	55	<0.2	
Landers Fork	187.2	2.04	8.31	9.71	132	2.9	<1	<5	100	24.52	<0.5	<0.5	<0.8	<5	0.4	2.0	9.84	0.7	1.30	<2	0.76	4.69	73	<0.2	
Arastra Creek	131.1	0.66	8.27	10.47	90	2.7	<1	<5	121	42.86	<0.5	<0.5	<0.8	18	3.2	11.7	10.98	18.2	13.35	<2	8.19	12.58	293	<0.2	
Nevada Creek	109.1	1.19	8.50	9.43	158	28.0	7.1	<5	229	30.99	<0.5	<0.5	<0.8	<5	0.5	2.0	13.91	0.6	0.97	<2	1.22	3.92	65	<0.2	
Northfork	87.1	6.23	8.37	10.28	135	4.0	<1	<5	245	21.29	<0.5	<0.5	<0.8	15	0.6	2.5	9.33	2.8	1.31	<2	1.11	3.53	60	<0.2	
Monture Creek	74.8	1.84	8.65	10.46	91	3.8	0.8	<5	102	16.97	<0.5	<0.5	<0.8	6	0.4	1.1	5.38	2.6	1.09	<2	0.45	3.10	30	<0.2	
Clearwater	55.8	1.81	8.65	9.57	68	1.8	3.1	<5	32	46.01	<0.5	<0.5	<0.8	21	2.6	14.2	9.35	5.5	6.20	<2	2.99	10.81	118	<0.2	
Elk Creek	46.6	0.13	8.55	9.97	149	10.6	3.1	7	89	30.24	<0.5	<0.5	<0.8	<5	0.4	1.1	8.02	0.6	1.39	<2	0.55	4.46	35	<0.2	
Gold Creek	21.8	0.87	8.66	9.66	109	2.1	0.4	<5	95	40.01	<0.5	<0.5	<0.8	8	1.8	2.4	18.28	2.99	3.71	<2	1.84	7.79	92	<0.2	
Union Creek	20.8	0.34	8.47	9.68	195	7.1	3.7	<5																	

(All water samples were below detection for: nitrite (<0.05 mg/L), nitrate (<0.05 mg/L), phosphate (<0.05 mg/L), F (<0.05 mg/L), Be (<0.05 µg/L), Ag (<1 µg/L), Cr (<1 µg/L), Mo (<1 µg/L), Pb (<6 µg/L), and V (<2 µg/L).)

Table 2. Mean concentrations of bed sediment (<63µm) samples.

	River Km	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Si	Sr	Ti	V	Zn			
		10	6.5	0.5	0.5	0.1	1	1	1	0.5	0.5	1.5	50	0.5	0.5	0.5	2	10	1.5	7	6	7	2	0.5	0.5	1	0.5			
<b>PQL</b>																														
<b>BLACKFOOT MAINSTEM</b>																														
BF bel Mike Horse Mine	212.5	5807	553.9 (<0.5)	148.8 (<0.1)	11814	115	63	5.6	2193	832	4.0	6732	21318 (<2)	24	64.8	805	8702	36342	4033	24.5	72	36	17377							
BF bel Meadow	210.0	18856	83.4	13.3	493.1	3.0	4309	32	40	8.7	1414	66963	822	7.0	3246	4610	2	36	34.4	1007	1263	3540	4611	18.8	120	51	5737			
BF ab Alice Cr	209.8	16681	73.4	6.5	665.3	2.1	4694	26	39	9.3	987	61943	915	8.1	3518	4271 (<2)		40	29.2	1149	1124	2571	1985	19.4	160	56	4106			
BF ab Hogum	203.3	10170	25.5 (<0.5)	854.9	1.4	4319	10	38	9.0	259	32048	720	8.8	3447	4901 (<2)			35	26.8	883	145	432	651	15.9	154	42	2273			
BF ab Landers Fork	193.2	6307	16.6	3.6	493.4	0.9	5866	3	13	9.9	81	21557	802	7.5	3278	1270 (<2)		52	15.2	320	43	426	489	24.6	142	39	959			
BF bel Landers Fork	187.7	6757	16.6	1.5	478.3	1.0	5969	3	13	10.7	86	20340	801	7.8	3297	901 (<2)		48	16.2	1283	38	470	429	30.4	134	36	656			
BF bel Lincain	186.6	5180	15.8	2.8	303.3	0.8	24547 (<1)		8	7.0	43	15284	700	10.0	6975	591 (<2)		46	9.9	851	20	251	265	330	24.1	104	23	279		
BF at Ogden Min Rd	175.9	6482	17.1	5.0	289.7	0.6	20224 (<1)		7	6.7	42	14104	872	11.4	6870	620 (<2)		53	11.3	853	18	269	277	209	111	20	93			
BF ab Nevada	153.3	5556	12.9	3.4	267.5	0.6	19896 (<1)		5	5.9	27	10699	603	9.1	6649	457 (<2)		44	7.7	874	13	266	239	22.1	103	16	53			
BF bel Nevada	104.5	5311	11.2	1.7	263.7	0.7	20252 (<1)		6	7.5	29	12040	748	9.7	6323	611 (<2)		62	9.3	933	13	390	247	31.1	121	15	54			
BF bel Monture Cr	74.4	4184	11.3	2.8	286.8	0.7	18881 (<1)		5	5.8	23	10428	689	7.2	5582	417 (<2)		55	7.3	974	12	596	187	23.1	94	13	41			
BF at Whitaker Bridge	30.3	5374	9.7	5.2	346.7	0.7	22165 (<1)		6	7.3	22	11321	837	9.5	6194	517 (<2)		77	8.2	950	11	735	211	28.0	116	14	43			
BF at Marco Flats	6	3437	8.2	3.3	194.1	0.5	17265 (<1)		4	5.0	17	8439	548	6.4	5185	230 (<2)		45	5.6	956	9	425	204	20.2	96	14	33			
<b>TRIBUTARIES</b>																														
Pass Creek	210.8	11305	28.6	4.2	610.7	1.2	5575	1	11	10.3	58	17026	982	14.4	4896	642 (<2)		49	12.3	955	57	650	231	17.8	154	28	187			
Meadow Creek	209.8	21246	72.5 (<0.5)	414.5 (<0.1)	4682	42	60	8.7	1680	577	5.8	2798	8896 (<2)					27	41.9	1001	2001	4958	6829	19.1	113	36	8079			
Alice Creek	198.1	4225	9.1	2.2	323.2	0.7	6754 (<1)		9	8.4	51	15810	610	5.8	3477	665 (<2)		37	11.2	861	14	228	338	14.1	133	35	42			
Hardscrabble Cr	198.6	5618	9.9	3.4	786.0	0.9	13602 (<1)		3	10.4	23	7822	595	4.3	2766	674 (<2)		64	6.6	1204	9	1278	271	44.1	93	9	48			
Hogum Creek	192.4	7853	16.0	3.8	557.7	1.8	7903 (<1)		13	21.9	23	17966	744	9.0	3821	1882 (<2)		96	34.7	1525	17	446	453	155.8	108	23	59			
Landers Fork	187.2	4906	13.4	3.6	245.7	0.7	32602 (<1)		6	7.9	27	13196	674	13.0	8639	385 (<2)		43	8.3	691	15	192	275	23.0	90	17	39			
Arastra Creek	131.1	10711	14.2	4.6	380.8	0.7	8170 (<1)		9	21.0	79	18507	840	18.6	5779	241 (<2)		94	12.5	1072	12	686	286	26.4	304	47	68			
Nevada Creek	109.1	4893	7.2	2.6	299.4	0.9	15800 (<1)		5	7.9	17	7269	921	5.8	4062	614 (<2)		132	10.2	1106	8	793	203	75.7	114	11	30			
Northfork	87.1	6175	29.6	4.3	295.1	0.7	25044 (<1)		6	7.8	35	17612	780	15.2	8518	341 (<2)		74	8.0	836	14	498	445	20.2	121	21	40			
Monture Creek	74.8	3089	<6.5)	3.3	365.5	0.3	4682 (<1)		3	-1	13	6879	471	5.0	2389	497 (<2)		22	4.1	705	7	518	172	12.0	57	5	22			
Cleawater	55.8	7173	<6.5)	2.3	466.2	1.0	6387 (<1)		4	7.5	14	10171	561	9.7	3522	588 (<2)		40	7.4	1003	10	1219	225	11.4	73	7	29			
Elk Creek	46.5	10064	<6.5)	4.6	254.4	0.8	14463 (<1)		6	15.8	17	14828	1814	16.7	8297	252 (<2)		105	8.6	1243	<6)	413	605	31.1	339	31	37			
Gold Creek	21.8	7244	<6.5)	3.1	290.8	0.8	8688 (<1)		5	6.6	15	8650	483	11.0	3600	442 (<2)		37	6.5	920	<6)	835	198	10.8	82	6	24			
Union Creek	20.9	8463	8.7	2.8	321.8	1.1	7704 (<1)		8	7.8	29	10523	1076	5.8	3757	1890 (<2)		78	11.1	645	17	737	229	19.9	120	12	67			



**Figure 1: Map of the Blackfoot River watershed with mainstem sampling sites (indicated by circles and river km designations) and sampled tributaries (indicated by name abbreviations).**

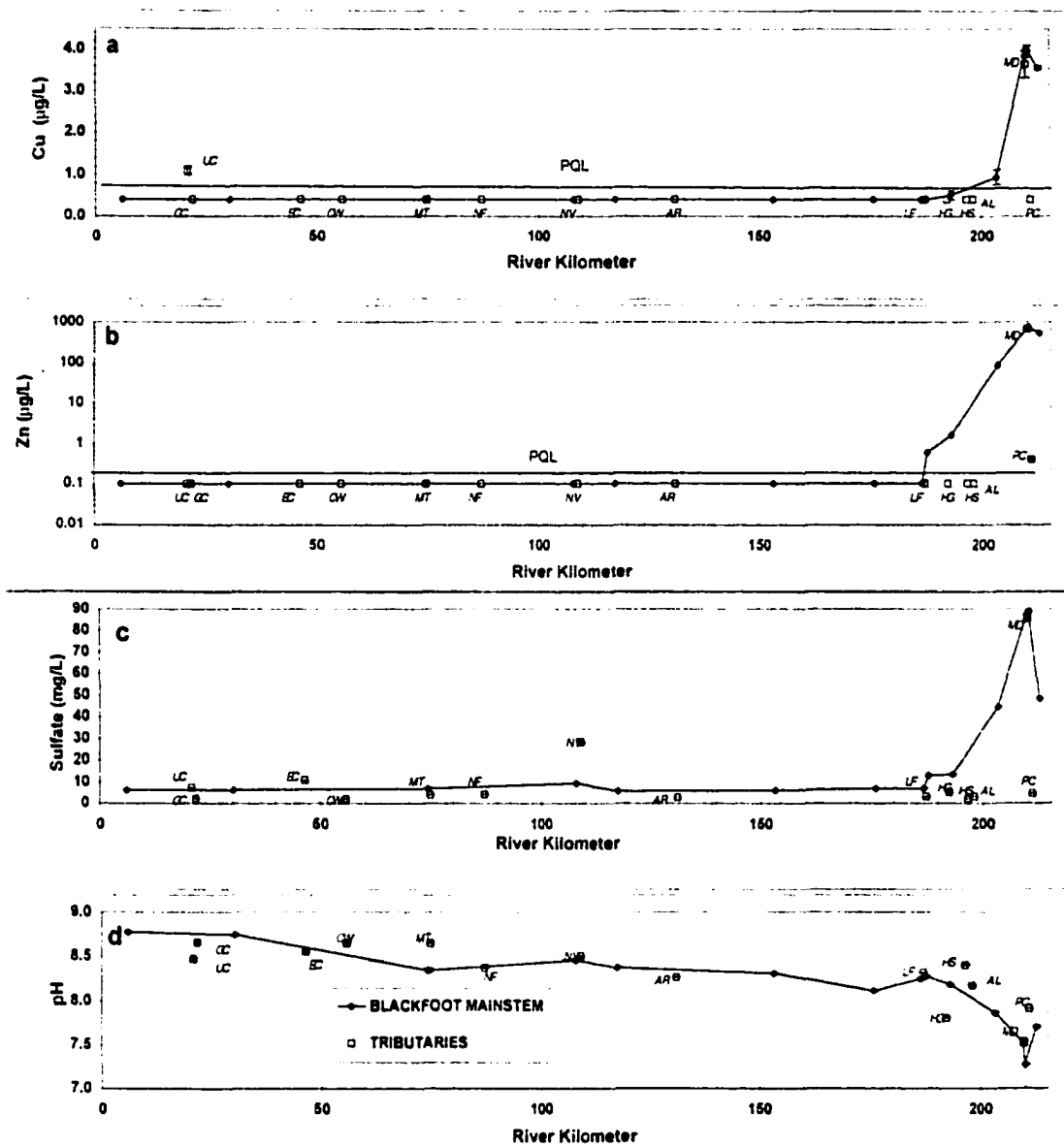


Figure 2 a-d: River kilometer vs. surface water a) Cu b) Zn (note log scale), c) sulfate, and d) pH. Solid, connected diamonds represent the mainstem samples; the squares represent tributary samples. Tributaries are identified by their abbreviations (listed in Figure 1).



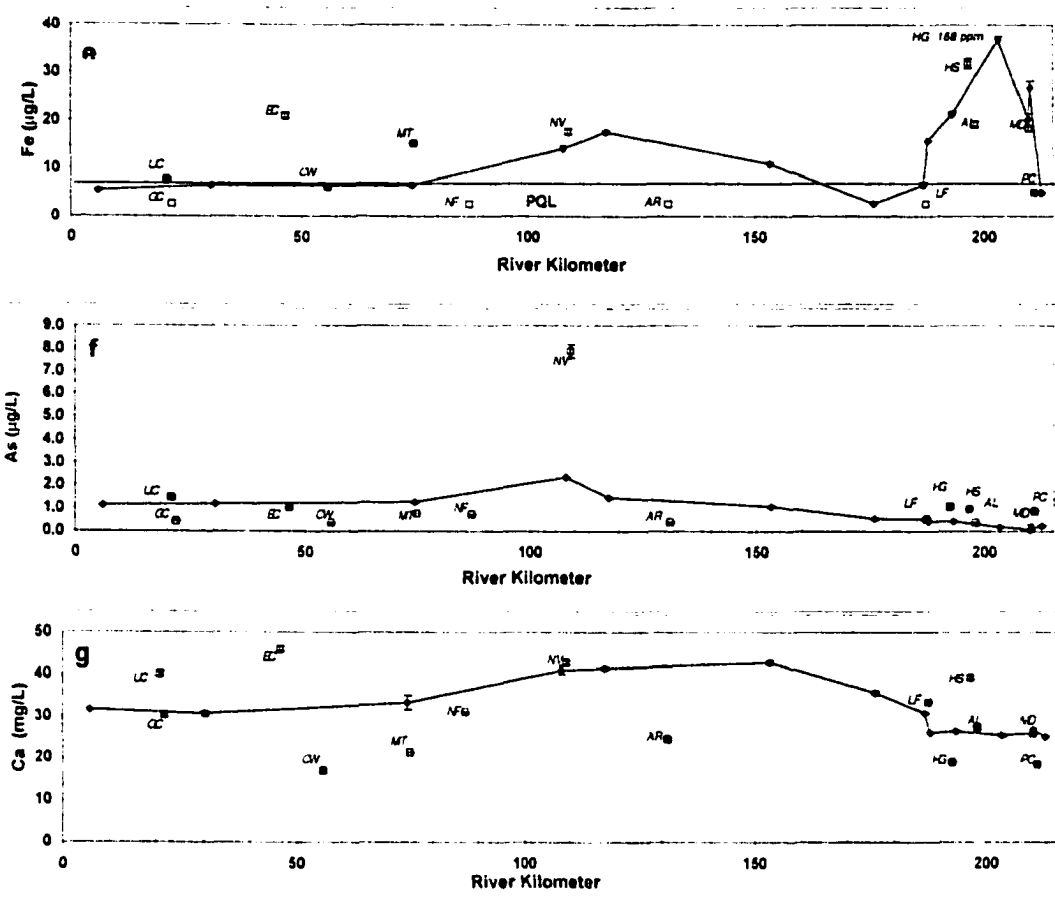


Figure 2 e-g: River kilometer vs. surface water e) Fe, f) As, and g) Ca  
 Solid, connected diamonds represent the mainstem samples; the squares represent tributary samples.  
 Tributaries with outlying concentrations are identified by their abbreviations (listed in Figure 1) to the left of their datapoints.

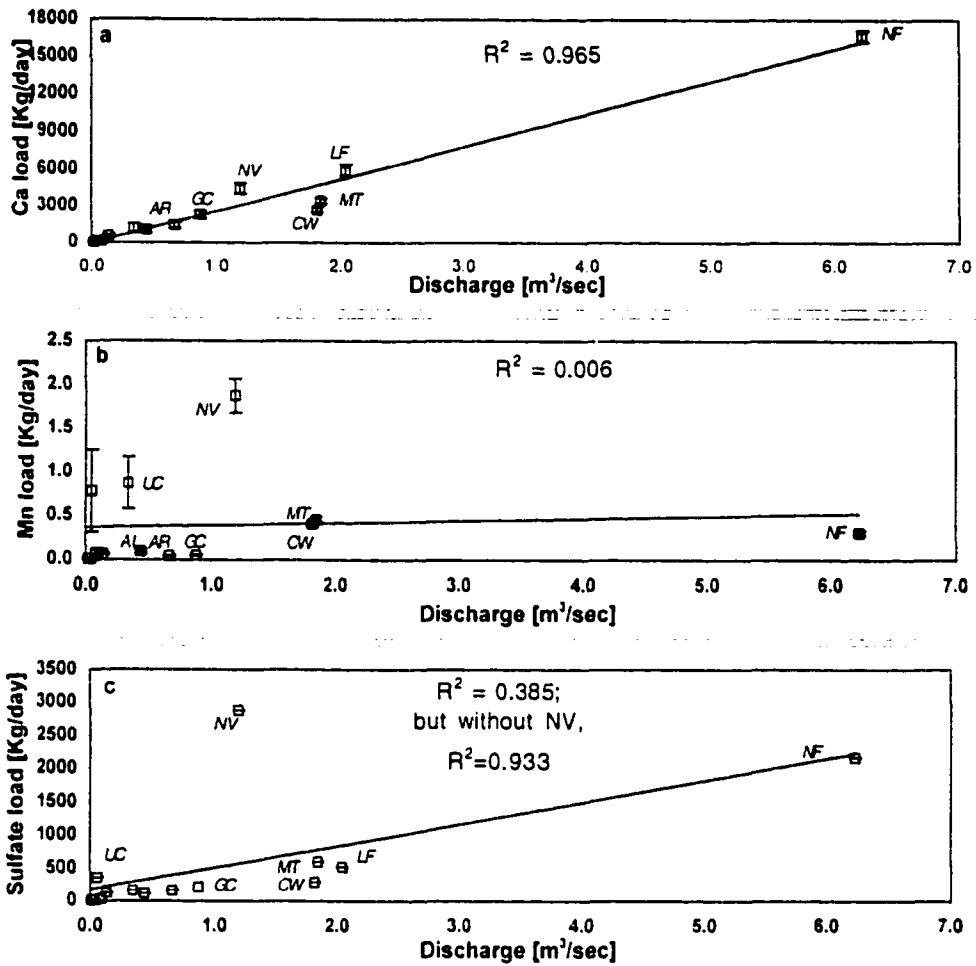


Figure 3: Tributary discharge vs. a) tributary Ca load, b) tributary Mn load, and c) tributary sulfate load

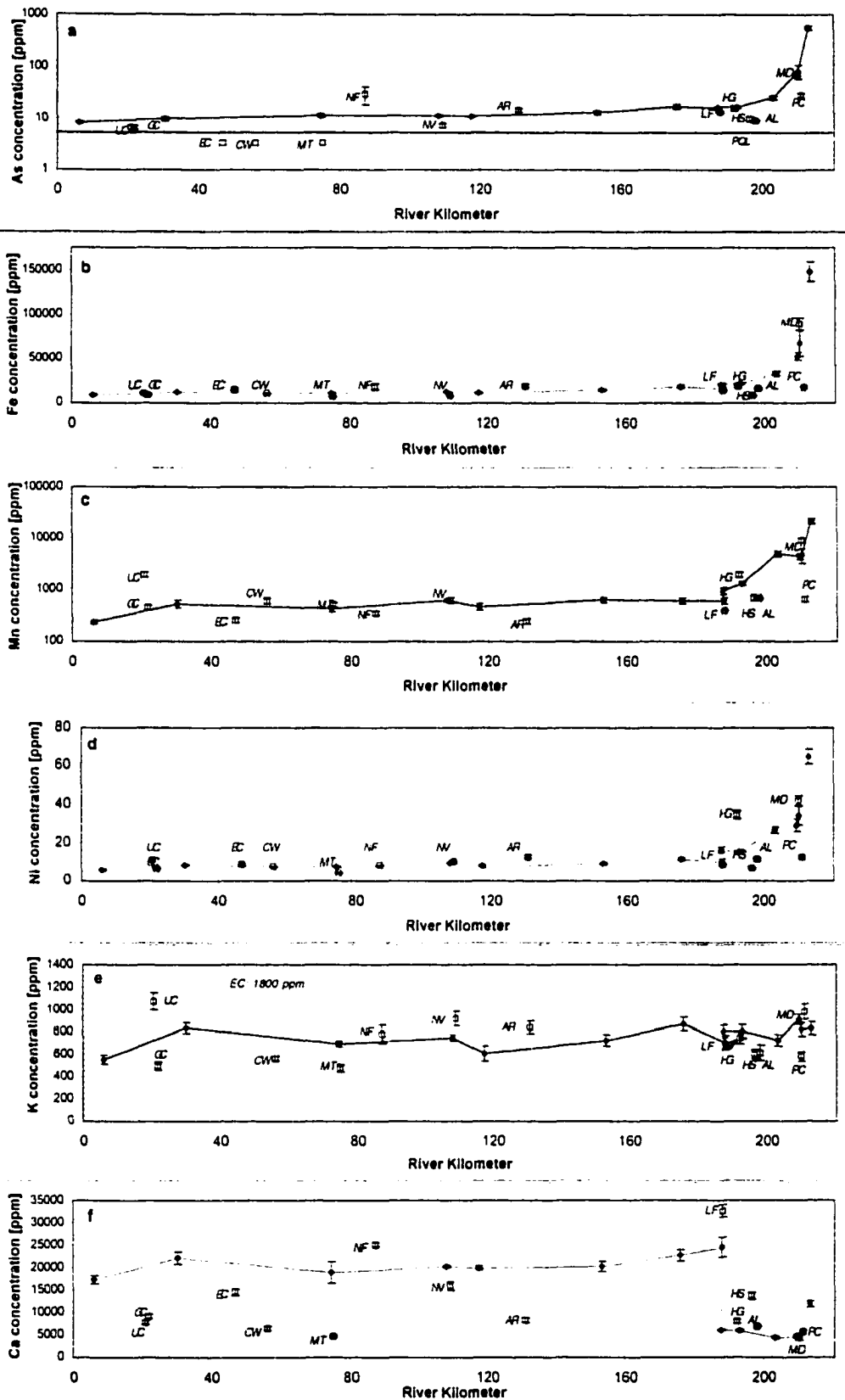


Figure 4: River Km vs. Bed sediment concentrations of a) As, b) Fe, c) Mn, d) Ni, e) K, and f) Ca (Solid triangles represent mainstem samples; squares represent tributaries)

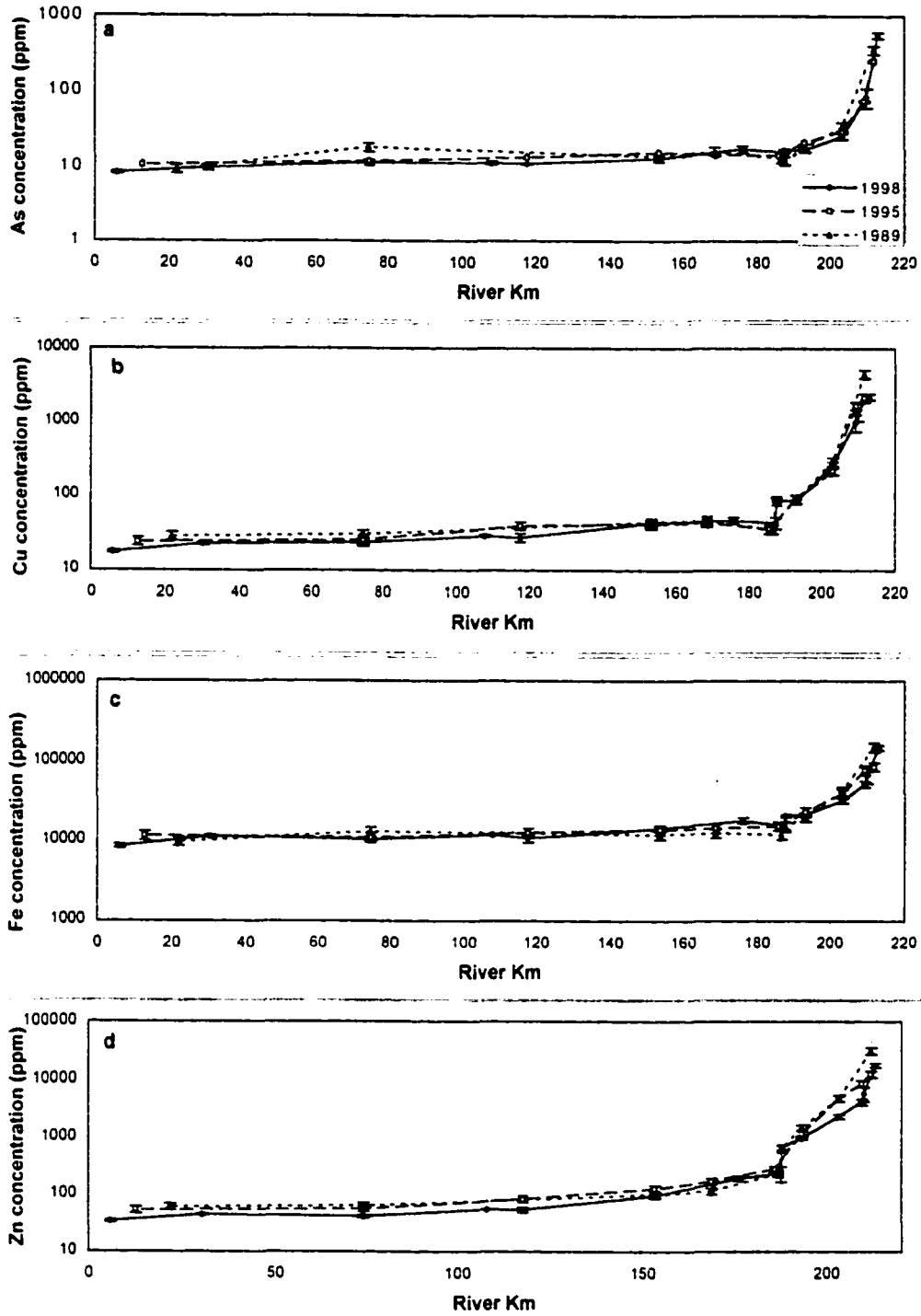


Figure 5: River Km vs mainstem bed sediment a) As, b) Cu, c) Fe, and d) Zn in 1989 (Moore et al., 1991), 1995 (Menges, 1997), and 1998 (this study).





Blackfoot Basin-wide Project Sediment Data Results (corrected for dilution and organo weights)

Table with 35 columns representing elements: Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Sr, Tl, V, Zn. Rows include various sediment types like Pass Creek, Postville Gulch, Meadow Cr., etc., with columns for concentration, units, and recovery percentages.

	Al	As	B	Be	Bi	Ca	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Si	Sn	Sr	Ti	V	Zn	
Norman 4	5400	11.8	(+0.5)	293	0.6	25000	(+1)	6	6	37.2	11871	586	11.2	7249	425.3	(+2)	43	7.8	795	16	421	234	(+3)	19.2	105	13	40
Mean	8175	29.6	4.3	295	0.7	25044	(+1)	6	8	34.8	11612	780	15.2	8518	341.1	(+2)	74	8.0	836	14	488	445	(+3)	20.2	121	21	40
Std Dev	729	22.7	3.0	29	0	818	0	1	2	7438	172	3	84	58	35	0	56	1	87	257	0	2	14	2	1		
%RSD	17	77	69.3	10	11	7		6	19	42	72	10	17	17	47	3	7	7	20	58			10	11	11	3	
Monroe Ct. BWS	3089	(+0.5)	(+0.5)	395	0.3	4652	(+1)	3	4	13.1	5879	471	5.0	7398	492.0	(+2)	22	4.1	705	7	518	172	(+3)	12.0	56.6	5	22
BF of Monroe-1	4071	9.8	2.1	323	0.7	15245	(+1)	5	6	18.0	10286	642	7.0	5350	523.0	(+2)	58	7.1	1007	11	562	219	(+3)	19.6	98.5	12	38
BF of Monroe-2	4213	9.6	2.7	331	0.7	16180	(+1)	5	6	20.0	9827	671	6.9	5038	484.8	(+2)	54	6.8	983	10	623	171	(+3)	19.0	87.0	11	38
BF of Monroe-3	3813	12.4	3.4	229	0.7	23752	(+1)	5	5	27.8	10213	686	6.5	5717	323.1	(+2)	51	7.1	951	15	488	190	(+3)	27.0	84.8	14	43
BF of Monroe-4	4551	14.6	3.4	268	0.7	21813	(+1)	6	6	28.5	11794	753	6.7	6341	338.0	(+2)	57	8.3	978	12	525	253	(+3)	25.8	96.4	15	44
BF of Monroe-4 d dup	4528	12.1	3.1	241	0.8	23124	(+1)	5	6	27.9	10879	780	6.3	6106	318.0	(+2)	54	7.8	936	14	487	198	(+3)	27.4	99.5	16	45
BF of Monroe-4 avg	4538	13.3	3	254	0.8	22368	(+1)	6	6	27.4	11387	796	6.5	6223	328.0	(+2)	56	8.0	958	13	511	206	(+3)	26.6	99.5	16	45
Mean	4184	11.3	3	287	0.7	18881	(+1)	5	6	23.3	10428	688	7.2	5682	417.2	(+2)	55	7.3	974	12	558	187	(+3)	23.1	94.5	13	41
Std Dev	268	2	1	47	0	4878	0	0	5	670	78	1	508	107	4	1	29	2	81	32	4	5	2	4			
%RSD	6	16	21	16	3	26		3	5	22	6	7	12	9	26	6	7	3	18	11	17		19	6	16	9	
Clearwater-1	7027	BPQL	2.2	478	1.0	5730	(+1)	4	7	13.6	9666	550	9.9	3602	882.9	(+2)	34	7.4	928	10	1008	223	(+3)	10.9	98.5	7	27
Clearwater-2	6932	BPQL	1.2	512	1.0	8086	(+1)	4	8	13.4	10187	524	8.5	3409	688.3	(+2)	44	7.6	968	11	1021	217	(+3)	10.6	98.9	7	28
Clearwater-3	7596	BPQL	3.4	408	1.0	7346	(+1)	4	8	15.3	10782	608	10.6	3854	404.6	(+2)	42	7.2	1114	10	1828	235	(+3)	12.7	100	7	32
Mean	7173	(+8.9)	2	466	1.0	6387	(+1)	4	8	14.1	10171	561	9.7	3522	588	(+2)	40	7.4	1003	10	1218	225	(+3)	11.4	72.9	7	29
Std Dev	338	1	53	0	849	0	0	7	6	598	43	1	124	157	5	0	98	1	355	9	1	23	0	3			
%RSD	5	49	11	3	13	10	2	7	8	8	11	4	27	14	7	10	8	28	4	10	32	1	10	32	1	10	
Elk Creek	10084	(+8.3)	4.6	794	0.9	14463	(+1)	6	16	17.2	14828	1814	16.7	8297	291.8	(+2)	109	8.8	1243	(+6)	413	805	(+3)	31.1	339	21	37
BF Whitaker-1	5723	11.2	6.0	372	0.8	24171	(+1)	6	8	22.2	11887	951	9.6	6385	561.4	(+2)	97	8.7	1014	12	987	182	(+3)	30.8	117	14	47
BF Whitaker-2	4687	10.9	7.5	357	0.7	24338	(+1)	5	8	20.7	10473	868	7.9	5793	738.4	(+2)	86	7.7	1001	10	917	213	(+3)	30.7	97.1	12	41
BF Whitaker-3	5470	9.8	6.2	335	0.7	18283	(+1)	5	8	21.9	11119	800	11.0	6733	350.7	(+2)	85	8.0	881	10	488	242	(+3)	24.7	128	16	42
BF Whitaker-4	5625	7.8	11.0	323	0.6	21757	(+1)	6	7	24.2	11854	729	9.4	5885	411.1	(+2)	96	8.4	903	13	577	208	(+3)	25.8	122	15	44
Mean	5374	9.7	5	347	0.7	22185	(+1)	6	7	22.3	11321	837	9.5	6194	517	(+2)	77	8.2	950	11	725	211	(+3)	28.0	116	14	43
Std Dev	463	7.7	3	22	0	2777	(+1)	0	1	642	95	1	448	171	18	0	87	1	237	25	3	13	1	3			
%RSD	8	17.1	55	6	8	13		6	11	7	6	11	23	23	22	6	7	12	12	12	12	12	11	12	11	8	
Union Cr.	8463	8.7	2.8	322	1.1	7704	(+1)	8	9	28.8	10623	1076	5.8	3757	880	(+2)	78	11.1	645	17	737	228	(+3)	19.9	120	12	47
Gold Cr.	7244	6.4	3.1	281	0.8	8988	(+1)	5	7	14.6	8950	493	11.0	3600	442.3	12.3	37	8.5	920	(+6)	335	198	(+3)	10.9	81.8	6	24
BF @ Marco 1	3478	8.7	2.4	183	0.5	17881	(+1)	4	5	17.2	8785	511	7.0	5381	224.0	(+2)	41	5.9	988	8	317	186	(+3)	20.5	98.0	18	33
BF @ Marco 2	4121	8.9	3.4	225	0.6	18983	(+1)	5	6	19.3	9530	648	8.1	5758	263.8	(+2)	48	6.4	928	9	421	234	(+3)	20.5	108	14	37
BF @ Marco 3	3112	7.8	3.5	203	0.6	19256	(+1)	4	5	17.1	7402	564	5.0	4787	243.2	(+2)	53	5.1	927	8	658	210	(+3)	22.8	86.0	11	32
BF @ Marco 4 DD	3285	7.1	(+0.9)	172	0.4	14702	(+1)	4	5	16.2	8652	478	5.6	4643	183.2	(+2)	37	5.9	878	10	300	180	(+3)	16.9	92.8	15	32
BF @ Marco 4	2940	7.6	3.6	164	0.4	15207	(+1)	4	4	16.3	7884	465	5.1	4821	182.7	(+2)	43	5.1	988	8	308	182	(+3)	17.1	87.7	13	31
BF @ Marco 4 L DUP	2908	7.4	2.4	158	0.5	14813	(+1)	4	5	16.1	7875	462	5.4	4811	187.5	(+2)	38	4.9	989	8	308	185	(+3)	17.0	86.5	14	30
BF @ Marco 4 avg	3037	7.3	2.1	185	0.5	14841	(+1)	4	4	16.2	8037	468	5.4	4825	191	(+2)	38	5.1	981	8	308	178	(+3)	17.0	86.5	14	31
Mean	3437	8.2	3.3	194	0.5	17265	(+1)	4	5	17.4	8439	548	6.4	5185	230	(+2)	45	5.6	958	9	425	204	(+3)	20.2	95.0	14	33
Std Dev	495	0.7	2	28	0	1899	0	1	1	921	78	1	474	31	7	1	32	0	184	25	2	10	3	3			
%RSD	14	8.7	56	13	12	11		8	12	7	11	14	23	6	13	15	11	3	2	18	12		12	11	19	8	



**Chapter 4:**  
**Temporal variations of the geochemistry**  
**in the Blackfoot and Clark Fork River basins**

**ABSTRACT**

Two rivers and two mountain streams in the Blackfoot and Clark Fork River basins were sampled over variable temporal scales within a 12 month period. Samples were collected at approximately the same time of day at least monthly, with supplemental sampling during spring runoff and fall precipitation events. Two 24-hour diel studies were also conducted at each site during low flow summer conditions. All samples were analyzed for both dissolved (operationally defined as  $<0.2 \mu\text{m}$ ) and total recoverable concentrations. Results show that for some parameters, short term variations (diel, or daily following precipitation events) are proportional to long-term variations, while other parameters cover significant portions of the seasonal variations in the short-term. Generally, the trace elements (Al, As, Cu, Fe, Mn, and Zn) behaved differently from the major elements (e.g. Ca, K, Mg, Na), which were better correlated with discharge. Suspended sediment, total recoverable trace metals, and some dissolved elements exhibited short-term flushing effects at the onset of high flow conditions. Diel cycling was observed for pH, dissolved oxygen, water temperature, dissolved inorganic carbon, total suspended sediment, and total recoverable metals at some or all sites. These results have important implications for the design of future monitoring studies of the geochemistry of surface waters.

**INTRODUCTION**

The spatial and temporal variations of the aqueous geochemistry of pristine and polluted streams and rivers are poorly defined. However, an understanding of these variations has potentially important implications for designing effective sampling and monitoring strategies and for the environmental regulation of pollution sources to rivers. Although numerous studies have made important contributions to the understanding of the time-dependent variability of the geochemistry of various freshwater systems, most were based on data from single study sites (e.g. Johnson and East, 1982; McKnight and Bencala, 1988; Fuller and Davis, 1989; van der Weijden and Middelburg, 1989; Cossa et al., 1990; Brick and Moore, 1996). Discrepancies among these and other studies in terms of sampling designs, sample processing, and analytical methods hinder the direct

comparison of datasets. On the other hand, studies that have described the spatial variations in the geochemistry of multiple numbers of streams typically lack the temporal resolution needed to put their samples into annual, seasonal, and daily contexts (e.g. Gibbs, 1973; Shiller and Boyle, 1985; Schemel et al., 2000; USGS, 2001).

Of the studies that have incorporated both spatial and temporal dimensions to their water quality research (e.g. Edwards, 1973; McKnight and Bencala, 1990; Carroll et al., 1998; Constanz, 1998; Evans and Davies, 1998; Clow and Mast, 1999; Meixner et al., 2000), not all have included trace metals into their evaluations, and even fewer studies have employed “clean” sampling and analytical methods. These methods have been recognized recently as being critical for the accurate assessment of trace metal concentrations in both pristine and contaminated waters (Horowitz et al., 1994; Benoit, 1994). It has been recommended that trace-metal research conducted without these methods should be viewed with extreme caution, and as a result, much of the trace metal data collected to date has been effectively invalidated (Shiller and Boyle, 1987; Benoit, 1994; Benoit, 1995; Taylor and Shiller, 1995; Windom et al., 1991). Of the published papers based on data generated using clean methods, many have again looked at either spatial or temporal aspects of aqueous geochemistry, but not both.

Many water quality studies take place during the late spring, summer, and early fall, and as a result, little is known about winter and early spring events. There are no known published clean-method studies examining seasonal variations in the Rocky Mountain region, where winter snowpacks create large streamflow surges in the spring and also where there are numerous streams and rivers contaminated by mining. Discharge is thought to be one of main controllers of the geochemistry of surface waters. It has been long reported that an inverse relationship exists between streamflow and the concentrations of major ions such as alkalinity, Ca, Mg, K, and Na, a trend explained by simple dilution from snowmelt and precipitation (Hem, 1970; Edwards, 1973; Whitfield and Clark, 1982; McKnight and Bencala, 1988).

However, research also suggests that these trends are not so simple and that many solutes and particulates can follow hysteresis patterns (Johnson and East, 1982; Williams, 1989; Campbell et al., 1995; Evans and Davies, 1998). Hysteresis patterns are formed by elemental concentrations along the rising limb of a hydrograph peak differing from the

those along the falling limb. The identification of hysteresis patterns in surface waters is important for designing monitoring studies, for making more informative comparisons among watersheds, and for evaluating the timing and nature of chemical sources to the stream channel (Hooper et al., 1990; Droppo and Jaskot, 1995; Sokolov and Black, 1996).

The initial stages of spring freshet may be characterized by a chemical surge of the dissolved major ion concentrations in the water channel. This phenomenon has been explained as a flushing of ions that have accumulated on snow crystals, in the soils, and in the groundwater over a relatively long winter residence period (Stottlemyer et al., 1997; Harrington and Bales, 1998; Marsh and Pomeroy, 1999). Such flushing events have been reported in the handful of hysteresis studies from alpine regions (Stottlemyer and Toczydlowski, 1990; Williams et al., 1993; Campbell et al., 1995). These events control the development of clockwise hysteresis patterns, in which solute concentrations are higher along the rising limb than on the falling limb. However, other research from similar regions have reported that some solutes may exhibit counter-clockwise hysteresis patterns as well (Stoddard, 1987; Stottlemyer and Troendle, 1992; Bhangu and Whitfield, 1997). These researchers have explained such trends by the volumetric dominance of dilute snowmelt over contributions from groundwater and soil water.

The seasonal variations of trace element concentrations have not been studied in nearly as much detail as that of the major ions. Because major ions are generally chemically conservative, their trends should be less complicated than those of the trace metals (Bencala et al., 1987; Wetherbee and Kimball, 1991). From the limited research using clean methods, the relationship between streamflow and trace element concentrations has been variable from site to site and no generalizations can be made. For example, Shafer et al. (1997) report 1- to 5- fold increases in filterable metal concentrations (and up to 17-fold increases in particulate metals) in two Wisconsin rivers during high flow events compared to baseflow. Similarly, Sherrell and Ross (1999) found highly significant positive correlations between discharge and dissolved metals in four acidic New Jersey streams. In contrast, Shiller (1997) reports that the dissolved metal concentrations in the Mississippi River do not correlate with discharge. Clearly,

more data are needed to elucidate any patterns in the discharge versus trace metal relationships in streams and rivers.

In addition to the need for better data on this issue, there are unanswered questions regarding how seasonal dynamics compare with those that occur on shorter timescales, as on storm-duration and diel scales. Studies of metal loading into rivers during storm events have shown that both particulate and dissolved metals can be mobilized into stream channels in mining-contaminated basins (Bradley and Lewis, 1982; Bird, 1987; Soulsby, 1995; Sanden et al., 1997). On a diel scale, processes such as photo-oxidation and -reduction of Fe, biologically- induced pH changes, bank vegetation-controlled changes in streamflow, and suspended sediment flux have been linked to diel cycles of dissolved and particulate trace elements in streams and rivers (McKnight et al., 1988; Fuller and Davis, 1989; Brick and Moore, 1996). Short-term variations have obvious implications for sampling designs and motivate the question of how seasonal geochemical cycles compare with what is seen on much narrower time scales. The purpose of this study is to answer some of these questions by examining the geochemical variability in the dissolved ( $<0.2\mu\text{m}$ ) and particulate phases in mining impacted and relatively pristine rivers in Montana on seasonal, short-term precipitation event, and hourly scales using clean sampling techniques.

## **METHODS**

### **1. Sampling design**

#### **a) Spatial design**

We chose four sites in western Montana as the focus of this study (Figure 1). Two sites are relatively small, moderately high mountain streams (elevation= 1450 m) and the other two sites are lower (1000 m and 1200 m) on much larger rivers draining 20-times the land area of the smaller streams. One of the two sites from each size category drains a region impacted by mining contamination, while the other drains relatively pristine areas.

The two smaller streams, at sites LF and BH, are located in the upper Blackfoot River watershed. The Landers Fork (LF) is a major tributary to the upper basin, and the

site along the Blackfoot River near Hogum Creek (BH) is located 6 km upstream of the Blackfoot-LF confluence. The Landers Fork drains 350 km<sup>2</sup>, while the Blackfoot at BH drains 254 km<sup>2</sup>. Site BH is ca. 20 Km downstream from the historic Upper Blackfoot Mining complex. Site LF is located only 1 km upstream from the confluence with the Blackfoot, and in the years of this and previous studies (Nagorski et al., 1998; Nagorski et al., 2001) it is typically several times larger in streamflow than BH. It drains the pristine Scapegoat Wilderness area, where elevations reach 2400 m, and it thus receives more snowpack than does site BH.

The other two sites, BFB and CFBM, are located on the lower Blackfoot River (near Bonner) and Clark Fork River (near Bearmouth), respectively. They were selected due to the presence of USGS gauging stations as well as their similar streamflow sizes at baseflow conditions. We acknowledge the potential conflict of non-independence for the lower Blackfoot site due to its location downstream of BH and LF. However, BFB is 187 km downstream from the headwater sites, and its flow during the study period was on average 10 times larger than the headwaters streams combined. Studies on the watershed (Spence, 1975; Moore et al., 1991; Menges, 1997; Nagorski et al. 2000) show that the impacts of the headwater mines generally are not detectable in the solute phase by about 20-30 Km downstream of the site. The major tributaries feeding the Blackfoot River between the headwater sites to the lower basin site drain large portions of wilderness areas, in addition to rural agricultural land, and there are no large-scale industries or urban areas.

In contrast, the site along the Clark Fork River is approximately 130 km downstream from Butte, the setting for one of the world's largest historical mining operations. Over a hundred years of mining and smelting in the upper Clark Fork basin and Flint Creek basin have contaminated the river to the extent that the river's approximately 200 km stretch between Butte and Missoula is the largest Superfund complex in the U.S.A. (Moore and Luoma, 1990). Although CFBM is located a good distance from the major mining contamination, it is still chronically impacted by metal pollution from the tailings on the floodplain, elevated metals in the streambed sediments, and other nonpoint sources (Moore and Luoma, 1990; Nimick and Moore, 1991).

## b) Temporal design

We sampled the sites on a monthly basis with supplemental high flow sampling during spring runoff and late summer precipitation events. Robertson and Roerish (1999) found that such a design was highly effective for one year studies aiming to estimate loads in small streams. Our monthly design consisted of a random weekend starting date in February, 2000, followed by a sampling date established at four week intervals from then on, through January, 2001 (thus a total of 13 “monthly” sampling events). We gave the four week rule an allowance of plus or minus two days in order to deal with adverse weather or other logistical inconveniences.

During spring runoff from mid-April through mid-June, we collected samples once or twice per week in order to capture as much flow variability as possible. Frequent site visitation was particularly important for sites BH and LF, as real-time streamflow data were unavailable. All 4 sites were visited for each event, except for one supplemental sampling event (on 4/14/00) when only BFB and CFBM were visited. As a result, BFB and CFBM had a total of 24 “seasonal” sampling events, while BH and LF had a total of 23.

Between September 1 and September 5, relatively large amounts of precipitation fell in the region following months of near-drought, warm, and dry weather (WRCC, 2001). In response, we took “rain event” samples every day or every-other day for almost two weeks. We sampled the lower sites closer to Missoula (BFB and CFBM) every day from September 1-9, and on September 11, and 12. Diel sampling events at BFB and CFBM during the next week provided additional site data. We sampled sites BH and LF on September 1, 3, 4, 5, 6, 8, and 10; their further distance from Missoula did not allow for as dense of a temporal resolution as at BFB and CFBM.

We visited each sample site at approximately the same time of day in order to minimize complicating any seasonal trends with diel trends. We visited CFBM consistently within a few hours of sunrise in the morning, BFB during the late mornings, BH in the early afternoon, and LC in the mid-afternoons.

We conducted diel studies at each of the four sites during relatively stable, low-flow conditions (in August and September). Low-flow summer conditions are believed to be optimal for maximum diel variation (Brick and Moore, 1996). For two non-

consecutive days at each site, we sampled once every two hours. Sites BH and LC are close enough in distance to allow concurrent diel sampling. Hence, we collected samples at BH every odd hour and at LC every even hour on 8/17/00-8/18/00 and on 8/20/00-8/21/00 beginning at 14:00 on each diel set. We sampled CFBM bi-hourly on 9/14/00 at 08:00 through 9/15/00 at 08:00, and on 9/18/00-9/19/00, also from 8:00 to 8:00. At BFB, we sampled the first set beginning on 9/12/00 at 8:00, and ending on 9/13/00 at 8:00. However, the second diel set at BFB (begun on 9/16/00 at 8:00) was hampered by a several hour-long lightning and wind storm just after the 20:00 sampling. Although little rain fell, the weather conditions prohibited safe sampling of the river. Because the gauging station indicated no change in streamflow over the following 24 hours, the sampling event was resumed starting at 20:00 on the following evening (9/17/00) and carried through until 8:00 on 9/18/00.

## 2. Streamflow measurement

We obtained streamflow (Q) values at BFB and CFBM from the USGS gauging stations at the sites. The estimated error of the Q measurements is 5% (M. White, USGS, personal communication). From the end of November through the end of the study period, Q measurements at BFB were unavailable due to ice at the site.

At BH and LF, we measured streamflow ourselves, given that there were no gauging stations at these sites. We made the measurements using a Price AA current meter or a pygmy meter, according to standard USGS protocol (Rantz et al., 1982). Our reproducibility of the Q measurements at site BH averaged 7%, although the highest error of 17% was made during the low flow period in December. At LF the mean measurement precision was 3%, with the largest error at 7%.

At LF, daily Q values were estimated from the nearest USGS gauging station on the Blackfoot River, 71 km downstream from LF. Despite the distance from LF, we found a good linear relationship between Q measurements we made at LF and the Q reported on the same dates at the gauging station ( $R^2=0.96$ ). Hence, we could monitor the approximate Q at site LF. Site BH did not correlate well with the USGS gauging station, and so we do not have any estimated data on the Q values at BH on days inbetween sampling events.

### 3. Sampling protocol

We strictly followed a meticulous clean protocol during all stages of sample handling. As described in Chapters 2 and 3, we extensively pre-cleaned all sample bottles before each sampling event, and we used clean sampling procedures to obtain width and depth-integrated water chemistry samples. We obtained three individual samples from each site on each sampling event, except for during the diel sampling when we took only one sample per bi-hourly event. The triplicate samples were never composited and were put through handling and analysis procedures independently. Following collection of the water chemistry samples, we took samples for total suspended sediment (TSS) analysis from the same areas from where we collected the water quality samples. We measured pH, DO, and stream temperature in situ, and again we did so at the same places along the channel transect from where we collected the water quality samples. We checked the pH and DO meter and recalibrated it if necessary before measuring at each site.

### 4. Laboratory protocol

All sample processing and analysis took place at the Murdock Environmental Biogeochemistry Laboratory at the University of Montana. Sample filtration methods are described in the Methods section of Chapters 2 and 3. Following filtration to  $<0.2\mu\text{m}$  (operationally defined as the “dissolved” phase), we decanted 100 mL for purposes of alkalinity measurement of the samples, and then we preserved the remaining volumes in the 1 liter sample bottles for total recoverable metal analysis with 3 mL of 6N trace metal grade  $\text{HNO}_3$  per liter of sample. Total recoverable metal digests were performed within 2 months of sample collection according to EPA Method 200.2 (EPA, 1991). All steps of the digestion process took place under the clean hoods as well. The resulting concentrations in the digested samples are called “total” concentrations in this report.

We quantified the total suspended sediment (TSS) within 1 week, but usually within 1 day, of sample collection. We did so by weighing the mass of particulates retained on a  $0.2\mu\text{m}$  filter following a vacuum-driven filtration of at least 300 mL (mean=1.5 liters) of sample. We measured DIC within two weeks using a Shimadzu



Carbon Analyzer. We determined alkalinity by titration with sulfuric acid to pH 4.5 within 3 days of sample collection. However, the large number of samples collected during the first couple weeks of September precluded the immediate alkalinity analysis on many of those samples. Some samples were kept in the refrigerator for 18 days before being analyzed for alkalinity, while the EPA recommended time limit is 14 days.

We measured arsenic concentrations on a HGAAS and all other elements using ultrasonic nebulization (Cetac, U-5000AT+) with a Thermo-Jarrel-Ash ICAPES (IRIS) as described in Chapters 2 and 3.

## 5. Laboratory QA/QC

We followed strict quality assurance and quality control protocols during all types of lab analysis. On the ICP we ran acidified blanks, fortified blanks, USGS Standards T143 and T145, sample analysis duplicates, and sample spikes at regular intervals so that at the end, 40-60% of the total analysis consisted of QA/QC evaluations. On the HGAAS, we analyzed at least one sample spike, one sample analysis duplicate, one or two checks of the USGS standards, a blank, and all 5 calibration standards with each set of 10 samples. When analyzing DIC, we again had at least one sample duplicate and one check of the blank and all 3 calibration standards with each set of 10 samples. The Practical Quantifiable Limit (PQL) on all instruments was defined as the minimum value at which elements could be detected with a maximum variability of 30% (Table 1). All QA/QC results are presented in Tables 1-7, and a summary follows.

*Laboratory blanks:* A total of 237 lab blanks were run on the ICP, and only trace amounts of Ba, Ca, Na, S, and Sr were detected in no more than 17 of the blanks (Table 1.1) All 262 lab blanks measured on the HGAAS and all 113 blanks run on the carbon analyzer were also below detection (Table 1.2). The highest TSS blank found was 0.1 mg/L (Table 1.2).

*Filtered field blanks:* The 48 filtered field blanks also had rare and insignificant concentrations of measured elements. Filtered Al, Ba, Ca, Mn, Si, and Sr were above the PQL in only 1 or 2 of the field blanks (Table 1.3). One of the 48 filtered field blanks had Fe at 41  $\mu\text{g/L}$ , substantially above its PQL of 5  $\mu\text{g/L}$ . Sodium's maximum field blank concentration of 0.6 mg/L likely accounts for some of the noise in Na concentrations at

sites LC, BFB, and BH, where Na concentrations were typically less than 4 mg/L. Although S concentrations were detected in 44 of the 48 field blanks, even the maximum concentration of 0.08 mg/L found is insignificant compared to values found in the environmental samples. Arsenic and DIC were below the PQL in all field blanks (Table 1.4). The highest alkalinity value measured in a field blank was 8.8 mg/L (Table 1.4).

*Digest blanks and digested field blanks:* Processing blanks through the digestion procedure resulted in some significant contamination. Elements which turned up at levels high enough to interfere with concentrations in environmental samples were Mn, Cr, Ni, P, Fe, and Zn (Tables 2.1 and 2.2). Manganese was detected (at 3 µg/L compared to its PQL of 0.5 µg/L) in only one of the 83 digest blanks and in none of the 45 digested field blanks. Although Fe was detected in less than a third of the digest blanks and digested field blanks, its maximum concentration of 0.07 mg/L exceeded Fe concentrations in many environmental samples. The Cr and Ni values in the blanks fully account for their concentrations in some of the digested samples, and so they were discarded from the dataset. Similarly, Zn contamination was problematic, with detections of up to 0.29 mg/L in 20 of the 45 digested field blanks and in 28 of the 83 digest blanks.

*External standards:* The mean concentrations of all elements (except Si) in USGS standards T-143 (n=151) and T-145 (n=102) as analyzed on the ICP fell within the reported acceptable ranges (Tables 3.1 and 3.2). These standards were also digested along with environmental samples for total recoverable determinations (Tables 4.1 and 4.2). Again, all but Si in both types of standards had mean measured concentrations within the reported acceptable range. However, Zn also violated the reported limit for USGS T-143 averaging 15% higher than the upper reported limit; its exceedance may be due to Zn contamination problems during the digest procedure, as evidenced by the blank recoveries. The USGS standards were also measured on the HGAAS, and the digested and non-digested USGS T-143 and T-145 (n= 107 and 164, respectively) standards fell within the acceptable ranges (Table 5.1).

*Internal standards:* An internal standard was measured 190 times on the ICP during sample analysis, and mean concentrations of all analytes were within 5% of the constructed value (Table 3.3). Exceptions to this are Be, Co, and Si, whose average

readbacks were within 8%, 6%, and 6% of the known values, respectively. On the HGAAS, the mean percent difference between known (lab-constructed) values and measured As concentrations was 8% (stdev=8%) for As concentrations of <0.5 µg/L and 3% (stdev=3%) for As concentrations >0.5 µg/L (Table 5.2). On the carbon analyzer, the average difference between the 350 lab standards and their known (lab-constructed) concentrations was 2% (stdev=2%) (Table 5.2).

*Analytical duplicates:* The mean percent difference between samples measured twice on all instruments was 6% or lower for all elements (Table 6.1 and 6.2). The only exception was for duplicate measurements of TSS samples, for which the mean percent difference between samples was 26%.

*Digest duplicates:* The mean percent difference between digest duplicates (the same sample digested separately twice) was 6% or less as well, except for Al, As, Cr, Fe, Ni, P, and Zn (average % differences= 11%, 8%, 22%, 7%, 25%, 11%, and 21%, respectively) (Tables 6.3 and 6.4). Most of these elements were also those that turned up in the blanks at significant levels.

*Spikes:* Forty-two blanks and up to 223 samples were spiked for most elements analyzed. Mean spike recoveries on all detectable elements were between 97% and 111% (Tables 7.1, 7.2, and 7.3). The only exception to this was Li, whose mean percent spike recovery was 84%.

## 6. Data analysis

Due to the non-normal distributions of the concentration data, the presence of outliers for numerous parameters, heterogeneity of the sample variances, and the failure of data transformations to correct these problems, non-parametric statistical methods were used to analyze the data. The program SPSS was used for all statistical tests following spreadsheet manipulation in Excel. One exception to this was for calculations of non-parametric multiple comparisons by simultaneous test procedures (STP), which were done manually according to Sokal and Rohlf (1995).

## **RESULTS AND DISCUSSION**

### **1. Seasonal variations**

#### **1. Streamflow variation**

At BFB, LF, and BH, peak Q occurred in late spring and early summer. At BFB and LF, runoff lasted between April and July (Figures 2 a,c). At BH, Q peaked early relative to BFB and LF (Figure 2d). Streamflow at BH on 4/22/00 was higher than on any other date, and it decreased steadily from then on.

There was a highly unusual Q pattern at CFBM during the study year (Figure 2b). Instead of being characterized by the typical snowmelt runoff peak, Q decreased from April through August. As a result, the hydrograph was approximately inverted. Streamflow averages for March through August were the lowest in the 8 year site record, and 7/31/00 marked the lowest Q (2180 L/s) ever recorded at the site. The low Q, caused by below normal snowpack and precipitation levels in the region, was further complicated by an unknown amount of irrigation withdrawal in the Clark Fork valley.

#### **2. Among-site comparisons of dissolved and total concentrations:**

Comparisons among sites (using the Kruskal-Wallis test) showed that pH, water temperature, and dissolved oxygen concentration were the only parameters that lacked significantly different distributions among the 4 study sites. Non-parametric multiple comparisons by STP identified the relative significant ( $p=0.05$ ) differences between sites for the rest of measured parameters, as listed in Table 8. Not included in the analysis were elements that were entirely or mostly below detection at all four sites.

The concentration distributions of most measured parameters (alkalinity, DIC, and dissolved (d) and total (t) As, Ca, Cu, K, Li, Mg, Mn, Mo, Na, P, S, Si, and Sr) were highest at site CFBM. The site was lowest in concentration only for  $Ba_d$  and  $Ba_t$ . The large sites (CFBM and BFB) had higher TSS,  $Al_i$ ,  $As_d$ , and  $Li_i$  concentrations and lower  $Ba_d$  and  $Ba_t$  concentrations than the small sites (LF and BH). The mining-impacted sites (CFBM and BH) had higher concentrations of  $Fe_d$ ,  $Mn_d$ ,  $S_d$ ,  $S_t$ ,  $Si_d$ ,  $Si_t$ ,  $Sr_d$ ,  $Sr_t$ , and  $Zn_t$  than the relatively pristine sites (BFB and LF). While BFB and BH had similar

distributions of alkalinity, DIC,  $Ca_d$ ,  $Ca_t$ ,  $K_d$ ,  $K_t$ ,  $Fe_d$ ,  $Mg_d$ ,  $Mn_t$ ,  $Na_d$ ,  $Na_t$ , and  $P_t$  concentrations, CFBM and LF had heterogeneous concentration distributions for all elements.

### 3. Differences in the dissolved and total concentrations

Differences between the dissolved and total concentrations of each detectable element were evaluated using the Wilcoxon Ranged Sign test, a non-parametric version of the paired t-test. This test was selected over the Wilcoxon Rank Sum test due to the lack of independence in the samples. Dissolved and total elements are not independent because the total fraction encompasses the dissolved fraction.

Arsenic (except for at CFBM), Ba, Cu, Fe, Mn, Mo, and P were significantly ( $p \leq 0.05$ ) higher in the total recoverable fractions compared to the dissolved fractions at the sites where they were detectable (Table 9). However, the dissolved and total fractions of most of these elements (As, Cu, Fe, Mn, and P) did not correlate well with one another (Table 10). (Exceptions to this are As at LF, where the correlation between dissolved and total concentrations was 0.91, and Mn at BFB, where  $r = 0.81$ .) For example, while dissolved Fe concentrations at CFBM remained within the narrow range of 0.011 to 0.020 mg/L over the 12 month study, total Fe concentrations varied almost 2 orders of magnitude, from 0.071 to 1.132 mg/L. This lack of association means that changes in the particulate metal concentrations occurred independently of variations in the dissolved concentrations. The implication of this result is that the dissolved phase of these elements cannot be assumed to represent the total recoverable phase, and vice versa, and so both phases need to be sampled for monitoring and interpreting water quality variations in these rivers.

At sites BFB and LF, dissolved Fe and Mn were following nearly identical trends as total Fe and Mn (except for Fe at LF, where it was BPQL), despite their poor correlations (Figure 3a, b). This suggests that these “dissolved” metals may in fact be colloidal instead of truly dissolved. Numerous studies have demonstrated that in order to obtain the truly dissolved fraction, samples must be filtered through membranes that are no larger than 0.01  $\mu\text{m}$  in size (Kimball et al., 1992; Benoit, 1995; Ross and Sherrell,

1999). Therefore, our operationally-defined “dissolved” fraction may not be an accurate description for some of the elements in the filtered fraction.

#### 4. Was streamflow a good predictor of dissolved and total concentrations?

Streamflow (Q) was significantly and inversely correlated (pearson correlation  $< -0.80$ ;  $p < 0.01$ ) at all four sites with dissolved (d) and total (t) Ca, Mg, and Sr only (Table 11 and Figure 4a-d). On a site-specific basis, significant inverse and good correlations ( $r < -0.80$ ;  $p < 0.01$ ) with streamflow were present also for alkalinity, DIC,  $As_d$ ,  $Ba_d$ ,  $Ba_t$ ,  $Li_d$ ,  $Li_t$ ,  $Na_d$ , and  $Na_t$  at BFB; for  $Li_d$  and  $Li_t$  at CFBM; for alkalinity, DIC,  $As_d$ ,  $Ba_d$ ,  $Ba_t$ ,  $K_d$ ,  $K_t$ ,  $Na_t$ ,  $S_t$ ,  $Si_d$ , and  $Si_t$  at LF; and for alkalinity, DIC,  $Ba_d$ ,  $Ba_t$ ,  $Li_t$ , and  $Na_t$  at BH. Significant positive, linear correlations with Q were present only for TSS,  $Mn_d$ ,  $Mn_t$ ,  $Fe_t$ ,  $Zn_d$  at site BH. Although  $Zn_t$  measurements are generally excluded from this report due to problems with contamination, it is worth noting that  $Zn_t$  was also correlated positively with Q at BH ( $r = 0.91$  and  $0.97$ , respectively, excluding an extreme outlier).

According to these results, the general pattern emerges that the major elements, Ba, and Sr were moderately well and inversely associated with Q, while many of the trace elements were poorly or positively correlated with Q. Hence, the processes controlling the major element concentrations in these streams and rivers were different from those controlling the inputs of trace metals. Based on other studies with similar results, a probable explanation for the behavior of the major elements is that in general, they were chemically conservative and were simply diluted by snowmelt during runoff (Bencala et al., 1987; McKnight and Bencala, 1988; Whitfield and Clark, 1992; Bhangu and Whitfield, 1997).

The mobilization of sediment and some trace metals during higher flows may be due to physical processes, as indicated by the positive association between TSS and total metal concentration with Q at BH. Physical mobilization of sediments from the streambed and floodplain may occur with high Q events because the higher stage and velocity of the river can and entrain more bottom sediments and access broader areas of the floodplain (Bradley, 1984; Whitfield and Clark, 1992; Droppo and Jaskot, 1995).

Yet, the chemical characteristics and availability of different sized sediments can vary substantially as well (Bradley and Lewis, 1982; Bird, 1987; Hatch et al., 1999). Hence, the size of the flow event may not necessarily correlate with the sediment and associated metal concentrations, as was the case at BFB, CFBM, and LF.

The mobilization of trace elements may also be chemical in nature, as suggested by the lack of predictability of the dissolved metal concentrations by Q, the most dominant physical factor. This lack of association between Q and dissolved trace elements such as As, Cu, Fe, Mn, Zn was most pronounced at site CFBM (Figure 5 a,b). The reactive nature of the trace elements makes them more susceptible to changing pH, redox, and temperature conditions, biological activity, and varying availability of complexing agents in the basin source areas and in the water channel (Forstner and Wittmann, 1979; Cossa et al., 1990; Shiller, 1997). The major source for the dissolved trace elements in the Clark Fork are the mining-contaminated floodplain soils and streambed sediments along most of the river corridor (Nimick and Moore, 1991; Axtmann et al., 1991). For example, trace metals that were immobilized in sulfide mineral complexes in the floodplain or in stagnant water areas may have become oxygenated and displaced into the water column at higher flows, where they temporarily remained out of equilibrium with Fe- or Mn-oxides/oxyhydroxides (Wetherbee and Kimball, 1991). They also may have been released into the river by the lifting of reduced bed sediments into the water channel, from hydrologic flushing of the hyporheic zone, or surface runoff that washed metal-rich salts off the floodplain (Lucy, 1996; Nagorski and Moore, 1999).

##### 5. Relationships between TSS and total recoverable elements

Correlations of TSS against the total recoverable elemental concentrations at each site reveal that total Al, Fe, and Mn are very well correlated ( $r \geq 0.88$ ,  $p < 0.01$ ) with the TSS concentration at all sites (except for Fe and Mn at LF, where they are below the PQL) (Table 12). Total Cu was also well correlated ( $r = 0.95$ ) with TSS at CFBM, while it was below the PQL at the other 3 sites. Good correlations indicate that the total metal concentrations could be reasonably well estimated using TSS, which is far easier and less expensive to measure. Unlike for the trace elements, the association between TSS and

most of the major elements was poor. Together with the insignificant differences between the dissolved and total recoverable phases of the major ions, this indicates that the available major elements are concentrated in the dissolved fraction rather than in the particulate load.

Not all elements correlated uniformly across the sites. For example,  $As_t$  was poorly correlated with TSS ( $r=0.38$  and  $-0.30$ ) at the two minimally contaminated sites (BFB and LF), while it correlated reasonably well ( $r=0.78$  and  $0.81$ ) at the two mining-impacted sites (CFBM and BH). This difference implies that the suspended sediments at CFBM and BH have approximately steady concentrations of As. Hence, when there were higher particulate levels in the river, the As concentrations increased accordingly. In contrast, the lack of a relationship between TSS and  $As_t$  at BFB and LF implies that the suspended sediments at these sites contained inconsistent concentrations of As.

One way of evaluating whether or not the mining-impacted sites had higher metal concentrations than the relatively pristine sites is to compare the total recoverable geochemistry. If rivers with similar TSS concentrations drain areas with similar physical and geochemical characteristics, the rivers also should have similar total recoverable metal concentrations. Considering that the TSS concentrations at CFBM (median=6.8 mg/L) were not statistically different ( $p<0.05$ ) from the TSS at BFB (median=5.5 mg/L), and that the TSS at BH (median=1.3) was not significantly different than the TSS at LF (median=1.7), one would expect that the concentrations of the total recoverable elements to be similar as well. Total Al, which is commonly used a correction factor for grain size variations, had identical median concentrations and concentration distributions at CFBM and BFB. However, median  $As_t$ ,  $Fe_t$ ,  $Mn_t$ ,  $S_t$ , and  $Zn_t$  concentrations were 13, 1.6, 4.7, 22, and 8.3 times higher, respectively, at CFBM than at BFB. Total Cu was at least 4.3 times higher at CFBM than at BFB (exact enrichment factors can not be calculated because  $Cu_t$  was below detection at BFB). Although median  $Al_t$  was twice as high at LF than at BH, median  $Fe_t$ ,  $Mn_t$ ,  $S_t$ , and  $Zn_t$  were 2.8, 4.8, 6.0, and 6.6 times higher, respectively, at BH than at LF. Therefore, both mining-impacted rivers were enriched in total-recoverable metals over their unmined counterparts.



## 6. Seasonal hysteresis at BFB, LF, and BH

Hysteresis patterns at sites BFB, LF, and BH were apparent for numerous parameters, while no hysteresis emerged from the CFBM data. At BFB, LF, and BH, pH and water temperature followed counter-clockwise hysteresis, meaning that they were lower along the rising limb of the hydrograph than on the falling limb (Figure 6a,b). The counterclockwise rotation in the pH loops indicates that earlier runoff was more acidic than later runoff, which presumably had more time to become buffered by materials in the watershed en route to the water channel.

Rotating in the other direction, dissolved oxygen, TSS,  $Al_t$ ,  $As_t$ ,  $K_d$ ,  $K_t$ ,  $Fe_t$ ,  $Mn_t$ ,  $S_d$ ,  $S_t$ , and  $Sr_t$  followed clockwise hysteresis patterns at the 3 sites (Figure 7a-d). These patterns for the dissolved elements ( $K_d$  and  $S_d$ ) suggest that the spring freshet exerted a piston-effect on relatively high-concentration solutes in ground water and soil water, or that the dissolved elements were preferentially eluted from the snowmelt (Stottlemyer and Toczydlowski, 1990; Williams et al., 1993; Campbell et al., 1995; Stottlemyer et al., 1997). Clockwise rotations for many of the total elements may have occurred due to flushing and subsequent depletion of sediments and other particulate matter in the channel and floodplain at the onset of high flow conditions (Williams, 1989; Droppo and Jaskot, 1995; Sokolov and Black, 1996).

Alkalinity,  $Ba_t$ ,  $Ca_d$ ,  $Ca_t$ ,  $Mg_d$ ,  $Mg_t$ , and  $Sr_d$  generally lacked open hysteresis loops at the sites (Figure 4a-d). Dissolved Ba at BFB was the only element with clear hysteresis, which rotated in a counter-clockwise direction. The lack of hysteresis loops means that the rising and falling limb concentrations were not distinct from one another due to linearity of the relationships or from cross-overs that prevented the formation of open loop patterns. Linear relationships indicate that concentration variations are in phase with Q variations. This can occur when the different geochemical sources have indistinguishable signatures or when the same sources are regulating the solute chemistry on the falling and rising limbs of the hydrograph. Cross-over patterns form as a result of inconsistent elemental concentrations of the various sources contributing to streamflow over the study period. A lack of clear hysteresis for these elements at LF was also found in the 1998 study (Nagorski et al., 2001). However, the same study identified counter-

clockwise hysteresis at BH for DIC, Ba, Ca, Li, and Si in 1998. It is possible that the difference between study years at BH may have been due to the better definition of the rising limb chemistry in 1998 than in 2000. While only 1 rising limb data point was collected in 2000, there were 3 such data points in 1998.

Several elements did not have consistent trends among sites BFB, LF, and BH. While DIC, Ba<sub>d</sub>, Na<sub>d</sub>, and Na<sub>t</sub> had no hysteresis loops at LF and BH, DIC and Ba<sub>d</sub> had counter-clockwise hysteresis and Na<sub>d</sub> and Na<sub>t</sub> had clockwise hysteresis at BFB. Dissolved Fe was below the PQL at LF and had no discernable pattern at BH, but had a clockwise pattern at BFB. Similarly, Li<sub>t</sub>, Mn<sub>d</sub>, and Ti<sub>t</sub> had clockwise rotation at BFB but were mostly or totally BPQL at LF and BH, so comparisons could not be made. Dissolved As had clockwise rotation at LF, no hysteresis at BH, and had counter-clockwise hysteresis at BFB if one discounts a single early season datapoint.

At BFB, the hysteresis loops for Ba, K, Na, Si, and Sr were more open than at sites LF and BH. This result is similar to those reported by Whitfield and Shreier (1981) and Whitfield and Clark (1992), who found wider hysteresis loops at sites further downstream than near the headwaters in several British Columbia streams and rivers. They hypothesized that such patterns may emerge due to the more numerous and chemically diverse sources available for contribution to the water channel at sites further downstream in the basins than those restricted to smaller drainage areas.

## 7. Discharge-concentration relationships at CFBM

At CFBM there was a complete absence of hysteresis patterns for all parameters measured. The hysteresis plots for CFBM show numerous cross-overs and overall disorder, as would be expected with an absence of a spring snowmelt hydrograph at the site (Figure 5a and 5b). The most prominent feature of CFBM's dataset is that TSS and total Al, As, Cu, Fe, Mn, P, and Ti were most highly concentrated on 6/1/00 and second most highly concentrated on 4/22/00 (Figure 8). On 6/1/00, the Montana Aquatic Life Standards for chronic and acute Cu (adjusted for hardness) were exceeded. Acute Cu violations also occurred on 4/22/00, while chronic exceedences occurred on 3/29/00, 4/14/00, 4/22/00 and 6/1/00.

The 6/1/00 sampling event captured the peak of a several-day long surge in streamflow caused by a large rain event the previous day (Figure 2b). On this day (5/31/00), 2.8 cm of precipitation was recorded in nearby Drummond, and this was the second largest single-day rain event of the year (WRCC, 2001). Streamflow on 6/1 was double that of the week before. Other researchers have also reported the flushing of suspended sediment and metals in industrialized watersheds at the onset of increasing Q levels (Bradley and Lewis, 1982; Bird, 1987; Sanden et al., 1997; Nagorski et al., 2001).

The sampling on 4/22/00 followed 1-2 weeks of intermittent rainfall that was also accompanied by fluctuations in the hydrograph, although these Q variations were not nearly as dramatic as on 6/1/00 (Figure 2b). Considering the 5% error on the Q values, the Q on 4/22/00 was no different from the Q on both 3/29/00 and 4/14/00, when TSS and metal concentrations were substantially lower. Therefore, the surge in TSS and associated metals occurred due to processes in the basin that supplied the river with sediment and its associated metals without significantly changing the Q values. One possible mechanism for this could be that early spring rains became absorbed by the soils, and this process of ground saturation forced later rainfall to enter the river as direct surface runoff, which could in turn carry floodplain soils and sediments with it into the water channel. As mentioned earlier, potential sources of metals-enriched sediments are abundant along the Clark Fork River floodplain due to the mining and smelting wastes in the watershed (Nimick and Moore, 1991).

#### 8. Is there evidence of spring flushing?

For some elements, a lack of good linear correlation with Q and a lack of clear hysteresis patterns may be explained by the interference of one or two data points collected during the early stages of runoff that appear to defy otherwise discernable patterns. These samples, which are characterized by a disproportionately large increase in concentration with the initial rise in Q at each site are termed "spring flushing" points. Many other researchers have identified such points in temporal sampling studies, although most of the focus in the literature has been on the flushing of atmospherically-derived acidic anions such as sulfate and nitrate from the snowpack (Williams et al., 1993; Campbell et al., 1995), with little attention given to major cation, trace element,

and particulate concentrations. The only known report of cation flushing in watersheds is from Sottlemeyer and Toczydlowski (1990), who found flushing of Ca, Mg, Na, K, and  $\text{NH}_4^+$  in a Michigan stream.

Examination of the patterns of the cross-over elements at BFB reveal that  $\text{As}_d$ ,  $\text{Ca}_d$ ,  $\text{Ca}_t$ ,  $\text{Mg}_d$ ,  $\text{Mg}_t$ , and  $\text{Sr}_d$  had open counter-clockwise hysteresis loops (which was found for  $\text{Ba}_d$ ), if a single early event data point is not considered (Figure 4a, Figure 9a,b). Conversely, the unusually high value for dissolved and total S in the early spring opened a loop in what would otherwise be a linear relationship between Q and S concentration (Figure 7d). Dissolved and total As, K, Li, Mn, Na, S, Si, and Sr surged in concentration on 3/29/00 at the site, when streamflow was at the very early stages of increasing spring runoff (Figure 10a,b). Of these elements,  $\text{As}_t$ , and total and dissolved K, Na, S, and Si were higher on 3/29 than on any other date during the 12 month study. Total Al, Fe, Mn, and Ti peaked 2 weeks later, on 4/14/00, following the sharpest hydrograph rise of the spring runoff event (Figure 10c,d). TSS concentrations were highest between 3/29/00 and 4/22/00.

At site CFBM, spring runoff flushing is not possible to identify due to the lack of a spring freshet peak. However, as discussed in the previous section, surges in TSS and associated total elements (Al, As, Fe, Mn, P, and Ti) occurred on 4/22/00 and 6/1/00. The flushing events on these dates are more accurately described as flushing by precipitation events rather than by large-scale melting of snowpack in the watershed.

At site LF, we captured 2 main peaks in TSS during early runoff; one was on 4/22/00 and the second was on 5/3/00 (Figure 11a). Total Al, Fe, Mn, and  $\text{Mn}_d$  had similar peaks on these dates (Figure 11b). Alkalinity and total Ba, Si, and Sr also had a flushing effect on the surface water (Figure 11c). Their concentrations were higher on 3/29/00 compared with 2/26/00, even though flow had increased from 490 to 720 L/s. Other than  $\text{Mn}_d$ , which is likely colloidal and not truly dissolved, no other dissolved elements exhibited early spring flushing. These results are different from those found at the site in the spring of 1998 (Chapter 2; Nagorski et al., 2001). At that time, dissolved Ca and Mg flushing was measured in the early spring freshet samples. These differences in the study years might be due to the sampling frequencies being too coarse to capture

short-term flushing events. In the 1998 study, total recoverable concentrations were not measured, and so between-year comparisons can not be made.

At site BH, spring flushing is evident for K, and S (Figures 12 a,b). Dissolved and total K concentrations increased by 10% on 3/29/00 compared with 2/26/00, even though discharge had also increased (from 540 to 770 L/s). More pronounced flushing is evident for S. Dissolved S (which was not different from total S) dropped sharply after rising though 4/22. It remained at relatively low levels during the summer months when most other major ions were at their highest. It had a secondary peak in mid June, and its largest peak was in November. Spring flushing of S was observed at the same site in 1998 by Nagorski et al., (2001). Although S flushing has been widely reported in the literature as occurring in watersheds draining snowpacks with atmospherically-derived S (Schemenauer et al., 1985; Campbell et al., 1991), S flushing was observed at BH and not at LF in both study years. This indicates that the upstream mining sources in the Blackfoot River might have been driving the S surges during high flow events, and not atmospheric inputs.

9. By what extent do concentrations change during high flow compared to low flow?

a) Elements with inverse, approximately linear relationships with Q:

At BFB, most elements that correlated inversely with Q (alkalinity, DIC, As<sub>d</sub>, Ba<sub>d</sub>, Ba<sub>t</sub>, Ca<sub>d</sub>, Ca<sub>t</sub>, Li<sub>d</sub>, Li<sub>t</sub>, Mg<sub>d</sub>, Mg<sub>t</sub>, Na<sub>d</sub>, Na<sub>t</sub>, Sr<sub>d</sub>, and Sr<sub>t</sub>.) decreased to 40-55% of baseflow concentrations when Q increased by a proportionally greater amount—by 8.5 times during the height of runoff. The exceptions were dissolved and total Li and Na, which were more dilute, at 22-30% of baseflow concentrations during peak flow. At CFBM, there was a 5.5-fold increase at the highest flow event sampled compared with the lowest Q sampled. Yet, the elements that correlated inversely with Q (Ca<sub>d</sub>, Ca<sub>t</sub>, Li<sub>d</sub>, Li<sub>t</sub>, Mg<sub>d</sub>, Mg<sub>t</sub>, Sr<sub>d</sub>, and Sr<sub>t</sub>) decreased to only 48-74% of their low-flow concentrations. More dramatically, at LF the highest Q was 28 times the low-flow Q, but the inversely-correlated elements (alkalinity, DIC, As<sub>d</sub>, Ba<sub>d</sub>, Ba<sub>t</sub>, Ca<sub>d</sub>, Ca<sub>t</sub>, K<sub>d</sub>, K<sub>t</sub>, Mg<sub>d</sub>, Mg<sub>t</sub>, Na<sub>t</sub>, S<sub>t</sub>, Si<sub>d</sub>, Si<sub>t</sub>, Sr<sub>d</sub>, and Sr<sub>t</sub>) remained at 42-70% of their baseflow concentrations. Finally, at site BH, the greatest difference in Q was a 16-fold increase during the peak of runoff

compared with baseflow. There, too, elements that correlated inversely with Q (alkalinity, DIC, Ba<sub>d</sub>, Ba<sub>t</sub>, Ca<sub>d</sub>, Ca<sub>t</sub>, Mg<sub>d</sub>, Mg<sub>t</sub>, Na<sub>t</sub>, Sr<sub>d</sub>, and Sr<sub>t</sub>) were diluted by a relatively small amount, to 50-64% of their baseflow concentrations.

In sum, the concentrations of most of these elements generally decreased by the narrow range of approximately 40-70% at all sites, even though the maximum Q values at each site varied from 5.5 to 28 times the baseflow levels. This suggests that despite the variations in the increases of flow due to varying amounts of presumably dilute spring freshet, the meltwaters were being approximately uniformly mitigated by other sources in the basin that had relatively high concentrations of major elements. That is, most of the water contributing to the high flow events at each site likely was routed through soil and aquifer materials and picked up solutes before reaching the stream channel, no matter how much meltwater there was (Campbell et al., 1995; Droppo and Jaskot, 1995; Stottlemyer et al., 1997).

Additionally, closer examination of the relationships between the elements and Q reveal that at BFB and LF, the concentrations of many of the elements leveled off past a certain high Q threshold (Figures 4a, 4c). What emerges is an "L" shape to the Q vs. concentration plots, in which the negative slope of the Q v. concentration relationship approaches zero at the higher flow levels. This is observed for DIC, Ba<sub>d</sub>, Ba<sub>t</sub>, Ca<sub>d</sub>, Ca<sub>t</sub>, Mg<sub>d</sub>, and Mg<sub>t</sub> at BFB, and for the aforementioned elements and alkalinity, and As<sub>d</sub>, As<sub>t</sub>, Si<sub>d</sub>, Si<sub>t</sub> and Sr<sub>t</sub> at LF. At BFB, the break in slope occurred when Q was approximately 5-times baseflow levels, and at LF when Q reached approximately 10-times baseflow levels. Sites CFBM and BH showed no similar L-shaped relationships. In a 1997-1998 study in Landers Fork and Upper Blackfoot, Nagorski et al. (2001) made similar observations for site LF. They too reported a stabilization of solute concentrations when Q exceeded 10 times baseflow levels. These results indicate that beyond a certain level of discharge, high flow input may be overwhelming the chemical signature contributed by water supplies that are dominant during low flow conditions.

b) Elements with positive linear relationships with Q:

BH was the only site where any measured parameters correlated positively and approximately linearly with Q. At this site, where Q was 16 times larger during the highest flows compared with the lowest flow, TSS increased by up to 39 times during high flow. Dissolved Mn increased by up to 6 times,  $Mn_t$  by 22 times, and  $Fe_t$  by 28 times. Therefore, increases in Q created disproportionately large increases in the suspended sediments and associated total metals. In this mining-impacted basin, this pattern may be explained by higher and faster flows being able to access greater volumes of metals-enriched streambed and floodplain sediment originating from the wastes produced by the historic mining operations near the headwaters.

## **II. Diel cycling**

Based on the 2 days of diel sampling at each site, diel cycle patterns were identified for pH, D.O., and water temperature at all 4 sites (Figures 13 a-c). Additionally, DIC had a diel pattern at BFB, CFBM, and BH (Figure 13d), and  $K_d$  and  $K_r$  cycled at site BH (Figure 13e). At site CFBM, TSS and total Al, Cu, Mn, Ti, and Zn showed a diel pattern as well (Figure 13f-h). TSS appeared to display diel cycling at BFB as well, although the trends are mostly within the precision errors of the TSS measurements (Figure 13i). Many trace elements were below detection at the sites, and so although diel cycling was not measured, it cannot be definitively ruled out with this dataset.

The pH, D.O., and water temperature patterns were similar at all sites, as these parameters increased after sunrise, peaked between noon and 18:00, and then decreased at nighttime. Not all sites had the same timing of minima and maxima, however. At BFB, pH peaked at 16:00, at CFBM it peaked at 12:00-13:00, at BH the peaks were at 15:00 and 17:00, and at LF the pH remained stable at its highest value over a relatively long period of time- from noon to 18:00. At BFB and CFBM, the D.O. peaks occurred approximately 2 hours later than the pH peaks. At BH and LF, the D.O. cycles were far less pronounced than they were at BFB and CFBM. At BH the peaks occurred at 15:00, while at LF the D.O. peak was at 18:00 on the first day and at 14:00 on the second day.

The water temperatures reached their daily maxima between 14:00 and 18:00 at the sites, slightly later than the air temperature maxima, which were measured between 13:00 and 15:00.

Diel cycling of DIC followed a trend opposite that of pH, D.O. and water temperature. DIC increased at night and decreased during the day. At BFB and CFBM, DIC peaked at 6:00-8:00, while at BH, concentrations were steadily higher between 23:00 and 9:00 compared to the daytime. This is consistent with pH, D.O., and inorganic carbon diel cycling found in other studies, which credit the process to regulation by photosynthesis and respiration of aquatic plants and algae (McKnight et al., 1988; Fuller and Davis, 1989; Brick and Moore, 1996) .

At site BH, the diel cycling of  $K_d$  and  $K_t$  exhibited nighttime increases as well. The difference between daytime and nighttime K concentrations was only approximately 10%, but the results are consistent on both days. The lowest concentrations were at about noon, and the highest occurred during the late evenings. The cause of this cycling is not known, but it is interesting to note that this element was one of only 3 which exhibited spring flushing at the site.

At CFBM, TSS and total Al, Cu, Mn, and Ti were 150-400% higher at night than during the day. These total metals correlated moderately well ( $r=0.66-0.75$ ) with TSS at the site over the diel timescale. Total Zn showed a similar pattern by being twice as concentrated at night as during the day, but these data are inconclusive due to the problems with Zn contamination. This observance of TSS and associated trace metal cycling is similar to the results found by Brick and Moore (1996) on the Clark Fork River near Deer Lodge, 92 km upstream of CFBM. Those researchers detected nighttime increases in TSS, dissolved Mn and Zn, and acid soluble Fe, Mn, Cu, and Zn. The cause for the nighttime increases in the suspended sediment and associated metals is unknown, although Brick and Moore (1996) suspected that nocturnal benthic insect activity could account for the differences.



### III. Rain-storm response

#### 1. Precipitation

In Butte, at the headwaters of the Clark Fork River, 1.14 cm of rain fell on 9/1 and 9/2, about twice the cumulative precipitation there (0.58 cm) from mid July-August 31. Similarly, in Drummond, only 9 miles from CFBM, only 0.18 cm fell between 7/10/00-8/31/00, compared with the 0.66 cm that fell on 9/1 and 9/2. A total of 1.57 cm fell from 9/1-9/6, and more rain (1.09 cm) fell on 9/11-9/13.

In the Blackfoot River basin, a similar pattern of early September rains followed many weeks of near-drought conditions. In Lincoln, the town approximately 15 km downstream of BH and LF, the cumulative precipitation of 1.57 cm on 9/1 and 9/2 exceeded the total precipitation (1.50 cm) of the 8 previous weeks. Similar levels of rainfall fell in the region through 9/5/00 and again from Sept 9-12. Midway down the basin, in the town of Ovando, there was 1.34 cm of precipitation on 9/3/00. This too was a drastic change from the previous 8 weeks, during which only 0.30 cm fell in the region.

All precipitation data comes from the WRCC (2001).

#### 2. Streamflow variation during storm

At BFB and LF, Q rose by approximately 20% following the onset of the September rains (Figure 14a,b). There was a larger relative change in Q at BH, where Q rose from 260 to 410 L/s between September 1-5 (Figure 14c). The largest Q response was at CFBM, where Q nearly doubled from 3100 L/s on 9/1/00 to 5800 L/s on 9/6/00 (Figure 14d).

#### 3. Water quality response to September rain events

a) Site BFB: Several parameters exhibited a response to the rain events and subsequent increase in Q. The pH level dropped on 9/2 and 9/3 by 0.1 units before going back up to 8.35-8.40 for the rest of the period. TSS decreased from 1.4-1.8 mg/L on 9/1 and 9/2 to 0.6 mg/L on 9/4/00, and then it went back up to 1.4-2.0 for the rest of the next week. The water temperature fell from 15°C to 11°C. Dissolved Mn was the only element which decreased in concentration over the first week of the rainy period (Figure

15a). By 9/6/00, it had dropped to 0.8  $\mu\text{g/L}$  from 1.1-1.2  $\mu\text{g/L}$  on 9/1 and 9/2, and after 9/6/00 it returned to its earlier concentrations.

Several elements increased in concentration over the course of rain-event study period. These included DIC, which increased by about 6%;  $\text{Fe}_d$  and  $\text{Fe}_t$ , which were rather noisy but overall increased by about 20%; and  $\text{K}_d$ ,  $\text{K}_t$ ,  $\text{Na}_d$ ,  $\text{Na}_t$ ,  $\text{S}_t$ ,  $\text{Si}_d$ ,  $\text{Si}_t$ , and  $\text{Sr}_d$  and  $\text{Si}_t$ , which increased by 10-20%. Dissolved S showed a stronger response; it increased by 30% between 9/1 and 9/12 (Figure 15b). Except for DIC and  $\text{Na}_t$ , these elements were among those that did not have good inverse, linear correlations with Q over the seasonal scale as well. Additionally, dissolved and total K, Na, S, Si, and Sr had concentration surges at the start of snowmelt in the spring. Their positive response to the increasing Q in September indicates that the rain created a flushing effect of those elements, rather than a diluting effect, just as the onset of spring runoff created a flushing effect in late March. This finding suggests that these elements are not predictable using Q alone in both short term (e.g. 1-2 weeks) and long term (e.g. several months of spring runoff) events in the watershed. Instead, information on the timing of relatively large surges in Q could be more useful in predicting the concentrations of these elements.

b) Site CFBM: This site, which had the largest Q response to the rainfall, exhibited some of the strongest geochemical responses. Total suspended sediment, which was relatively low from 9/1 to 9/4, (at 2.0-3.1 mg/L), increased sharply on 9/5, when it rose to 8.2 mg/L (Figure 16a). It continued to increase to 15 mg/L steadily through 9/12, except for a dip to 6.0 mg/L on 9/6. Total Al, Cu, Fe, Mn, P, Ti, and Zn followed almost identical patterns, increasing by 3-8 times over the 12 day study period (Figure 16b). As discussed earlier, these trace metals were generally well associated with TSS on the seasonal scale as well. Also increasing with Q were  $\text{Ba}_d$ ,  $\text{Ba}_t$ ,  $\text{Si}_d$  and  $\text{Si}_t$ , which rose by approximately 20% and whose trends were similar to those of the trace metals mentioned above (Figure 16c). Dissolved and total K also rose through 9/6/00, although unlike TSS and the associated metals, their concentrations dropped during the second half of the sampling event.

Dissolved and total Li, Mg, S, and Sr behaved in an opposite manner. These elements declined in concentration by 10-25% as the Q rose (Figure 16d). Dissolved and

total Li, Mg, and Sr also had good linear inverse correlations with Q on the seasonal scale, again suggesting that the system responded similarly to a significant rain event as it did to higher water during the spring earlier in the year.

c) Site LF: At this site, most changes that occurred over the rain event were within the measurement errors. No trends in concentrations are observed for this sampling period. The one exception is that dissolved S rose steadily by approximately 10%, from 0.93 mg/L on 9/1 to 1.00 mg/L on 9/10 (Figure 17). However, considering that the highest field blank reading on S was 0.08 mg/L, this trend may not be accurate. Nonetheless, it is interesting to note that in the fall of 1998, Nagorski et al. (2001) also found a surge in dissolved S at the same site. They hypothesized that the increases to S could have been due to delivery by rainfall directly, or by precipitation-induced flushing of S in adjacent aquifers—processes which have been identified by other researchers as likely sources for autumn S increases in watersheds (Williams et al., 1993 and Campbell et al. 1995).

d) Site BH: At this site, only a few parameters had measurable responses to the increase in Q. DIC, Ca, Mg, Si, and Sr concentrations dipped between 9/4-9/6, although these decreases were only 3-10%, which is close to the precision limits of the analytical measurements. Water temperature fell from 15 to 10°C. TSS decreased from 0.5 mg/L on 9/1 to 0.2 mg/L on 9/4, and then rebounded to 0.6 by 9/8.

The largest change in concentrations was for dissolved and total S. Its concentration was 3.6 mg/L on 9/1 and 9/3, and then it increased until 9/4, when its concentration was approximately 20% higher, at 4.4 mg/L. On 9/8 and 9/10, its concentration was still higher (at 4.0-4.1 mg/L) than it was at the start of the sampling event. Interestingly, this element exhibited flushing patterns at the site during spring runoff earlier in the year and also during the spring of 1998 (Nagorski et al. 2001). These results again indicate that the geochemical response to the high precipitation event was similar to the spring runoff response.

#### **IV. Comparison of seasonal, rain-event, and diel scale variabilities**

##### **1. How do diel variations compare with seasonal variations?**

The range (maximum value- minimum value) in diel concentrations was compared with the range in seasonal (12-month) concentrations, although extreme outliers (values > 3 times the interquartile range) were excluded (Table 13 a-d). These outliers were removed from the comparison in order to avoid inflating range values with data that were highly unusual within each temporal set because of possible sample contamination problems. Most of the elements that had extreme outliers were the total recoverable metals.

Based on calculations of the percent of the seasonal range captured by the diel range for each parameter, the data were separated into three groups: parameters whose diel range (1) was  $\geq$  than seasonal range; (2) was 50-99% of the seasonal range; and (3) was  $<$ 50% of the seasonal range.

Only 3 analytes fell within the first category. At site CFBM, the D.O. (in terms of percent saturation) was 135% greater over the 48 hour study period in September than during the 12 month seasonal study. The second element,  $Mo_i$  at CFBM, also had a diel range that exceeded the seasonal range. While the seasonal concentrations ranged from less than the PQL (0.003 mg/L) to 0.005 mg/L, the diel concentrations ranged from 0.003 to 0.009 mg/L. The relatively high diel  $Mo_i$  concentrations occurred between 9:00 and 21:00 on 9/18/00 for unknown reasons. The one other element with a diel range capturing the seasonal range was dissolved As at site BH. There, the seasonal range was from 0.2 to 0.4  $\mu$ g/L, while the diel concentration varied from 0.3 to 0.5  $\mu$ g/L—although these concentrations are very close to the PQL of 0.2  $\mu$ g/L.

The second category, in which the diel range covered 50-99% of the seasonal range, is comprised of: D.O. (mg/L) and  $As_d$  at BFB; pH, D.O. (mg/L) and  $Ca_d$  at CFBM; pH, water temperature, D.O. (% saturation),  $As_i$ ,  $K_d$ , and  $Si_d$  at BH; and pH, water temperature, D.O. (% saturation), and  $As_d$  at LF.

All other elements fell into the third category, in which the ranges of diel concentrations were less than 50% the seasonal ranges. Yet, several parameters were in the higher end of this category. For example, the diel ranges of pH, water temperature,

and D.O. at BFB were 32-46% of the seasonal ranges. The TSS and associated total metals at CFBM had high percentages as well. The diel TSS range spanned 46% of the seasonal variation;  $As_d$  and  $As_t$  spanned 33-36%;  $Cu_t$  was 21% the seasonal range;  $Fe_d$  and  $Fe_t$  spanned 22 and 28%, respectively, and  $Mn_d$  and  $Mn_t$  covered 26 and 28% of the seasonal variation. At all sites, most of the major elements had diel concentration ranges which were between 5 and 30% of the seasonal ranges.

An important point to consider with these values, especially for those elements that are close to the detection limits is that portions of the variability may be due to instrument measurement error. That is, the relatively large diel variations may be due a combination of real environmental change and of laboratory measurement error. Nonetheless, the results show that for whatever the reason, diel processes can cause as much change as seasonal processes. This result underscores the importance of sampling at consistent times of the day when aiming to evaluate long-term or spatial trends in trace metal geochemistry.

Only a few other researchers have compared diel variations to seasonal variations in rivers. McKnight and Bencala (1988) reported that during the 48 hour period they studied, the Fe changes in the Snake River, Colorado reflected 47% of the total variability seen over 6 years at the site. Similarly, Constanz (1998) found that the diurnal surface water temperature in 2 large Sierra Nevada streams captured 30-40% of the annual variation.

## 2. How does the September rain event geochemistry compare with the diel and seasonal-scale variations?

Examination of the boxplots in Figures 19-22 reveals that the amount of geochemical variability encountered at all 4 sites during the first 2 weeks of September was typically much smaller than the seasonal variability. The range in concentrations during the September rain event was more similar to those found during the diel studies for most measured parameters. However, the diel variability was generally larger than the rain event variability for the parameters with strong diel cycling, such as pH, DO (% saturation), and temperature. As noted earlier, both the seasonal and September sampling events took place at consistent times of day at each site.

With the exception of dissolved Mo at CFBM, there were no cases of the September rain event variability exceeding the seasonal variability. However, at CFBM the rain event produced nearly the same amount of concentration variation as was observed over the 12 month seasonal study for TSS, Al<sub>t</sub>, Cu<sub>t</sub>, Fe<sub>t</sub>, Mn<sub>t</sub>, P<sub>d</sub>, P<sub>t</sub>, S<sub>d</sub>, S<sub>t</sub>, Si<sub>t</sub>, and Zn<sub>t</sub>. (Figure 20). As described earlier, the September rain event triggered a 7-fold increase in TSS and a 3 to 8-fold increase in total recoverable metals. Put into the context of the overall seasonal variability, this relatively short-term rain event created conditions in the Clark Fork that reflected much of the variability seen on the seasonal scale.

These results, illustrated by the boxplots in Figures 19-22, indicate that the measured geochemistry of these rivers is highly dependent on the sampling design and frequency. From these results emerge the obvious implications for the design of future sampling projects. Without taking into account the time of day and sampling intensively during short term periods of variable climatic conditions, any attempts to characterize the seasonal or annual variations in surface waters may produce skewed and unrepresentative samples which may inaccurately portray the geochemical dynamics in rivers.

## **SUMMARY AND CONCLUSIONS**

The findings of this project indicate that major variations in the geochemistry of streams and rivers in Montana may occur within diel, daily, and seasonal time scales. Within the same water bodies, some constituents vary predictably and conservatively according to changes in streamflow, while others behave irregularly and in response to a complex combination of physical and chemical dynamics in the basin source areas.

The Clark Fork River, which lacked the typical spring runoff hydrograph peak due to abnormally dry conditions in the watershed and large irrigation withdrawals, had higher concentrations of most measured elements than the 3 other sites over the 12 month study period. The mining-impacted sites (CFBM and BH) had higher concentrations of S and some metals (Fe, Mn, and Zn) than the relatively pristine sites (BFB and LF).

On the seasonal scale, streamflow generally correlated inversely with many of the major elements, and it was positively or poorly associated with TSS and trace metals. As

a result, predicting the geochemistry of most solutes and particulates in this river cannot be done accurately using streamflow alone. While the major elements were conservatively diluted by snowmelt (generally by 40-70%), the trace metals were appeared to be sensitive to changing particulate availability and chemical variations in the watershed.

Numerous elements at BFB, LF, and BH exhibited hysteresis patterns, in which falling limb concentrations were different from rising limb concentrations. Some elements had different types of relationships with Q at each of the study sites, indicating that watershed-specific processes regulate the timing of their geochemical variations. Most total recoverable metals followed TSS trends, which had clockwise hysteresis. This rotation direction is likely due to the washing out and subsequent depletion of sediments in the watershed that had built up over low-flow winter conditions.

In contrast, most major elements exhibited linear relationships or cross-over hysteresis patterns with Q. Many of the elements without open hysteresis loops would have had counter-clockwise rotation if a small number of early spring data points were not considered. These early spring surges in concentrations are thought to be produced by flushing mechanisms, in which accumulated stored solutes are suddenly displaced into the stream channel by the meltwater, or by preferential elution from the snow itself. Spring flushing was found for TSS, Al<sub>t</sub>, As<sub>d</sub>, As<sub>t</sub>, Fe<sub>t</sub>, K<sub>d</sub>, K<sub>t</sub>, Li<sub>d</sub>, Li<sub>t</sub>, Mn<sub>t</sub>, Na<sub>d</sub>, Na<sub>t</sub>, S<sub>d</sub>, S<sub>t</sub>, Si<sub>d</sub>, Si<sub>t</sub>, Sr<sub>d</sub>, Sr<sub>t</sub> and Ti<sub>t</sub>, at BFB, which also had wider hysteresis loops for many elements than at LF and BH. Spring flushing was also identified for alkalinity, Al<sub>t</sub>, Ba<sub>t</sub>, Fe<sub>t</sub>, Mn<sub>d</sub>, Mn<sub>t</sub>, Si<sub>t</sub>, and Sr<sub>t</sub> at LF, and for dissolved and total K and S at BH.

At CFBM, there were no discernable relationships between Q and concentration for most parameters. The highest concentrations of TSS and associated metals occurred on days following relatively large rain events in the basin, indicating that rain-generated surface runoff can supply the river with mining-contaminated floodplain sediments or water and degrade the water quality 130 km downstream from the historic mining center.

Many elements that exhibited flushing effects at the start of spring runoff behaved similarly when relatively large September precipitation events ended 2 months of near-drought conditions in the region. Both dissolved and total recoverable concentrations of

many elements climbed with increasing Q produced by the fall rain. At CFBM, particularly large rises in metal concentrations were observed during this short-term sampling event.

Dissolved oxygen, pH, and water temperature had diel cycles at all sites, and DIC cycled at 3 sites. Such cycles are thought to be dependent on photosynthesis and respiration patterns by plants and algae in the streams and rivers. At CFBM, suspended sediment and associated total recoverable metals were higher at night than during the day on both 24-hour sampling events. These findings are similar to those found further upstream in a 2 day study by Brick and Moore (1996), who hypothesized that enhanced benthic insect activity at night may account for the diel changes. The reproducibility of their results in this project suggests that nighttime increases in suspended sediment and associated metals may be a common occurrence in the river. It is recommended that future studies be conducted on this issue and on the possibility that suspended sediment variations occur on a diel scale in other rivers as well.

The range of diel variations rivaled the seasonal variations for many elements. Major parameters such as pH, DO, TSS, and some total recoverable metals varied almost as much or even more on the diel scale as they did on the seasonal scale at some or all sites. The range in geochemical concentrations observed on the scale of the September rain event was typically smaller than the seasonal variability and similar to the diel-scale variability. Yet, some parameters varied a relatively large amount during the late summer rains as well. Most prominently, TSS and total recoverable metals at CFBM varied almost as much during the 2 weeks of rain as they did on the entire seasonal scale. These results advocate for the need to sample at consistent times of the day and over variable climatic conditions when attempting to characterize long-term geochemical trends in streams and rivers.



**Tables 1.1-1.4: Laboratory and Field Blanks**

Table 1.1

Summary: ICAPES measurement of Lab Blanks					
Element	Units	PQL	Total number of blanks	Number of blanks below PQL	Highest conc. found
Al	mg/L	0.01	237	237	(BPQL)
Ba	mg/L	0.0005	237	237	(BPQL)
Be	mg/L	0.0001	237	220	0.0003
Ca	mg/L	0.07	237	234	0.13
Cd	mg/L	0.001	237	237	(BPQL)
Co	mg/L	0.003	237	237	(BPQL)
Cr	mg/L	0.005	237	237	(BPQL)
Cu	mg/L	0.003	237	237	(BPQL)
Fe	mg/L	0.005	237	237	(BPQL)
K	mg/L	0.20	237	237	(BPQL)
Li	mg/L	0.002	237	237	(BPQL)
Mg	mg/L	0.10	237	237	(BPQL)
Mn	mg/L	0.0005	237	237	(BPQL)
Mo	mg/L	0.003	237	237	(BPQL)
Na	mg/L	0.18	237	231	0.31
Ni	mg/L	0.001	237	237	(BPQL)
P	mg/L	0.01	237	237	(BPQL)
Pb	mg/L	0.02	237	237	(BPQL)
S	mg/L	0.007	237	223	0.023
Si	mg/L	0.02	237	237	(BPQL)
Sn	mg/L	0.0025	237	237	(BPQL)
Sr	mg/L	0.0005	237	235	0.0008
Ti	mg/L	0.005	237	237	(BPQL)
V	mg/L	0.005	237	237	(BPQL)
Zn	mg/L	0.001	237	237	(BPQL)

PQL= Practical Quantifiable Limit

BPQL= Below Practical Quantifiable Limit

Table 1.3

Summary: ICAPES measurement of FA Field Blanks					
Element	Units	PQL	Total number of blanks	Number of blanks below PQL	Highest Conc. found
Al	mg/L	0.01	48	47	0.06
Ba	mg/L	0.0005	48	45	0.0014
Be	mg/L	0.0001	48	48	(BPQL)
Ca	mg/L	0.07	48	47	0.13
Cd	mg/L	0.001	48	48	(BPQL)
Co	mg/L	0.003	48	48	(BPQL)
Cr	mg/L	0.005	48	48	(BPQL)
Cu	mg/L	0.003	48	48	(BPQL)
Fe	mg/L	0.005	48	47	0.041
K	mg/L	0.20	48	48	(BPQL)
Li	mg/L	0.002	48	48	(BPQL)
Mg	mg/L	0.10	48	48	(BPQL)
Mn	mg/L	0.0005	48	47	0.0006
Mo	mg/L	0.003	48	48	(BPQL)
Na	mg/L	0.18	48	25	0.61
Ni	mg/L	0.001	48	48	(BPQL)
P	mg/L	0.01	48	48	(BPQL)
Pb	mg/L	0.02	48	48	(BPQL)
S	mg/L	0.007	48	4	0.077
Si	mg/L	0.02	48	46	0.23
Sn	mg/L	0.0025	48	48	(BPQL)
Sr	mg/L	0.0005	48	47	0.0007
Ti	mg/L	0.005	48	48	(BPQL)
V	mg/L	0.005	48	48	(BPQL)
Zn	mg/L	0.001	48	48	(BPQL)

FA= Filtered and acidified

TR= Total recoverable; digested according to EPA Method XXX.

Table 1.2

Summary: Laboratory blanks measured on TSS filters, AAS and Carbon Analyzer					
Analyte	Units	PQL	Total number of blanks	Number of blanks BPQL	Highest conc. found
TSS	mg/L		9	-	0.1
Arsenic	µg/L	0.2	262	262	(BPQL)
DIC	mg/L	1.0	113	113	(BPQL)

Table 1.4

Summary: Field Blanks measured on AAS, Alkalinity titrator, and Carbon Analyzer					
Analyte	Units	PQL	Total number of blanks	Number of blanks BPQL	Highest conc. found
As (FA and TR)	µg/L	0.2	96	96	(BPQL)
Alkalinity	mg/L	4	48	13	8.8
Inorganic C	mg/L	1.0	48	48	(BPQL)

**Tables 2.1-2.3: Digested field blanks and digest blanks**

Table 2.1

Summary: ICAPES measurement of TR Field Blanks					
Element	Units	PQL	Total number of blanks	Number of blanks below PQL	Highest Conc. found
Al	mg/L	0.01	45	39	0.03
Ba	mg/L	0.0005	45	45	(BPQL)
Be	mg/L	0.0001	45	45	(BPQL)
Ca	mg/L	0.07	45	42	0.14
Cd	mg/L	0.001	45	45	(BPQL)
Co	mg/L	0.003	45	45	(BPQL)
Cr	mg/L	0.005	45	42	0.018
Cu	mg/L	0.003	45	45	(BPQL)
Fe	mg/L	0.005	45	30	0.069
K	mg/L	0.20	45	45	(BPQL)
Li	mg/L	0.002	45	45	(BPQL)
Mg	mg/L	0.10	45	45	(BPQL)
Mn	mg/L	0.0005	45	45	(BPQL)
Mo	mg/L	0.003	45	45	(BPQL)
Na	mg/L	0.18	45	42	0.28
Ni	mg/L	0.001	45	38	0.004
P	mg/L	0.01	45	36	0.03
Pb	mg/L	0.02	45	45	(BPQL)
S	mg/L	0.007	45	33	0.078
Si	mg/L	0.02	45	39	0.05
Sn	mg/L	0.0025	45	45	(BPQL)
Sr	mg/L	0.0005	45	45	(BPQL)
Ti	mg/L	0.005	45	45	(BPQL)
V	mg/L	0.005	45	45	(BPQL)
Zn	mg/L	0.001	45	25	0.29

Table 2.2

Summary: ICAPES measurement of TR Digest Blanks					
Element	Units	PQL	Total number of blanks	Number of blanks below PQL	Highest Conc. found
Al	mg/L	0.01	83	83	(BPQL)
Ba	mg/L	0.0005	83	81	0.001
Be	mg/L	0.0001	83	83	(BPQL)
Ca	mg/L	0.07	83	77	0.14
Cd	mg/L	0.001	83	83	(BPQL)
Co	mg/L	0.003	83	83	(BPQL)
Cr	mg/L	0.005	83	81	0.017
Cu	mg/L	0.003	83	83	(BPQL)
Fe	mg/L	0.005	83	76	0.069
K	mg/L	0.20	83	83	(BPQL)
Li	mg/L	0.002	83	83	(BPQL)
Mg	mg/L	0.10	83	83	(BPQL)
Mn	mg/L	0.0005	83	82	0.0031
Mo	mg/L	0.003	83	83	(BPQL)
Na	mg/L	0.18	83	78	0.26
Ni	mg/L	0.001	83	74	0.006
P	mg/L	0.01	83	65	0.07
Pb	mg/L	0.02	83	83	(BPQL)
S	mg/L	0.007	83	69	0.065
Si	mg/L	0.02	83	77	0.03
Sn	mg/L	0.0025	83	83	(BPQL)
Sr	mg/L	0.0005	83	81	0.0007
Ti	mg/L	0.005	83	83	(BPQL)
V	mg/L	0.005	83	83	(BPQL)
Zn	mg/L	0.001	83	55	0.24

Table 2.3

Summary: Digest Blanks measured on AAS					
Analyte	Units	PQL	Total number of blanks	Number of blanks below PQL	Highest conc. found
Arsenic	µg/L	0.2	79	79	(BPQL)

**Tables 3.1-3.3: Summary of standards measured on ICAPES during sample analyses.**

Table 3.1

Summary: USGS Standard T-143 measured on ICAPES (n = 151)			
Element	Units	Reported Mean (Range)*	Measured Mean (Std. Dev.) w/in Reported Range?
Al	µg/L	22.1 (16.6)	21 (1)
Ba	µg/L	81.9 (9)	81 (3)
Be	µg/L	8.5 (1.32)	8 (2)
Ca	mg/L	53.7 (4.4)	52.8 (1.6)
Cd	µg/L	19.1 (3)	18 (1)
Co	µg/L	17 (2.4)	17 (4)
Cr	µg/L	37 (5.2)	36 (1)
Cu	µg/L	22.3 (3.8)	23 (1)
Fe	µg/L	222 (28)	236 (6)
K	mg/L	2.5 (0.42)	2.5 (0.4)
Li	µg/L	18 (4.2)	16 (1)
Mg	mg/L	10.4 (1)	10.4 (0.3)
Mn	µg/L	18.2 (3.8)	17.2 (0.5)
Mo	µg/L	36.1 (8.6)	37 (1)
Na	mg/L	34 (3.2)	33.5 (1.0)
Ni	µg/L	71 (10)	73 (2)
P	µg/L	(Not reported)	-
Pb	µg/L	83.4 (14.2)	87 (2)
S	mg/L	(Not reported)	-
Si	mg/L	10.94 (1.64)	12.9 (0.5)
Sn	µg/L	(Not reported)	-
Sr	µg/L	306 (30)	303 (10)
Ti	µg/L	(Not reported)	-
V	µg/L	30 (6)	28 (1)
Zn	µg/L	20 (4.4)	17 (1)

\*Reported Range is 2 pseudosigmas from the mean

Table 3.2

Summary: USGS Standard T-145 measured on ICAPES (n = 102)			
Element	Units	Reported Mean (Range)*	Measured Mean (Std. Dev.) w/in Reported Range?
Al	µg/L	67.6 (22)	65 (2)
Ba	µg/L	37.1 (3.8)	36 (1)
Be	µg/L	9.04 (1.4)	8.5 (0.2)
Ca	mg/L	30.7 (2.6)	30.2 (1.2)
Cd	µg/L	9.33 (1.64)	8.6 (0.6)
Co	µg/L	10 (1.8)	10 (0.3)
Cr	µg/L	15.3 (2.8)	14 (1)
Cu	µg/L	11 (2.8)	11 (1)
Fe	µg/L	101 (16)	107 (3)
K	mg/L	2.13 (0.32)	2.2 (0.1)
Li	µg/L	27.3 (5)	25 (2)
Mg	mg/L	8.68 (0.9)	8.6 (0.2)
Mn	µg/L	20.9 (3)	19.9 (0.6)
Mo	µg/L	9.23 (2.58)	9.1 (3)
Na	mg/L	41.2 (3.8)	41.0 (1.4)
Ni	µg/L	11 (2.6)	12 (1)
P	µg/L	(Not reported)	-
Pb	µg/L	12.7 (2.4)	(BPQL)
S	mg/L	(Not reported)	-
Si	mg/L	5.28 (0.66)	6.4 (0.3)
Sn	µg/L	(Not reported)	-
Sr	µg/L	203 (18)	204 (6)
Ti	µg/L	(Not reported)	-
V	µg/L	11.7 (3.4)	11 (0.4)
Zn	µg/L	10 (4.8)	7 (1)

\*Reported Range is 2 pseudosigmas from the mean

Table 3.3

Summary: Internal standard measured on ICAPES (n = 190)			
Element	Units	Known value	Measured Mean (Std. Dev.)
Al	mg/L	0.5	0.48 (0.01)
Ba	mg/L	0.5	0.49 (0.01)
Be	mg/L	0.5	0.46 (0.01)
Ca	mg/L	1.0	0.60 (0.39)
Cd	mg/L	0.5	0.48 (0.01)
Co	mg/L	0.5	0.53 (0.01)
Cr	mg/L	0.5	0.50 (0.01)
Cu	mg/L	0.5	0.49 (0.01)
Fe	mg/L	0.5	0.50 (0.01)
K	mg/L	5	4.96 (0.08)
Li	mg/L	0.5	0.48 (0.01)
Mg	mg/L	1.0	0.93 (0.22)
Mn	mg/L	0.5	0.50 (0.01)
Mo	mg/L	0.5	0.51 (0.01)
Na	mg/L	1.0	0.96 (0.27)
Ni	mg/L	0.5	0.51 (0.01)
P	mg/L	0.5	0.49 (0.02)
Pb	mg/L	0.5	0.50 (0.01)
S	mg/L	0.5	0.49 (0.02)
Si	mg/L	0.5	0.47 (0.08)
Sn	mg/L	0.5	0.46 (0.01)
Sr	mg/L	0.5	0.50 (0.01)
Ti	mg/L	0.5	0.49 (0.01)
V	mg/L	0.5	0.50 (0.02)
Zn	mg/L	0.5	0.50 (0.01)

**Tables 4.1-4.2: Summary of standards digested with TRM samples and measured on ICAPES during sample analyses.**

Table 4.1

Summary: Digested USGS Standard T-143 measured on ICAPES (n = 61)				
Element	Units	Reported Mean (Range)*	Measured Mean (Std. Dev.) w/in Reported Range?	Measured Mean
Al	µg/L	22.1 (16.6)	25 (4)	YES
Ba	µg/L	81.9 (9)	80 (2)	YES
Be	µg/L	8.5 (1.32)	7.9 (0.2)	YES
Ca	mg/L	53.7 (4.4)	51.2 (2.4)	YES
Cd	µg/L	19.1 (3)	18 (1)	YES
Co	µg/L	17 (2.4)	17 (0.4)	YES
Cr	µg/L	37 (5.2)	36 (3)	YES
Cu	µg/L	22.3 (3.8)	23.0 (0.8)	YES
Fe	µg/L	222 (28)	242 (16)	YES
K	mg/L	2.5 (0.42)	2.6 (0.1)	YES
Li	µg/L	18 (4.2)	17 (1)	YES
Mg	mg/L	10.4 (1)	10.3 (0.3)	YES
Mn	µg/L	18.2 (3.8)	17.3 (0.6)	YES
Mo	µg/L	36.1 (8.6)	37 (1)	YES
Na	mg/L	34 (3.2)	33 (1)	YES
Ni	µg/L	71 (10)	72 (2)	YES
P	µg/L	(Not reported)	-	-
Pb	µg/L	83.4 (14.2)	86 (2)	YES
S	mg/L	(Not reported)	-	-
Si	mg/L	10.94 (1.64)	12.8 (0.5)	NO
Sn	µg/L	(Not reported)	-	-
Sr	µg/L	306 (30)	302 (9)	YES
Ti	µg/L	(Not reported)	-	-
V	µg/L	30 (6)	28 (1)	YES
Zn	µg/L	20 (4.4)	28 (32)	NO

\*Reported Range is 2 pseudosigmias from the mean

Table 4.2

Summary: Digested USGS Standard T-145 measured on ICAPES (n=24)				
Element	Units	Reported Mean (Range)*	Measured Mean (Std. Dev.) w/in Reported Range?	Measured Mean
Al	µg/L	67.6 (22)	71 (9)	YES
Ba	µg/L	37.1 (3.8)	37 (1)	YES
Be	µg/L	9.04 (1.4)	8.5 (0.2)	YES
Ca	mg/L	30.7 (2.6)	29.7 (1.2)	YES
Cd	µg/L	9.33 (1.64)	8.7 (0.7)	YES
Co	µg/L	10 (1.8)	10 (0.3)	YES
Cr	µg/L	15.3 (2.8)	14 (1)	YES
Cu	µg/L	11 (2.8)	11.7 (0.4)	YES
Fe	µg/L	101 (16)	109 (4)	YES
K	mg/L	2.13 (0.32)	2.2 (0.05)	YES
Li	µg/L	27.3 (5)	25 (2)	YES
Mg	mg/L	8.68 (0.9)	8.55 (0.22)	YES
Mn	µg/L	20.9 (3)	19.9 (0.4)	YES
Mo	µg/L	9.23 (2.58)	8.9 (0.4)	YES
Na	mg/L	41.2 (3.8)	41.0 (1.2)	YES
Ni	µg/L	11 (2.6)	12 (1)	YES
P	µg/L	(Not reported)	-	-
Pb	µg/L	12.7 (2.4)	(BPQL)	-
S	mg/L	(Not reported)	-	-
Si	mg/L	5.28 (0.66)	6.2 (0.2)	NO
Sn	µg/L	(Not reported)	-	-
Sr	µg/L	203 (18)	206 (5)	YES
Ti	µg/L	(Not reported)	-	-
V	µg/L	11.7 (3.4)	10.6 (0.5)	YES
Zn	µg/L	10 (4.8)	10 (2)	YES

\*Reported Range is 2 pseudosigmias from the mean

**Tables 5.1-5.2**  
**External and Internal Standards Measurements**

Table 5.1

<b>Summary: External standards measured on AAS</b>			
<i>Concentrations in <math>\mu\text{g/L}</math>.</i>			
Standard	Reported value (Range)*	Measured values or mean (std. dev.)	Measured values within Report. Range?
USGS T-143 (n =42)	15.2 (2.4)	14.3 (0.9)	YES
USGS T-143 (Digested) (n =65)	15.2 (2.4)	13.8 (2.1)	YES
USGS T-145 (n =143)	9.88 (2.08)	8.8 (1.0)	YES
USGS T-145 (Digested) (n =21)	9.88 (2.08)	9.8 (5.4)	YES

\*Reported Range is 2 pseudosigmas from the mean

*Note: USGS Standards T-121, T-143, and T-113 were diluted to 10%, and USGS Standards T107, T-119, and T-145 were diluted by 50% for analysis in order to fall within the range of calibration of the AAS.*

Table 5.2

<b>Summary: Internal standards (fortified lab blanks) measured on AAS, and Carbon Analyzer</b>	
Standard	Mean (Std. Dev.) % difference of fortified lab blank and measured concentration
Arsenic (< or = 0.5 $\mu\text{g/L}$ ) (n =649)	8% (8%)
Arsenic (>0.5 $\mu\text{g/L}$ ) (n =664)	3% (3%)
Inorganic C (n =350)	2% (2%)

**Tables 6.1-6.4: Precision results on all instruments**

Table 6.1

<b>Summary: Results of analytical duplicates on ICAPES</b>		
Element	Number of dupl. pairs above PQL	Mean (stdev) of % differences of all dupl. pairs
Al	92	3% (9%)
Ba	58	1% (2%)
Be	4	1% (1%)
Ca	182	2% (2%)
Cd	2	1% (1%)
Co	2	1% (1%)
Cr	10	1% (2%)
Cu	56	5% (6%)
Fe	167	2% (2%)
K	182	2% (3%)
Li	139	2% (3%)
Mg	182	1% (2%)
Mn	162	2% (3%)
Mo	64	3% (4%)
Na	181	2% (3%)
Ni	35	5% (6%)
P	108	4% (5%)
Pb	2	1% (0%)
S	182	1% (2%)
Si	182	1% (2%)
Sn	0	-
Sr	182	1% (2%)
Ti	25	2% (3%)
V	2	1% (0%)
Zn	93	3% (4%)

Table 6.3

<b>Summary: Results of digest duplicates as analyzed on ICAPES</b>		
Element	Number of dupl. pairs above PQL	Mean (stdev) of % differences of all dupl. pairs
Al	65	11% (18%)
Ba	83	2% (2%)
Be	4	6% (7%)
Ca	83	3% (2%)
Cd	0	-
Co	0	-
Cr	8	22% (30%)
Cu	24	4% (5%)
Fe	83	7% (10%)
K	83	3% (5%)
Li	65	3% (6%)
Mg	83	2% (2%)
Mn	74	5% (10%)
Mo	23	5% (6%)
Na	83	4% (5%)
Ni	22	25% (42%)
P	50	11% (12%)
Pb	0	-
S	80	3% (2%)
Si	80	2% (2%)
Sn	0	-
Sr	83	2% (2%)
Ti	23	5% (4%)
V	0	-
Zn	64	21% (29%)

Table 6.2

<b>Summary: AAS, alkalinity titration, and carbon analyzer replicate comparisons</b>		
Analyte	Number of replicate sets above PQL	Mean (stdev) % difference or % RSD of replicate sets
Total Susp. Sed.	110	26% (25%)
Arsenic	183	6% (6%)
Alkalinity	89	1% (1%)
Inorganic C	79	1% (1%)

PQL= Practical Quantifiable Limit

%RSD= Percent relative standard deviation

Table 6.4

<b>Summary: Results of digest duplicates as analyzed on AAS</b>		
Element	Number of dupl. pairs above PQL	Mean (stdev) of % differences of all dupl. pairs
As	75	8% (12%)

**Tables 7.1-7.3: Summary of spike recoveries measured on all instruments.**

Table 7.1

Summary: ICAPES Spike recoveries on blanks			
Element	Unit	Spike values	Number of blanks spiked
Al	mg/L	0.5	42
Ba	mg/L	0.5	42
Be	mg/L	0.1	42
Ca	mg/L	20	42
Cd	mg/L	0.2	42
Co	mg/L	0.2	42
Cr	mg/L	0.5	42
Cu	mg/L	0.5	42
Fe	mg/L	0.5	42
K	mg/L	5	42
Li	mg/L	0.6	42
Mg	mg/L	5	42
Mn	mg/L	0.5	42
Mo	mg/L	0.2	42
Na	mg/L	10	42
Ni	mg/L	0.5	42
P	mg/L	1	42
Pb	mg/L	0.5	42
S	mg/L	5	42
Si	mg/L	5	42
Sn	mg/L	0.2	42
Sr	mg/L	0.5	42
Ti	mg/L	0.1	42
V	mg/L	0.2	42
Zn	mg/L	0.5	42

Table 7.2

Summary: ICAPES Spike recoveries on samples				
Element	Unit	Spike values (mg/L)	Number of samples above PQL for the element spiked	Mean (Stand. Dev.) percent recovery
Al	mg/L	0.5 or 0.125	108	97 (19)
Ba	mg/L	0.5 or 0.125	223	97 (4)
Be	mg/L	0.1 or 0.125	9	102 (2)
Ca	mg/L	20	223	98 (10)
Cd	mg/L	0.2 or 0.05	0	-
Co	mg/L	0.2 or 0.05	0	-
Cr	mg/L	0.5 or 0.125	12	104 (3)
Cu	mg/L	0.5 or 0.125	55	98 (5)
Fe	mg/L	0.5 or 0.125	210	104 (5)
K	mg/L	5	223	100 (3)
Li	mg/L	0.6 or 0.150	192	84 (5)
Mg	mg/L	5	223	102 (6)
Mn	mg/L	0.5 or 0.125	195	101 (3)
Mo	mg/L	0.2 or 0.05	68	103 (3)
Na	mg/L	10	223	98 (4)
Ni	mg/L	0.5 or 0.125	47	101 (3)
P	mg/L	1 or 0.25	117	100 (4)
Pb	mg/L	0.5 or 0.125	0	-
S	mg/L	5	223	107 (9)
Si	mg/L	5	223	108 (7)
Sn	mg/L	0.2 or 0.05	0	-
Sr	mg/L	0.5 or 0.125	223	97 (5)
Ti	mg/L	0.1 or 0.025	25	101 (4)
V	mg/L	0.2 or 0.05	0	-
Zn	mg/L	0.5 or 0.125	94	100 (4)

Table 7.3

Summary: AAS Spike (fortified sample) recoveries			
Analyte	Unit	Spike Value	Number of samples above PQL
Arsenic	µg/L	1.0	170

PQL= Practical Quantifiable Limit  
 %RSD= Percent relative standard deviation

**Table 8: Summary of results of non-parametric multiple comparisons among sites.**

PARAMETER:	ORDER
Q	BFB>CFBM>LF>BH
TSS, Al <sub>t</sub>	BFB=CFBM>LF=BH
Alk, Ca <sub>t</sub>	CFBM>BFB=BH; BFB=LF, CFBM>LF, LF>BH
DIC, Ca <sub>d</sub> , (Cu <sub>d</sub> ), (Cu <sub>t</sub> ), Li <sub>d</sub> , Mg <sub>t</sub> , (Mo <sub>d</sub> ), Mo <sub>t</sub> , P <sub>d</sub>	CFBM>BFB=LF=BH
As <sub>d</sub>	CFBM>BFB>LF>BH
Ba <sub>d</sub> , Ba <sub>t</sub>	LF=BH>BFB>CFBM
Fe <sub>d</sub>	CFBM=BH>BFB>LF
K <sub>d</sub> , K <sub>t</sub> , Mn <sub>t</sub> , Na <sub>d</sub> , Na <sub>t</sub>	CFBM>BFB=BH>LF
Mg <sub>d</sub>	CFBM>BH>BFB; BFB=LF, CFBM>LF, BH=LF
Mn <sub>d</sub> , S <sub>d</sub> , S <sub>t</sub> , Si <sub>d</sub> , Si <sub>t</sub> , Sr <sub>d</sub> , Sr <sub>t</sub>	CFBM>BH>BFB>LF
As <sub>t</sub>	CFBM>BFB=LF>BH
Fe <sub>t</sub>	BFB=CFBM>LF; BFB=BH, CFBM>BH, BH=LF
Li <sub>t</sub>	CFBM>BFB>LF=BH
P <sub>t</sub>	CFBM>BFB=BH; BFB>LF, CFBM>LF, BH=LF
Zn <sub>t</sub>	CFBM=BH>BFB=LF

In parentheses: elements that were above the PQL only at site CFBM



**Table 9**

Summary of Wilcoxon Signed Ranks Test results (p-values) comparing the seasonal dissolved and total concentrations of each element				
	BFB	CFBM	LF	BH
As <sub>d</sub> v. As <sub>t</sub>	0.007**	0.092	0.004**	0.000**
Ba <sub>d</sub> v. Ba <sub>t</sub>	0.000**	0.000**	0.004**	0.005**
Ca <sub>d</sub> v. Ca <sub>t</sub>	0.032*	0.300	0.584	0.403
Cu <sub>d</sub> v. Cu <sub>t</sub>	(BPQL)	0.000**	(BPQL)	(BPQL)
Fe <sub>d</sub> v. Fe <sub>t</sub>	0.000**	0.000**	(BPQL)	0.000**
K <sub>d</sub> v. K <sub>t</sub>	0.000**	0.819	0.004**	0.021*
Li <sub>d</sub> v. Li <sub>t</sub>	0.006**	0.150	0.152	0.301
Mg <sub>d</sub> v. Mg <sub>t</sub>	0.054	0.174	0.903	0.761
Mn <sub>d</sub> v. Mn <sub>t</sub>	0.000**	0.000**	(BPQL)	0.000**
Mo <sub>d</sub> v. Mo <sub>t</sub>	(BPQL)	0.04*	(BPQL)	(BPQL)
Na <sub>d</sub> v. Na <sub>t</sub>	0.002**	0.135	0.004**	0.007**
P <sub>d</sub> v. P <sub>t</sub>	0.000**	0.000**	(BPQL)	(BPQL)
S <sub>d</sub> v. S <sub>t</sub>	0.048*	0.276	0.005**	0.089
Si <sub>d</sub> v. Si <sub>t</sub>	0.003**	0.001**	?	0.951
Sr <sub>d</sub> v. Sr <sub>t</sub>	0.083	0.211	0.042**	0.070
Zn <sub>d</sub> v. Zn <sub>t</sub>	0.002**	?	0.000**	0.000**

\* Test is significant at the 0.01 level

\*\* Test is significant at the 0.05 level

**Table 10**

Dissolved vs. total metal concentration: correlation coefficients

	BFB	CFBM	LF	BH
As <sub>d</sub> v. As <sub>t</sub>	0.47*	0.45*	0.91**	-0.16
Ba <sub>d</sub> v. Ba <sub>t</sub>	0.97**	0.87**	0.98**	0.98**
Ca <sub>d</sub> v. Ca <sub>t</sub>	0.96**	0.79**	0.95**	0.96**
Cu <sub>d</sub> v. Cu <sub>t</sub>	(BPQL)	0.24	(BPQL)	(BPQL)
Fe <sub>d</sub> v. Fe <sub>t</sub>	0.55**	0.60**	(BPQL)	-0.39
K <sub>d</sub> v. K <sub>t</sub>	0.98**	0.99**	0.90**	0.94**
Li <sub>d</sub> v. Li <sub>t</sub>	0.94**	0.94**	0.95**	0.87**
Mg <sub>d</sub> v. Mg <sub>t</sub>	0.99**	0.98**	0.96**	0.96**
Mn <sub>d</sub> v. Mn <sub>t</sub>	0.81**	-0.45*	(BPQL)	0.73**
Mo <sub>d</sub> v. Mo <sub>t</sub>	(BPQL)	0.28	(BPQL)	(BPQL)
Na <sub>d</sub> v. Na <sub>t</sub>	0.99**	0.97**	0.84**	0.90**
P <sub>d</sub> v. P <sub>t</sub>	0.60**	0.54**	(BPQL)	(BPQL)
S <sub>d</sub> v. S <sub>t</sub>	1.00**	0.97**	0.75**	0.97**
Si <sub>d</sub> v. Si <sub>t</sub>	0.74**	0.79**	0.94**	0.52*
Sr <sub>d</sub> v. Sr <sub>t</sub>	0.99**	0.98**	0.97**	0.98**

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

Table 11

<b>Moderate to good correlations between Q and TSS, dissolved (d) elements, and total recoverable (t) elements at all sites .</b>				
<b>All other elements lacked good and significant correlations with Q.</b>				
<b>(Seasonal data only; n =23 for LF and BH; n =24 for CFBM; n =21 for BFB)</b>				
Parameter	Site BFB	Site CFBM	Site LF	Site BH
TSS	0.67**	0.64**	0.66**	0.85**
Alkalinity	-0.96**	-0.77**	-0.91**	-0.95**
DC	-0.95**	-0.55**	-0.96**	-0.93**
t_Al	0.48*	0.70**	0.58**	0.66**
d_As	-0.82**	-0.40*	-0.81**	-0.48*
t_As	-0.27	0.37	-0.68**	0.56**
d_Ba	-0.91**	-0.48*	-0.96**	-0.95**
t_Ba	-0.94**	-0.21	-0.95**	-0.96**
d_Ca	-0.96**	-0.89**	-0.94**	-0.95**
t_Ca	-0.96**	-0.82**	-0.93**	-0.95**
t_Cu	BPQL	0.66**	BPQL	BPQL
d_Fe	0.01	0.58**	-0.25	0.01
t_Fe	0.52**	0.68**	0.55*	0.88**
d_K	-0.71**	-0.69**	-0.95**	-0.70**
t_K	-0.59**	-0.66**	-0.85**	-0.62**
d_Li	-0.92**	-0.89**	-0.69**	-0.75**
t_Li	-0.85**	-0.91**	-0.75**	-0.81**
d_Mg	-0.94**	-0.80**	-0.94**	-0.94**
t_Mg	-0.96**	-0.80**	-0.93**	-0.96**
d_Mn	0.14	0.25	0.45*	0.88**
t_Mn	0.56**	0.39*	0.65**	0.85**
d_Na	-0.84**	-0.68**	-0.79**	-0.77**
t_Na	-0.86**	-0.74**	-0.89**	-0.90**
d_S	-0.75**	-0.73**	-0.68**	0.39
t_S	-0.75**	-0.78**	-0.41	0.34
d_Si	-0.70**	-0.38	-0.94**	-0.70**
t_Si	-0.28	-0.15	-0.91**	-0.66**
d_Sr	-0.94**	-0.93**	-0.97**	-0.92**
t_Sr	-0.93**	-0.90**	-0.96**	-0.93**
t_Ti	0.26	0.71**	BPQL	
d_Zn	-0.30	0.10	BPQL	0.91**
t_Zn	0.48**	0.45*		0.79**

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

**Table 12**

TSS vs. total metal concentrations: correlation coefficients

TSS vs.:	BFB	CFBM	LF	BH
Al <sub>t</sub>	0.89**	0.97**	0.99**	0.88**
As <sub>t</sub>	0.38	0.78**	-0.30	0.81**
Ba <sub>t</sub>	-0.67**	0.31	-0.70**	-0.76**
Be <sub>t</sub>	(BPQL)	0.83**	(BPQL)	(BPQL)
Ca <sub>t</sub>	-0.64**	-0.50*	-0.66**	-0.77**
Cu <sub>t</sub>	(BPQL)	0.95**	(BPQL)	(BPQL)
Fe <sub>t</sub>	0.91**	0.95**	0.95**	0.98**
K <sub>t</sub>	0.03	-0.60	-0.33	-0.22
Li <sub>t</sub>	-0.45*	-0.53**	-0.53**	-0.64**
Mg <sub>t</sub>	-0.67**	-0.45*	-0.70**	-0.77**
Mn <sub>t</sub>	0.92**	0.88**	0.99**	0.98**
Na <sub>t</sub>	-0.39	-0.37	-0.54**	-0.67**
P <sub>t</sub>	0.78**	0.89**	0.05	0.35
S <sub>t</sub>	-0.24	-0.58**	-0.11	0.35
Si <sub>t</sub>	0.38	0.26	-0.50*	-0.29
Sr <sub>t</sub>	-0.55**	-0.48*	-0.69**	-0.71**
Ti <sub>t</sub>	0.81**	0.97**	(BPQL)	(BPQL)

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

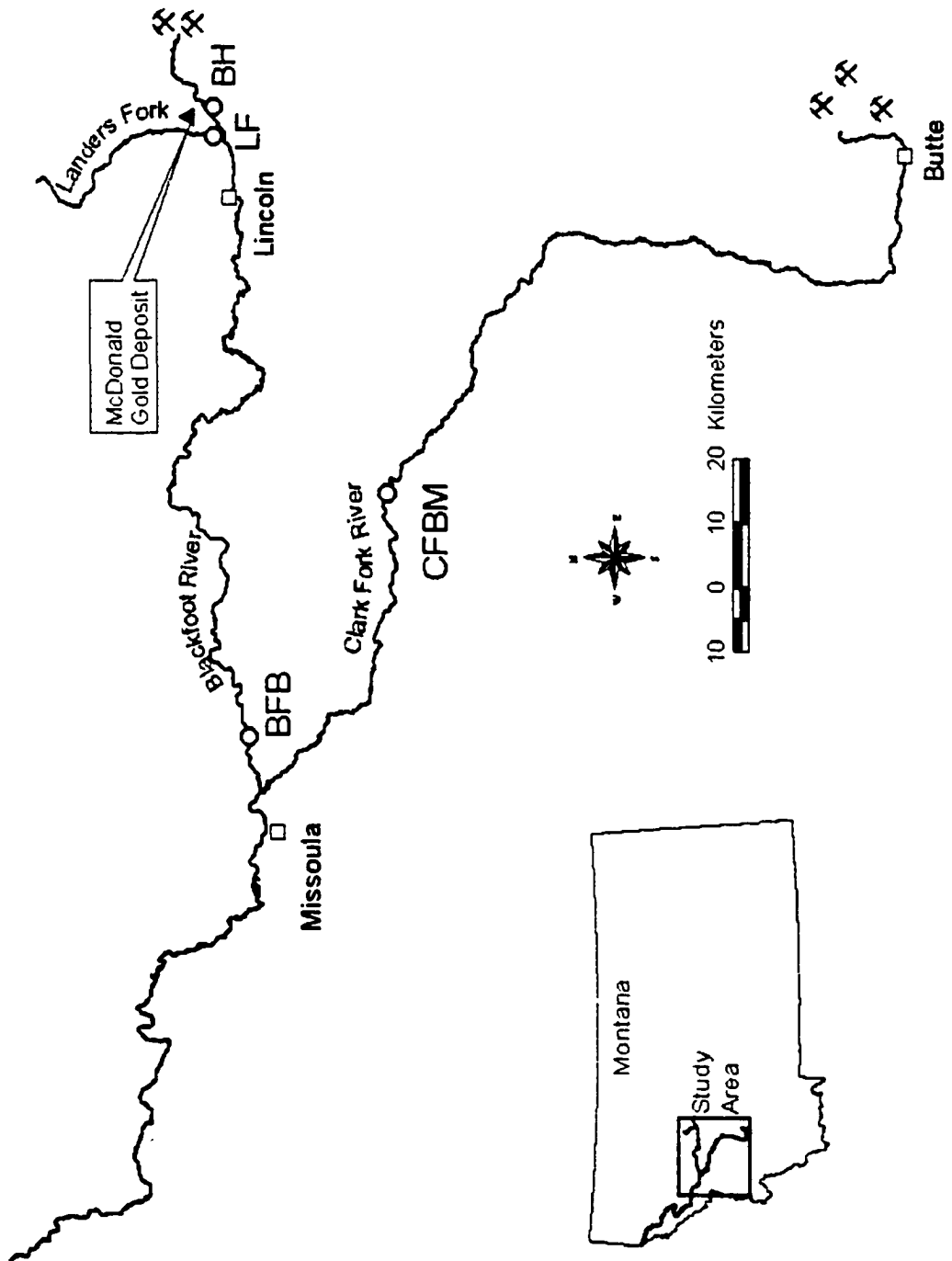
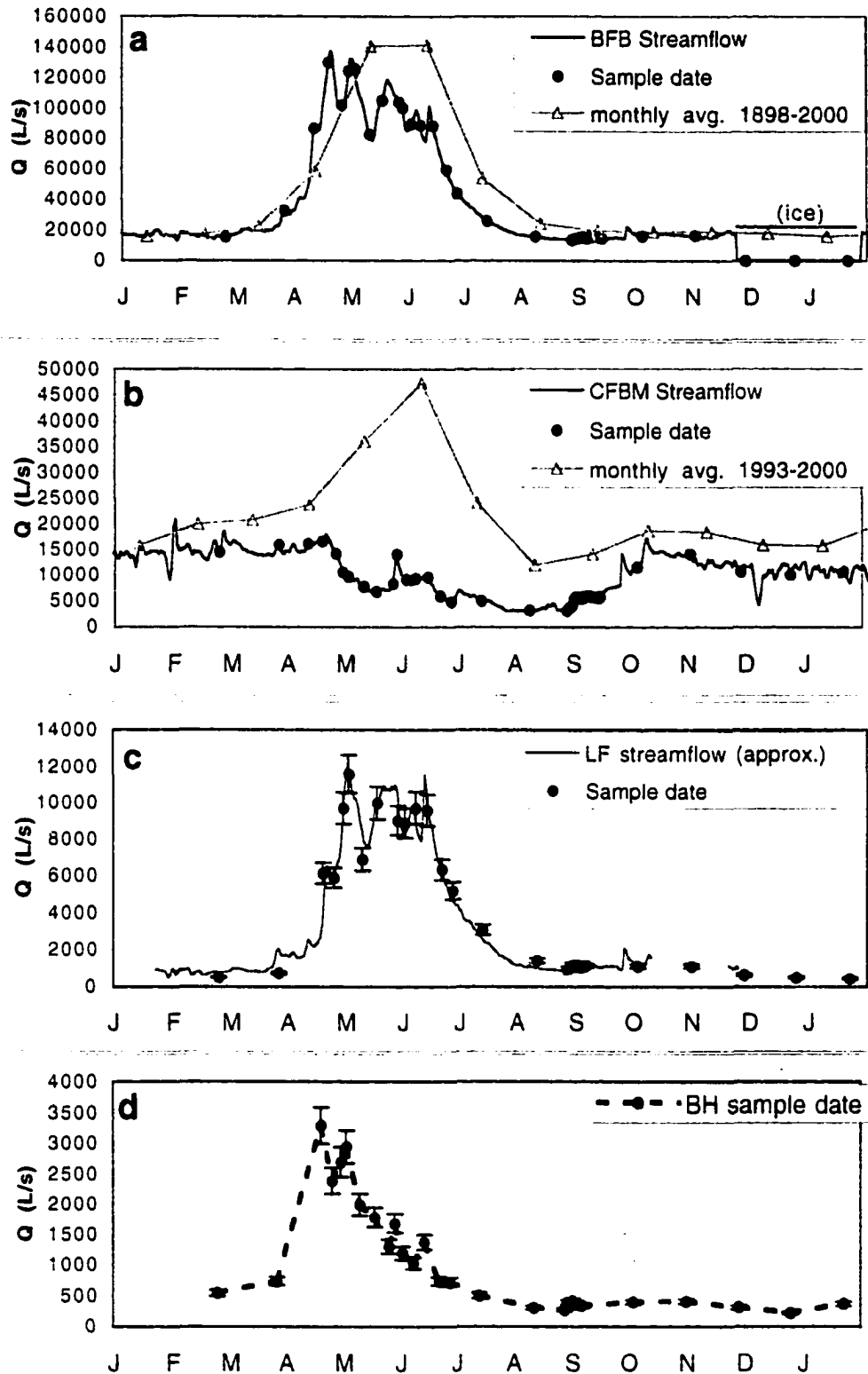
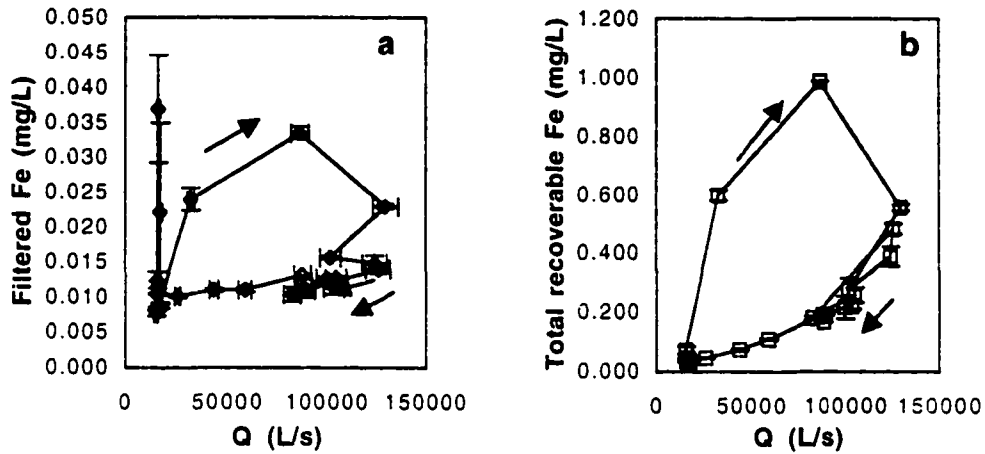


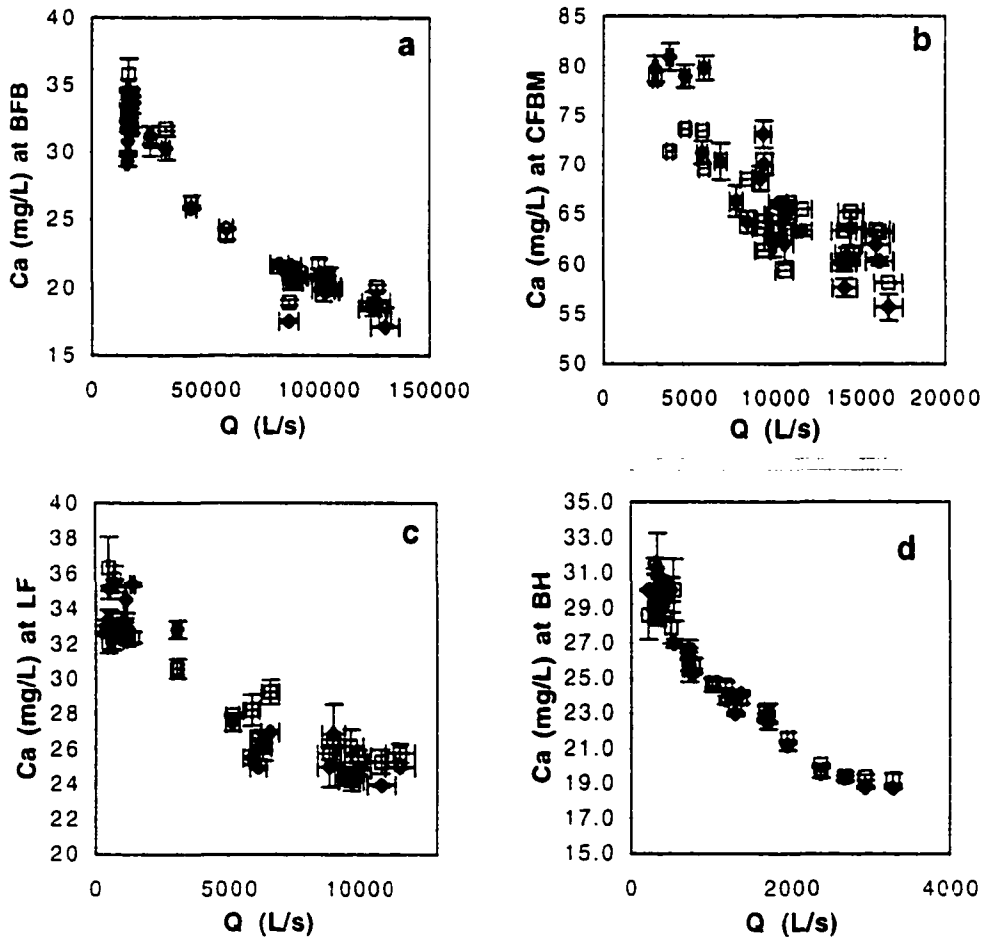
Figure 1: Site location map



**Figure 2:** Hydrographs for the four study sites: a) BFB, b) CFBM, c) LF, and d) BH. The approximated hydrograph at LF is based on a downstream gaging station on the Blackfoot River where Q was well correlated ( $R^2=0.96$ ) with Q measurements at LF.



**Figure 3:** Streamflow vs. (a) filtered ("dissolved") Fe and (b) total recoverable Fe at BFB. Error bars in these and all other plots represent the 95% confidence interval based on the triplicate samples collected per event.



**Figure 4:** Streamflow vs. Ca at a) BFB, b) CFBM, c) LF, and d) BH.

In these and all subsequent plots, filtered samples are denoted by triangles, and total recoverable concentrations by squares.

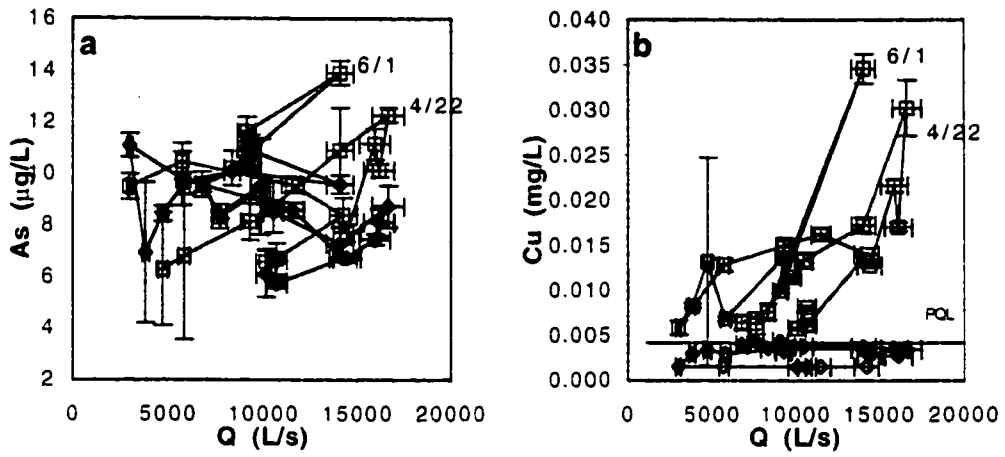


Figure 5: Streamflow vs. a)As and b) Cu at site CFBM. Sampling dates are connected in chronological order.

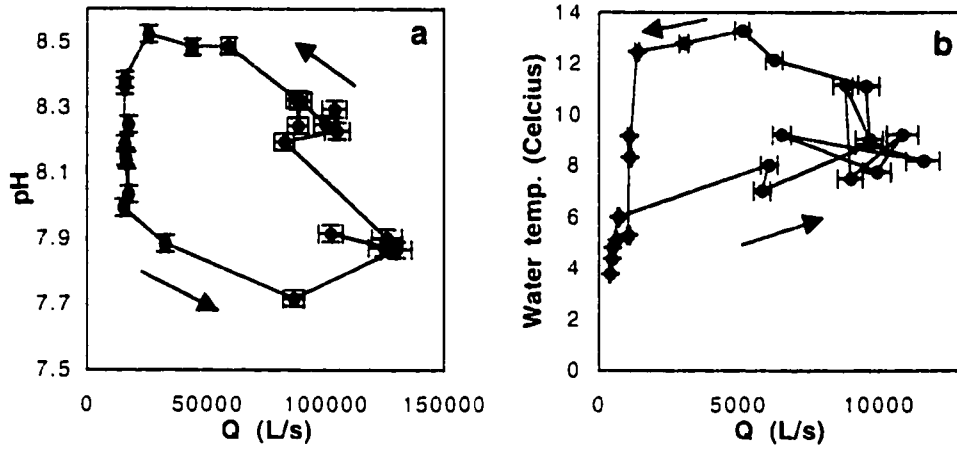
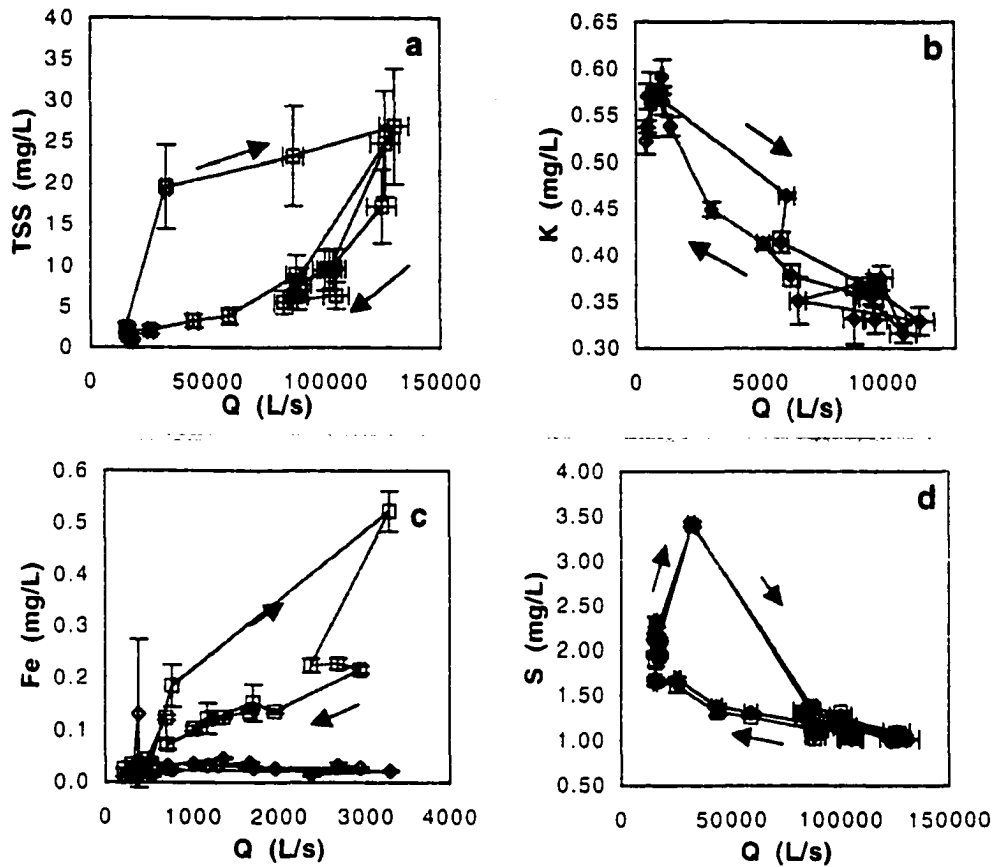
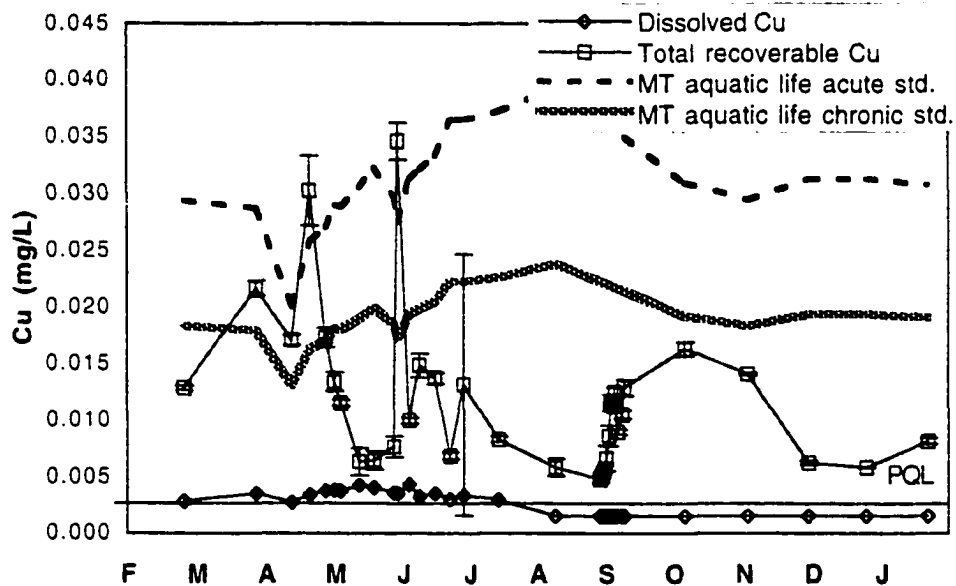


Figure 6: Streamflow vs. a) pH at BFB and b) water temperature at LF



**Figure 7:** Streamflow vs. a) TSS at BFB, b) dissolved K at LF, c) dissolved and total Fe at BH, and d) dissolved and total S at BFB. Sampling dates are connected in chronological order.



**Figure 8:** Date vs. Cu at CFBM, with MT aquatic life acute and chronic standards.



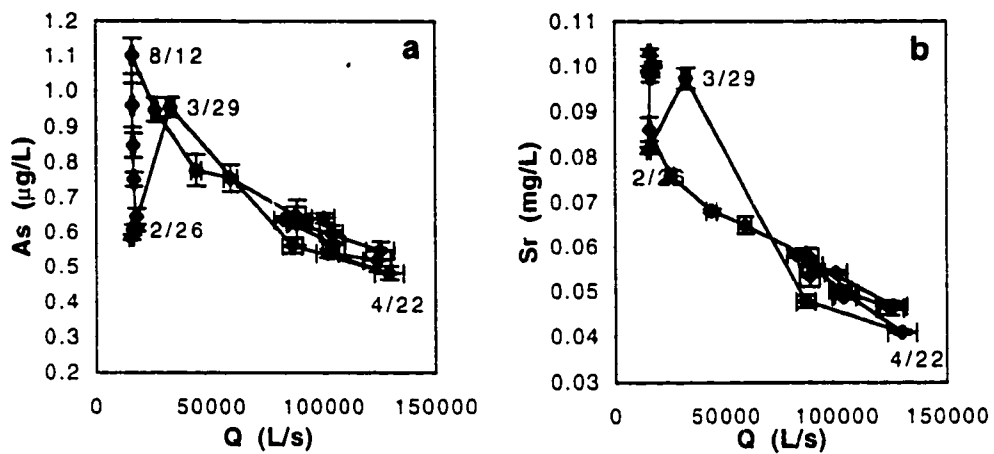


Figure 9: Streamflow vs. a) dissolved As and b) Sr at BFB

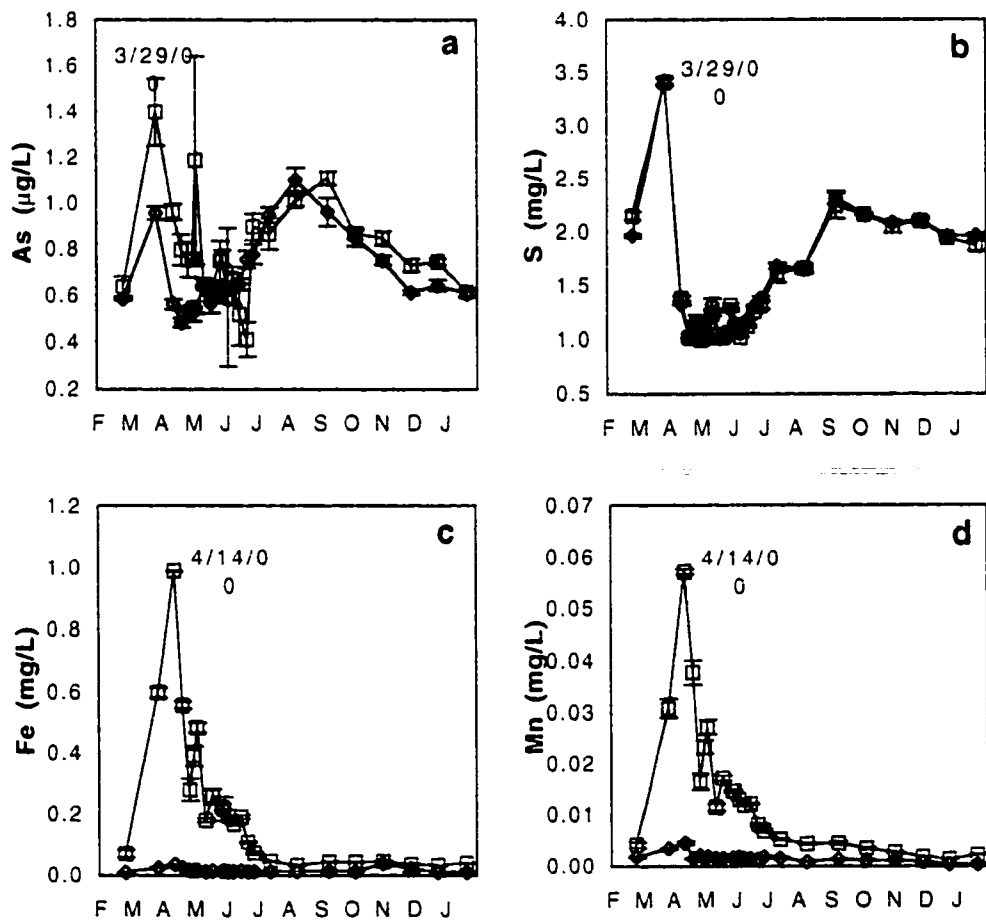


Figure 10: Date v. a) As, b) S, c) Fe, and d) Mn at BFB. Triangles denote dissolved concentrations and squares denote total recoverable concentrations.

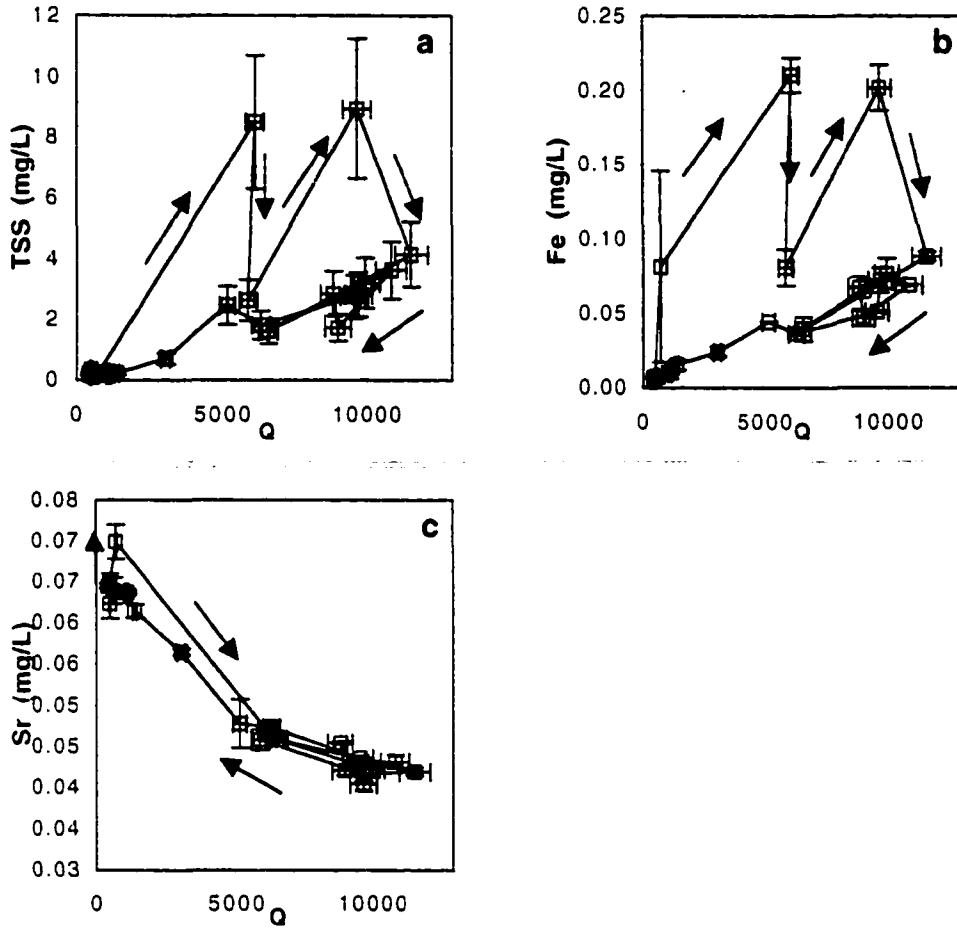


Figure 11: Streamflow vs. a) TSS, b) total Fe, and c) total Sr at LF.

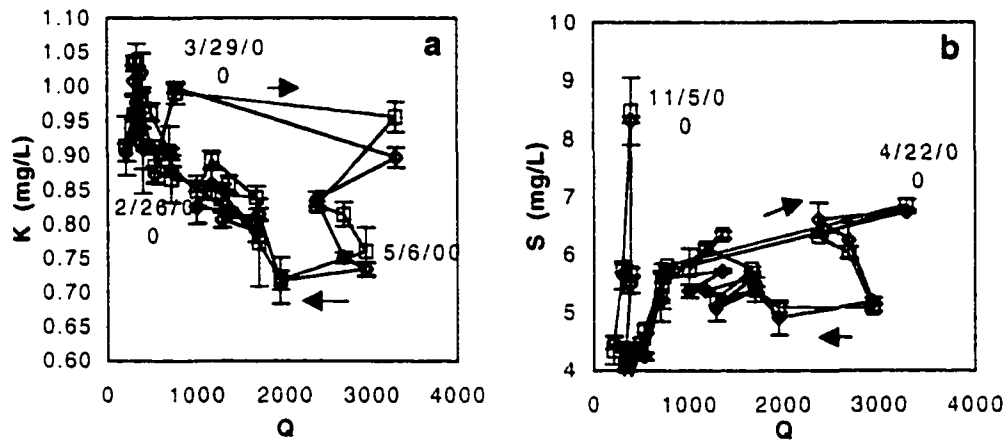
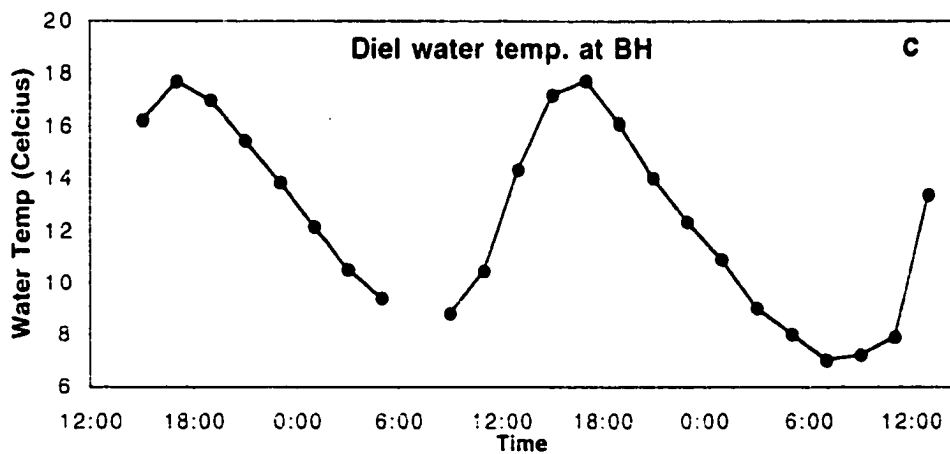
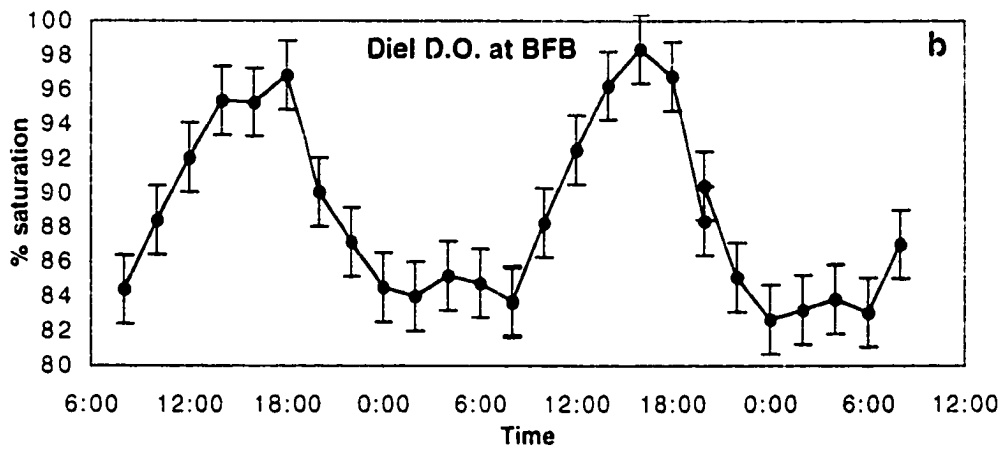
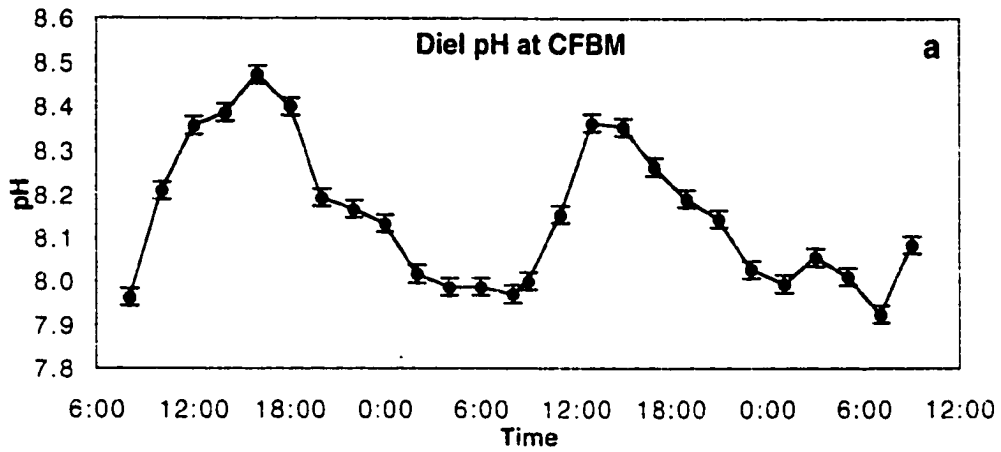
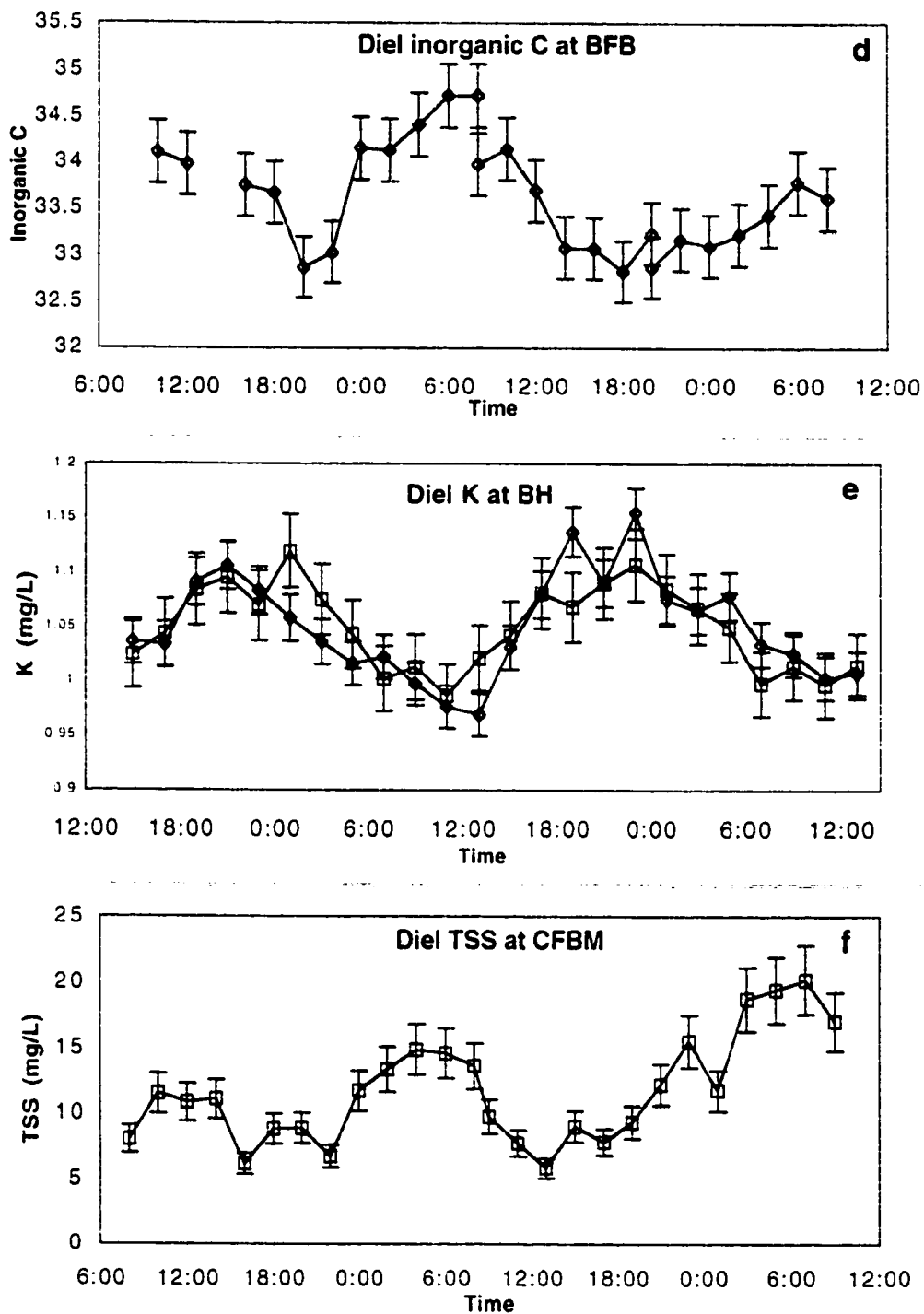


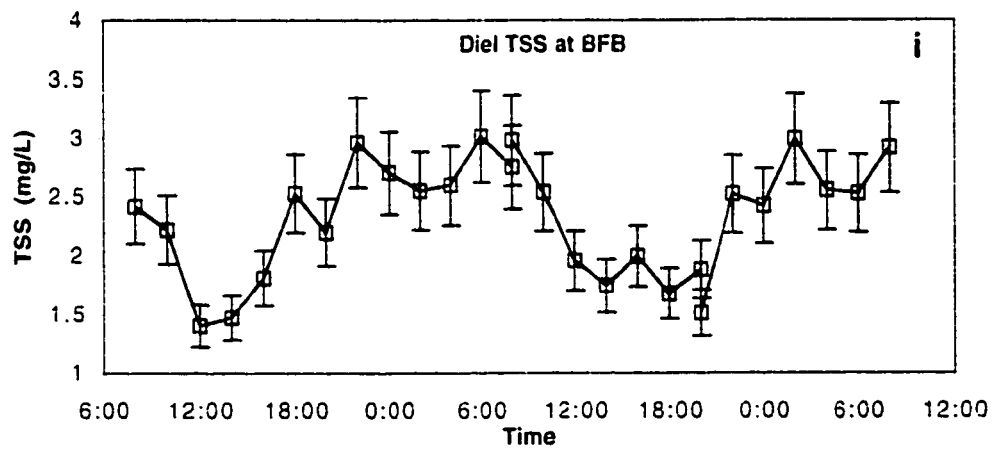
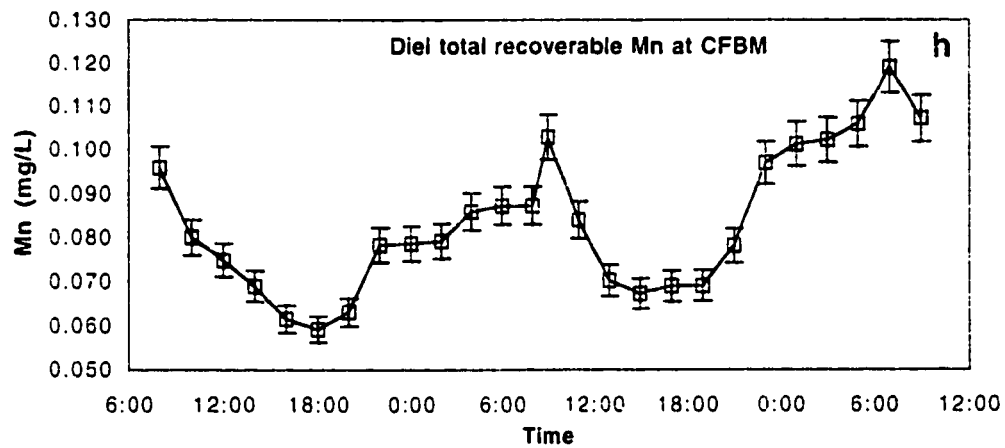
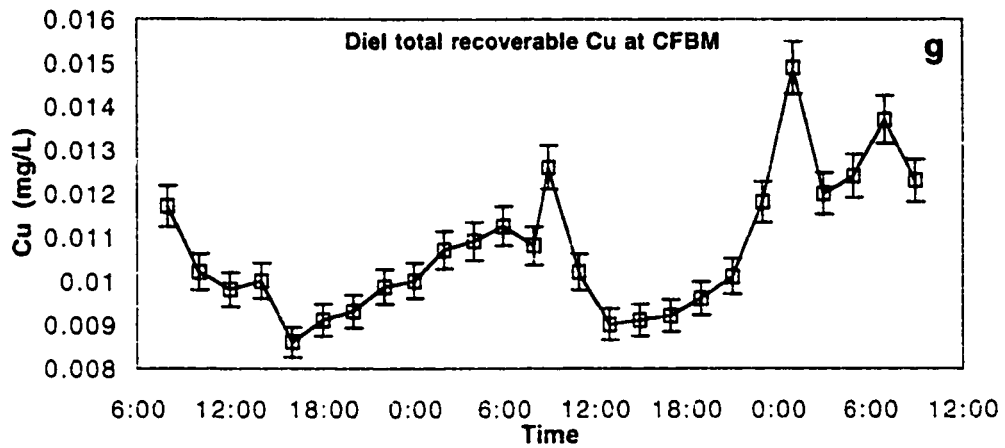
Figure 12: Streamflow vs. a) K and b) S at site BH.



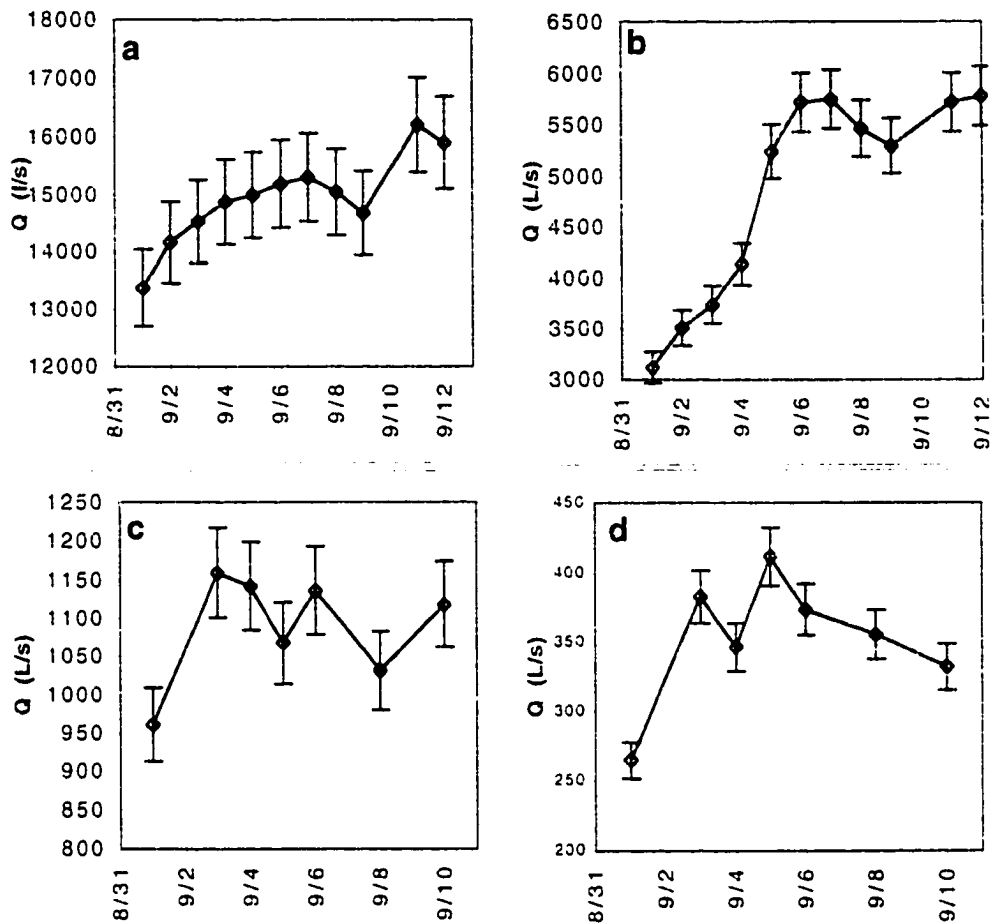
**Figure 13:** Diel variations of a) pH at CFBM, b) D.O. at BFB, and c) water temperature at BH.



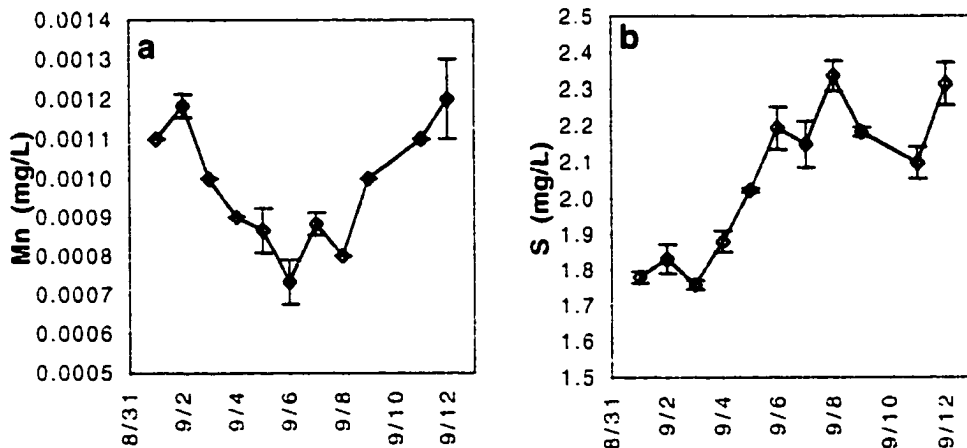
**Figure 13:** Diel variations of d) DIC at BFB, e) dissolved and total recoverable K at BH, and f) TSS at CFBM



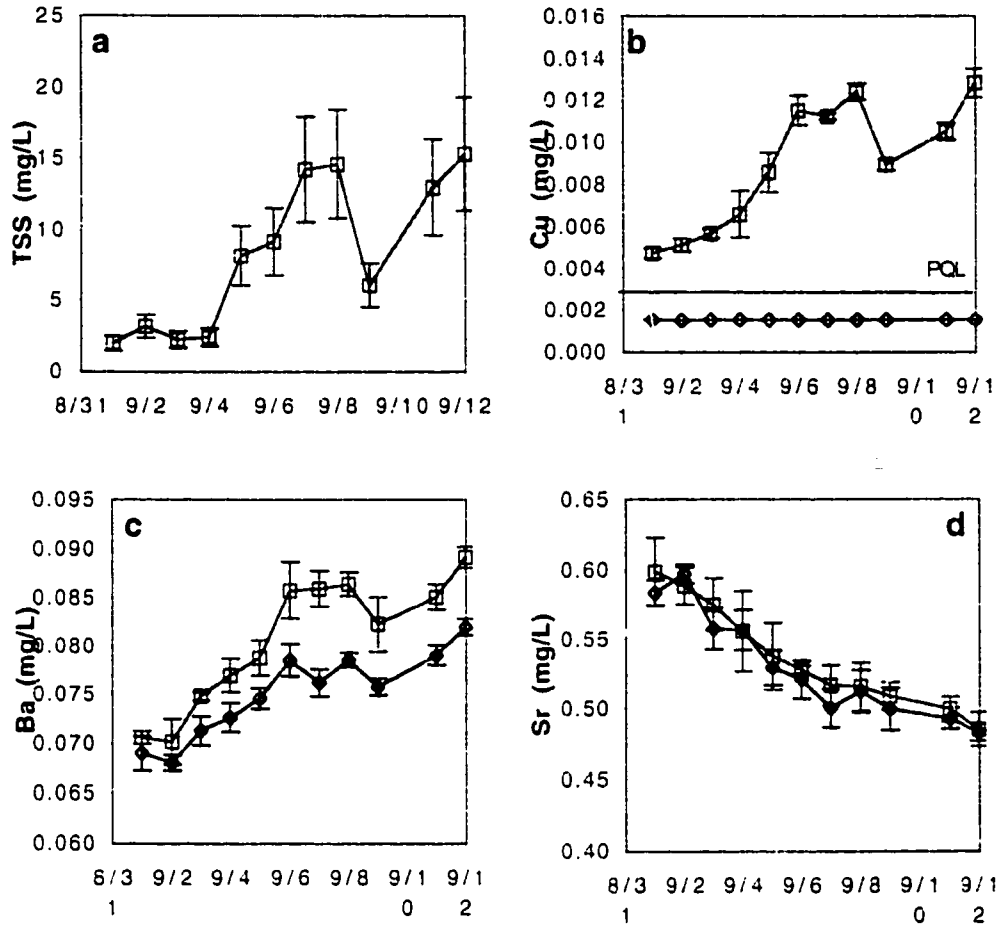
**Figure 13:** Diel variations of g) total Cu at CFBM, h) total Mn at CFBM, and i) TSS at BFB.



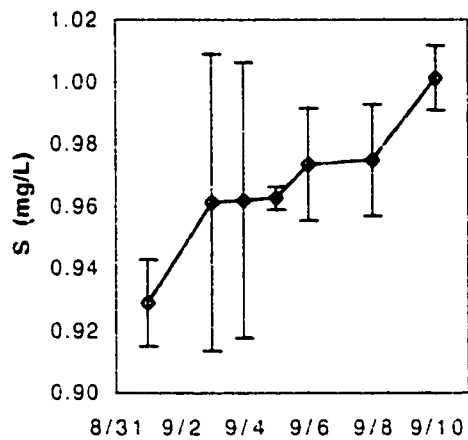
**Figure 14:** Streamflow during the first 2 weeks of September at a) BFB, b) CFBM, c) LF and d) BH.



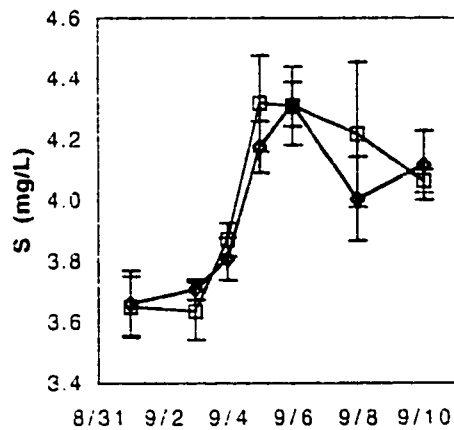
**Figure 15:** a) Dissolved Mn and b) Dissolved S at site BFB during the first 2 weeks of September.



**Figure 16:** a) TSS, b) Cu, c) Ba, and d) Sr at CFBM during the first 2 weeks of September



**Figure 17:** Dissolved S at site LF during the first two weeks of September.



**Figure 18:** Dissolved and total S at site BH during the first two weeks of September.

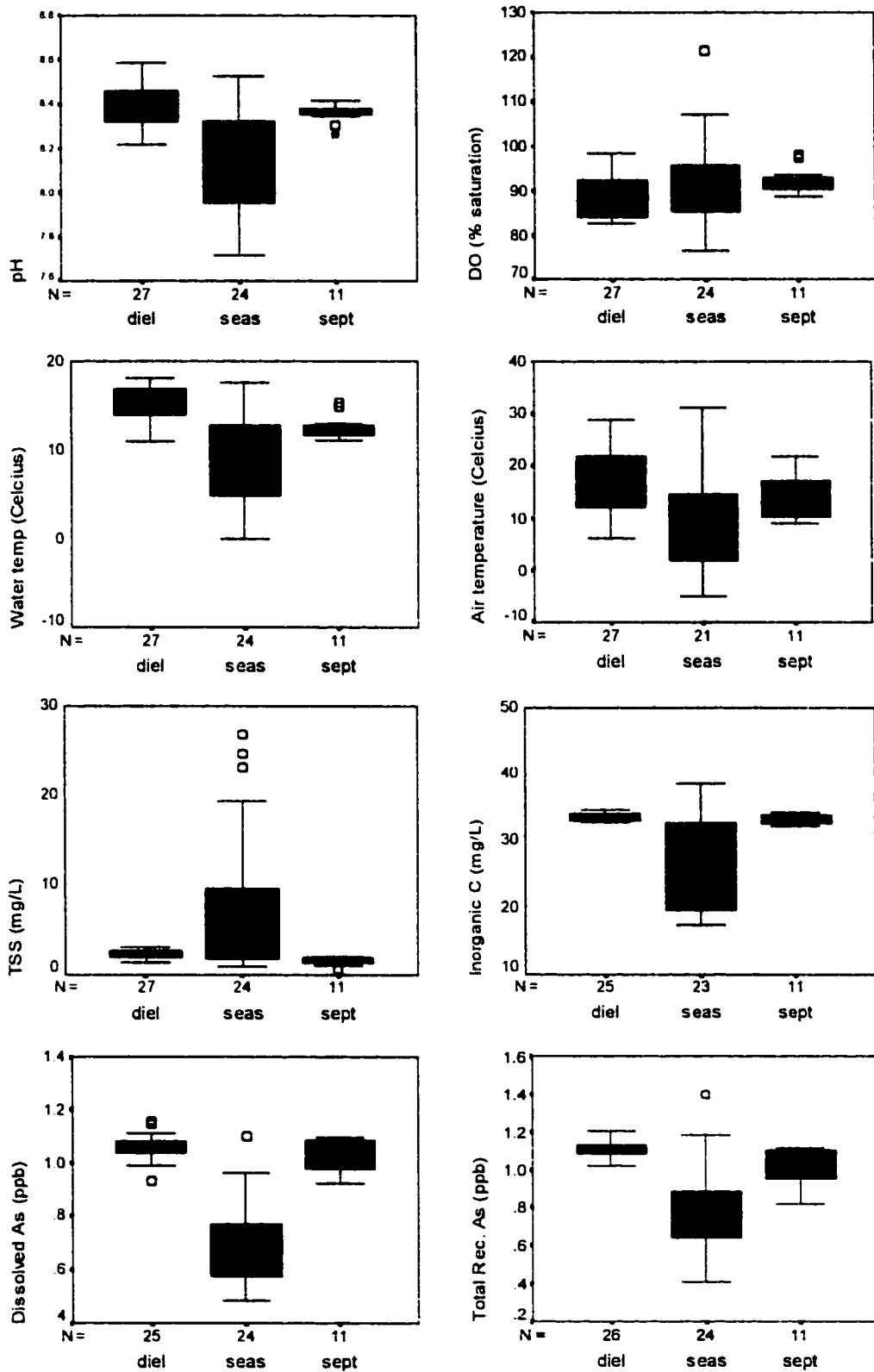


Figure 19: Boxplots of Diel, Seasonal, and September rain event variability at site BFB.



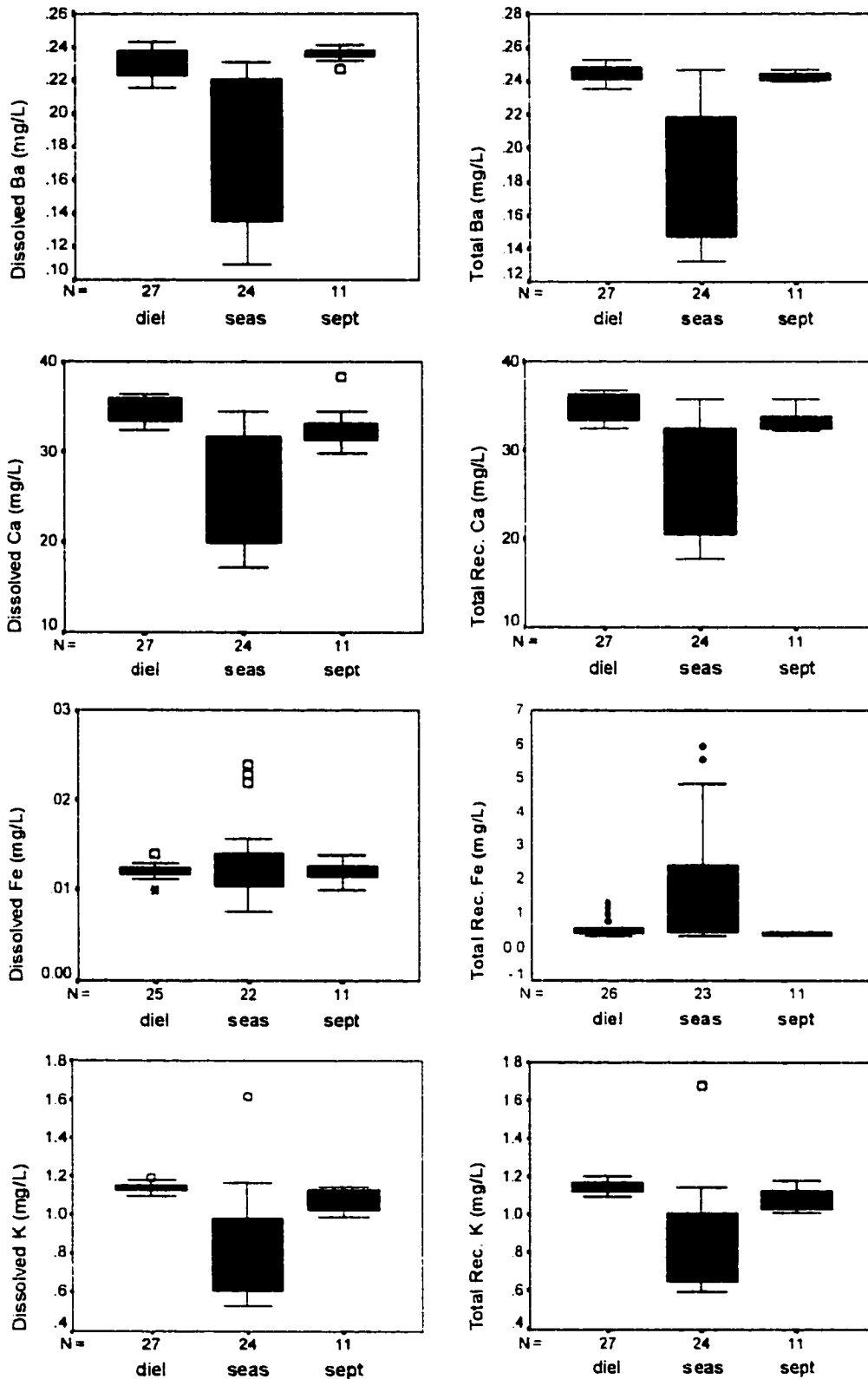


Figure 19, continued: Boxplots of Diel, Seasonal, and September rain event variability at site BFB.

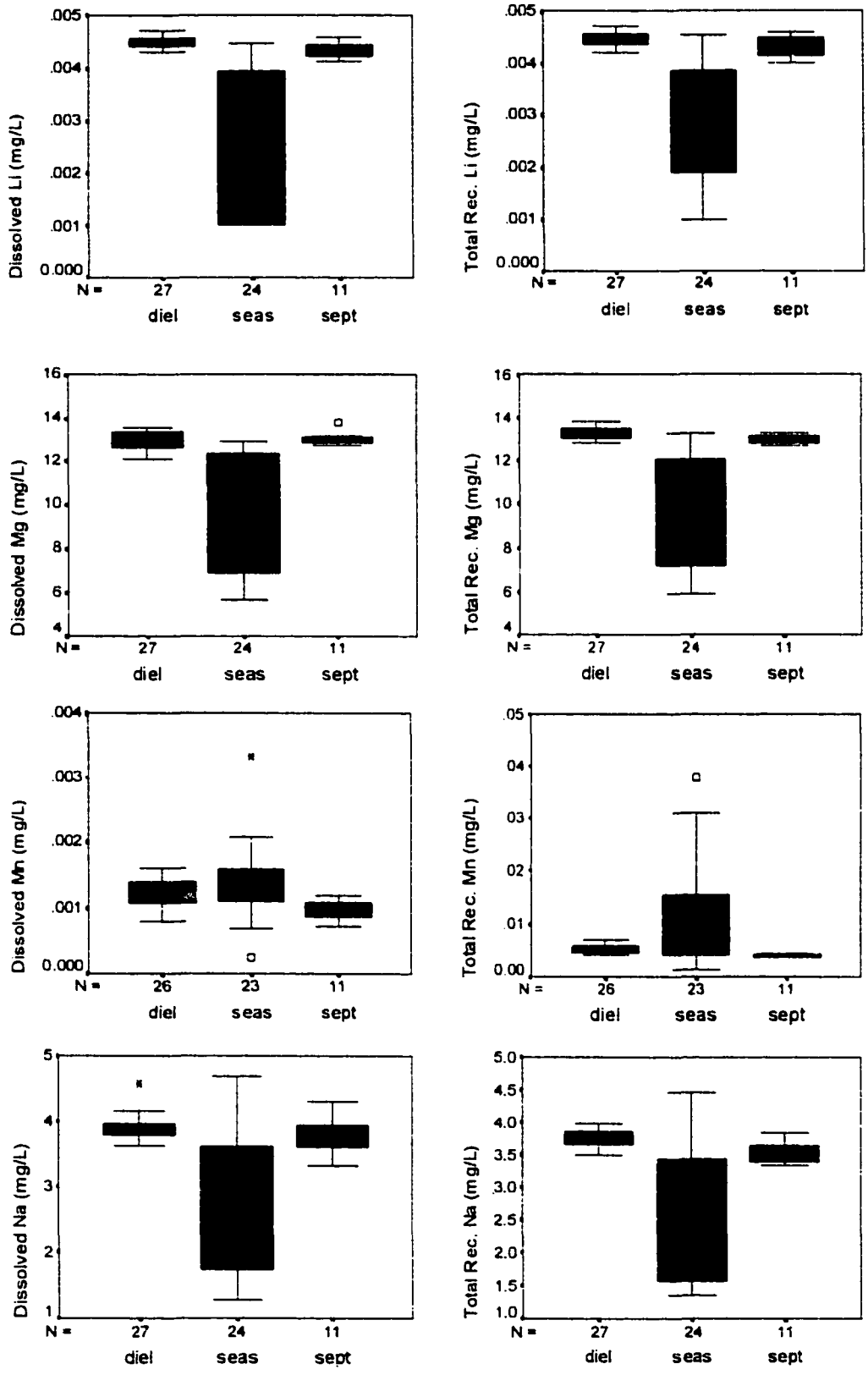


Figure 19, continued: Boxplots of Diel, Seasonal, and September rain event variability at site BFB.

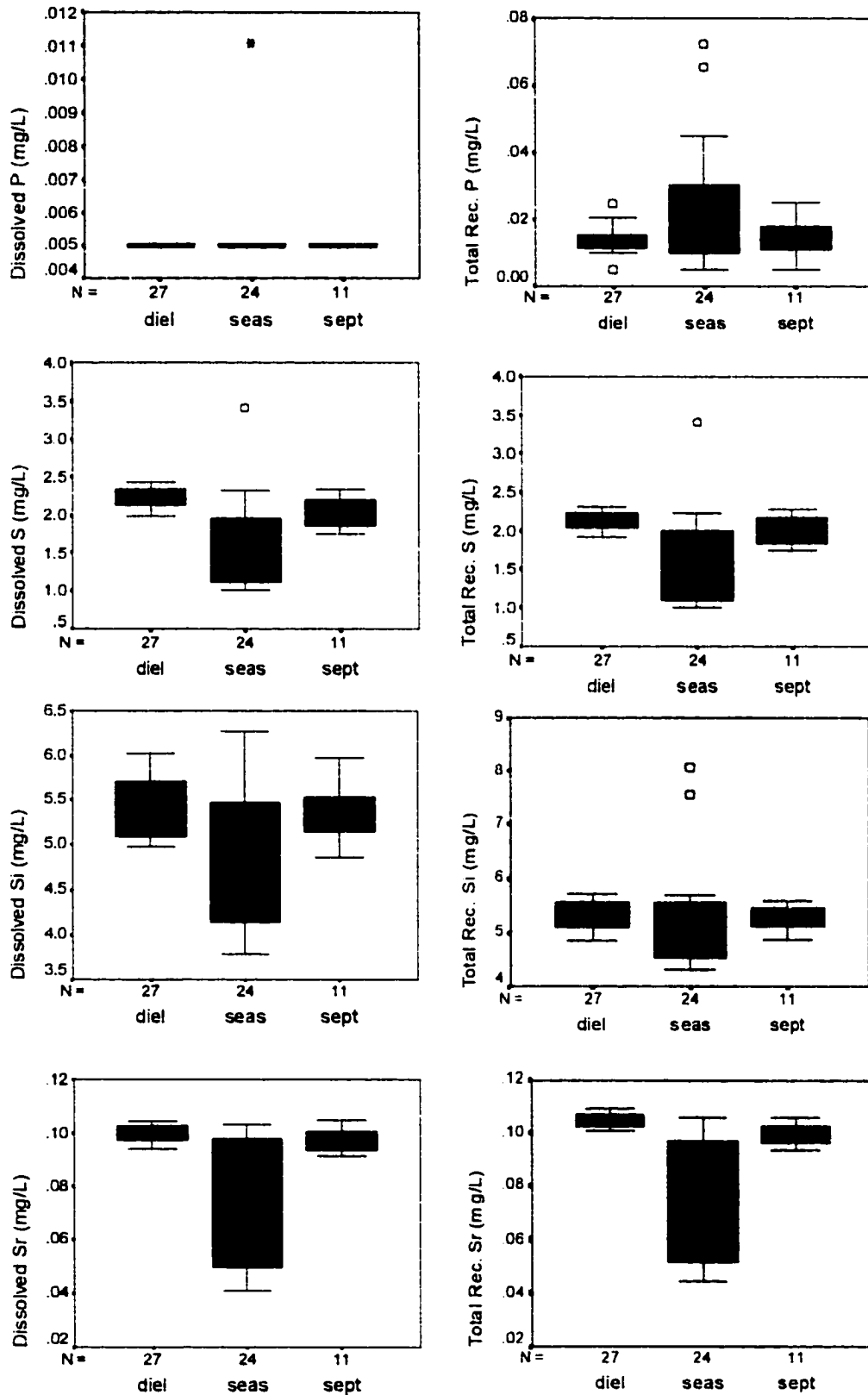


Figure 19, continued: Boxplots of Diel, Seasonal, and September rain event variability at site BFB.

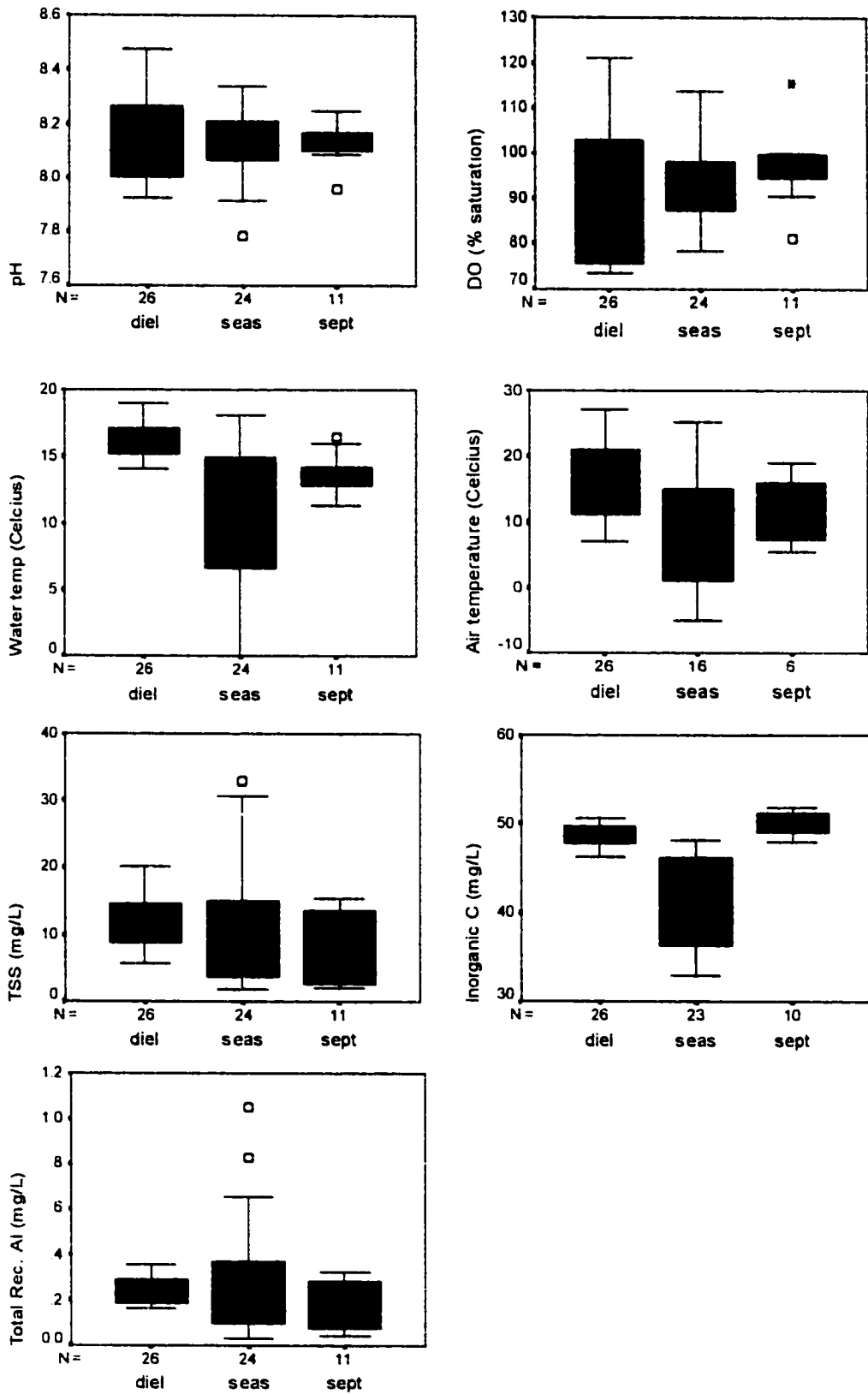


Figure 20: Boxplots of diel, seasonal, and September rain event variability at site CFBM.

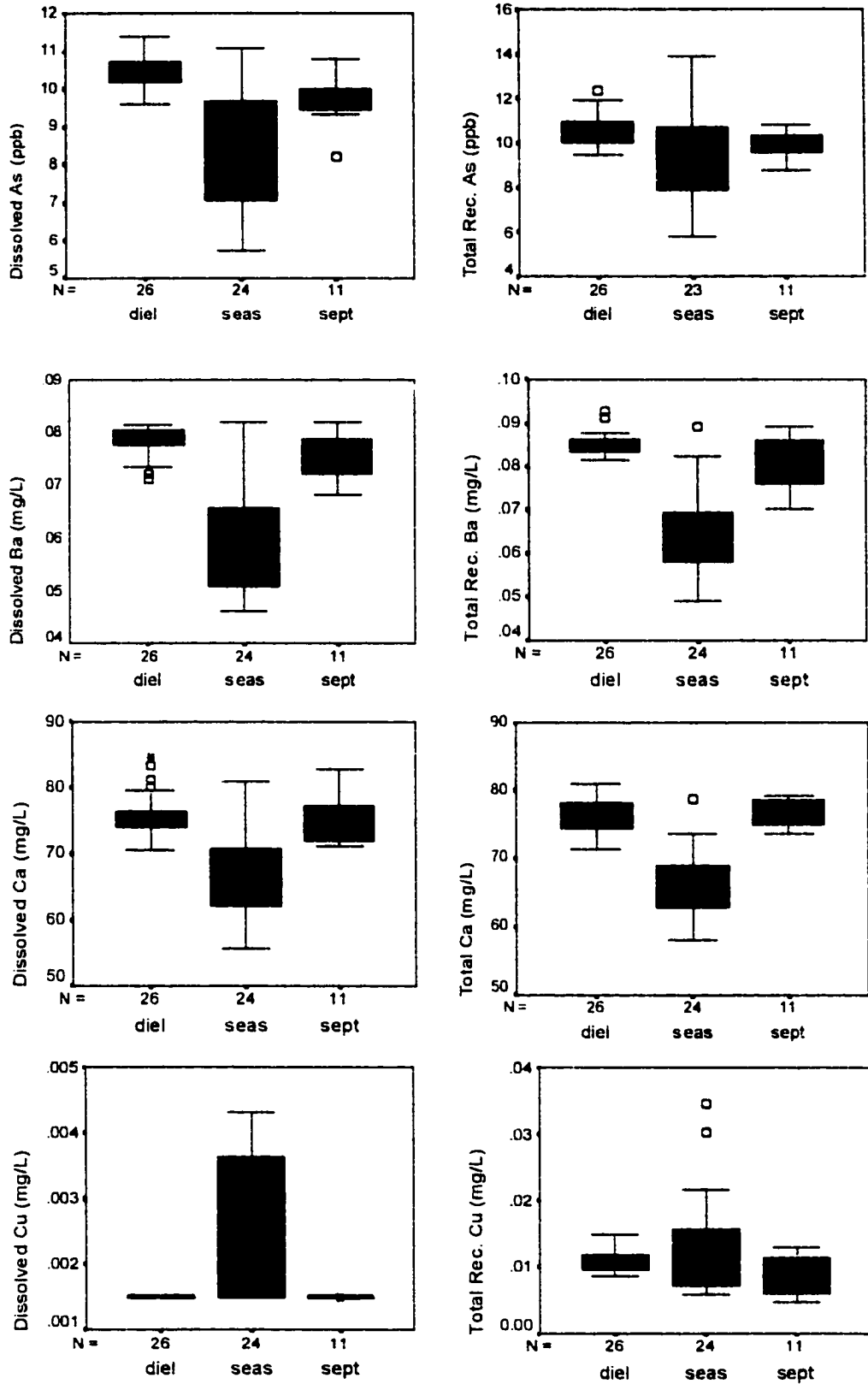


Figure 20, continued: Boxplots of diel, seasonal, and September rain event variability at site CFBM.

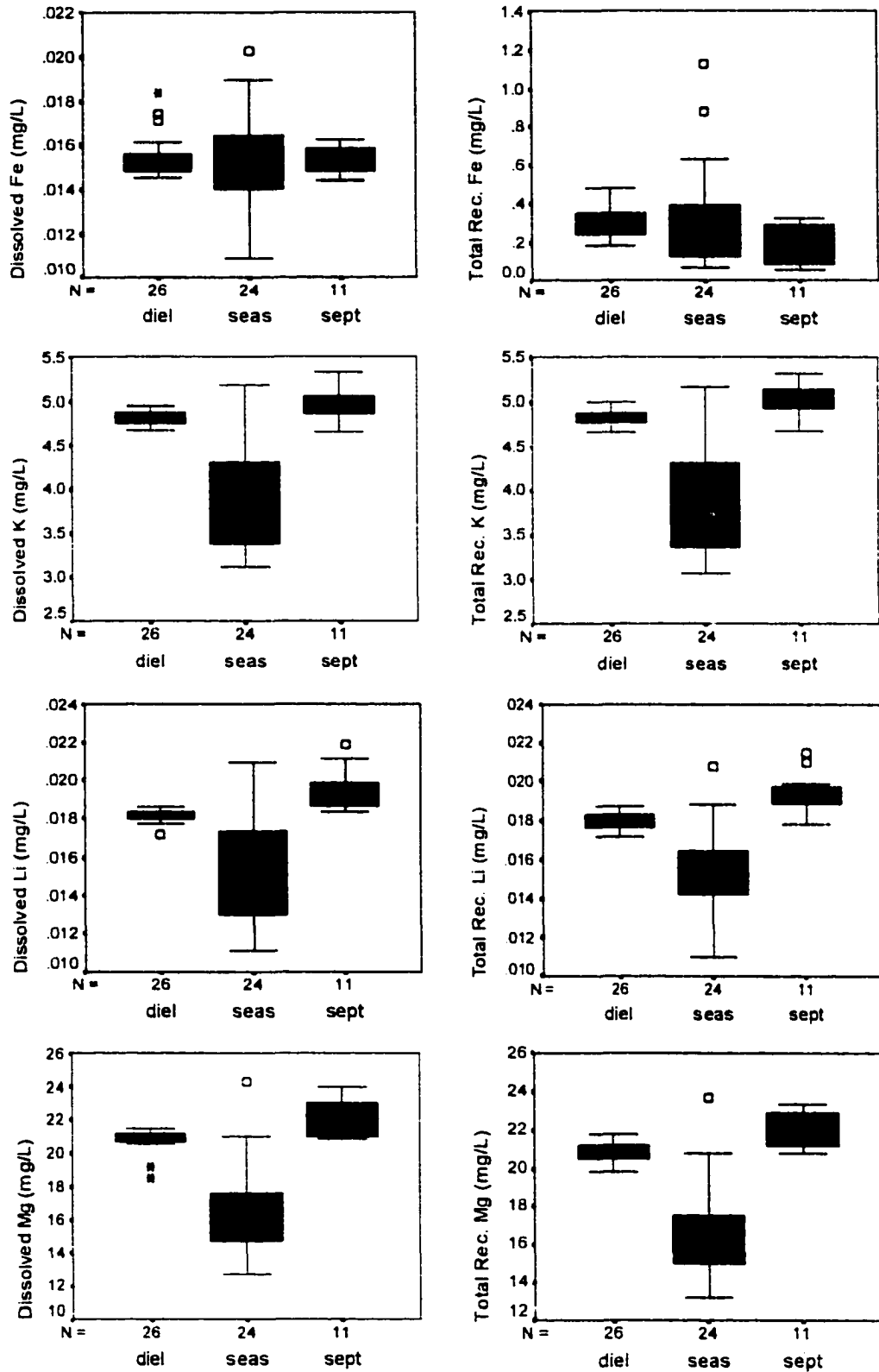


Figure 20, continued: Boxplots of diel, seasonal, and September rain event variability at site CFBM.

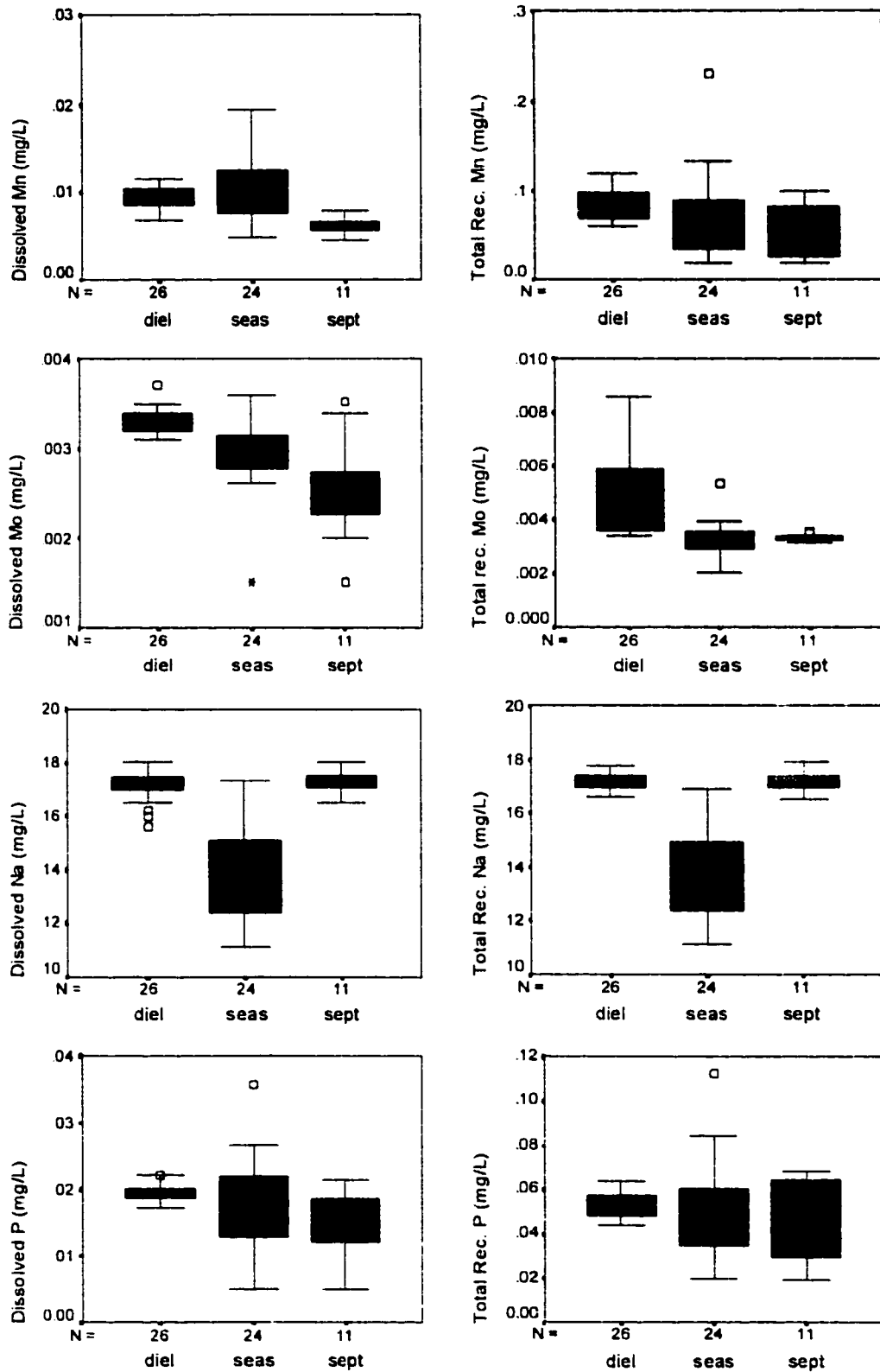


Figure 20, continued: Boxplots of diel, seasonal, and September rain event variability at site CFBM.

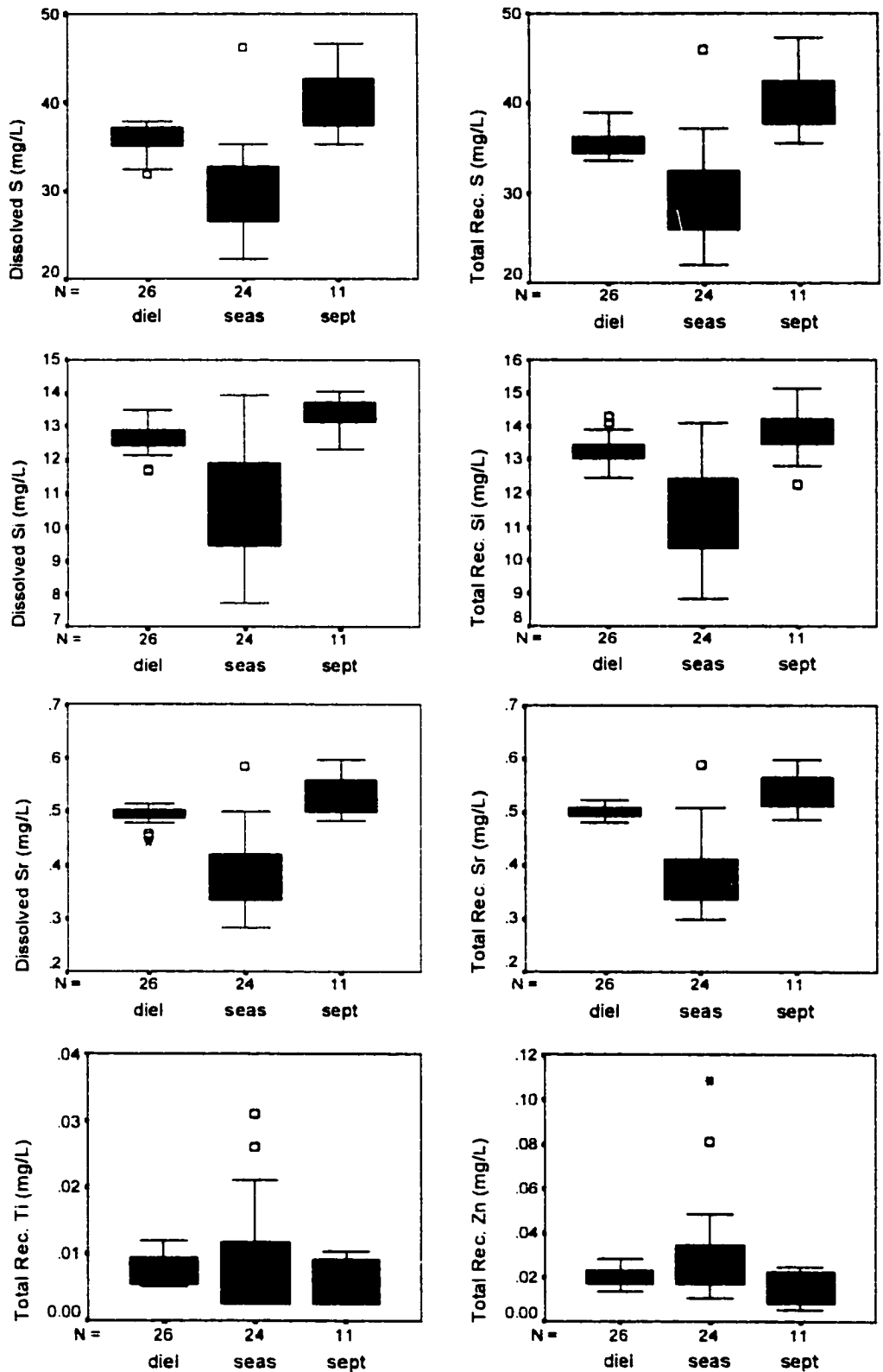


Figure 20, continued: Boxplots of diel, seasonal, and September rain event variability at site CFBM.



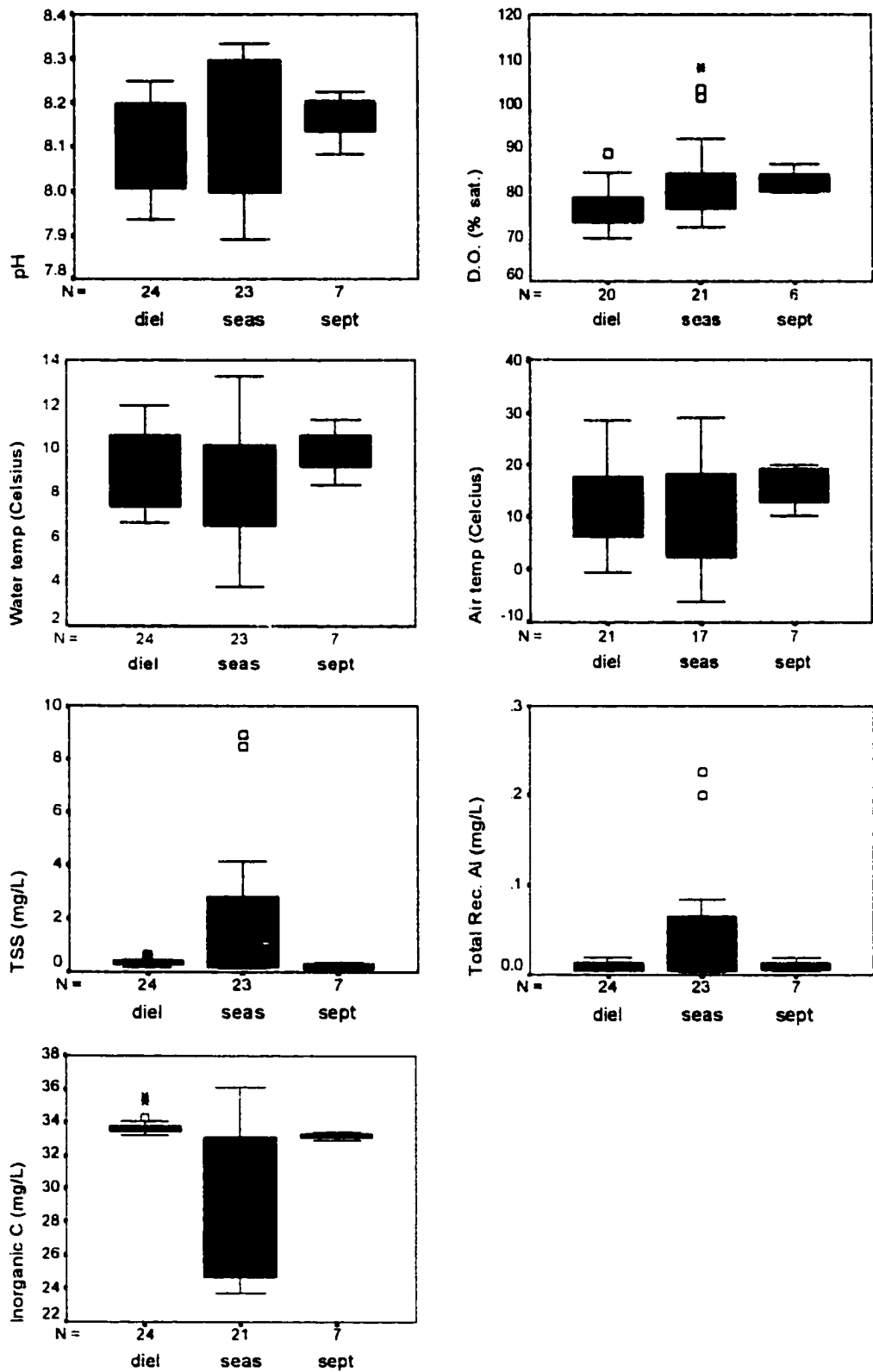


Figure 21: Boxplots of diel, seasonal, and September rain event variability at site LF.

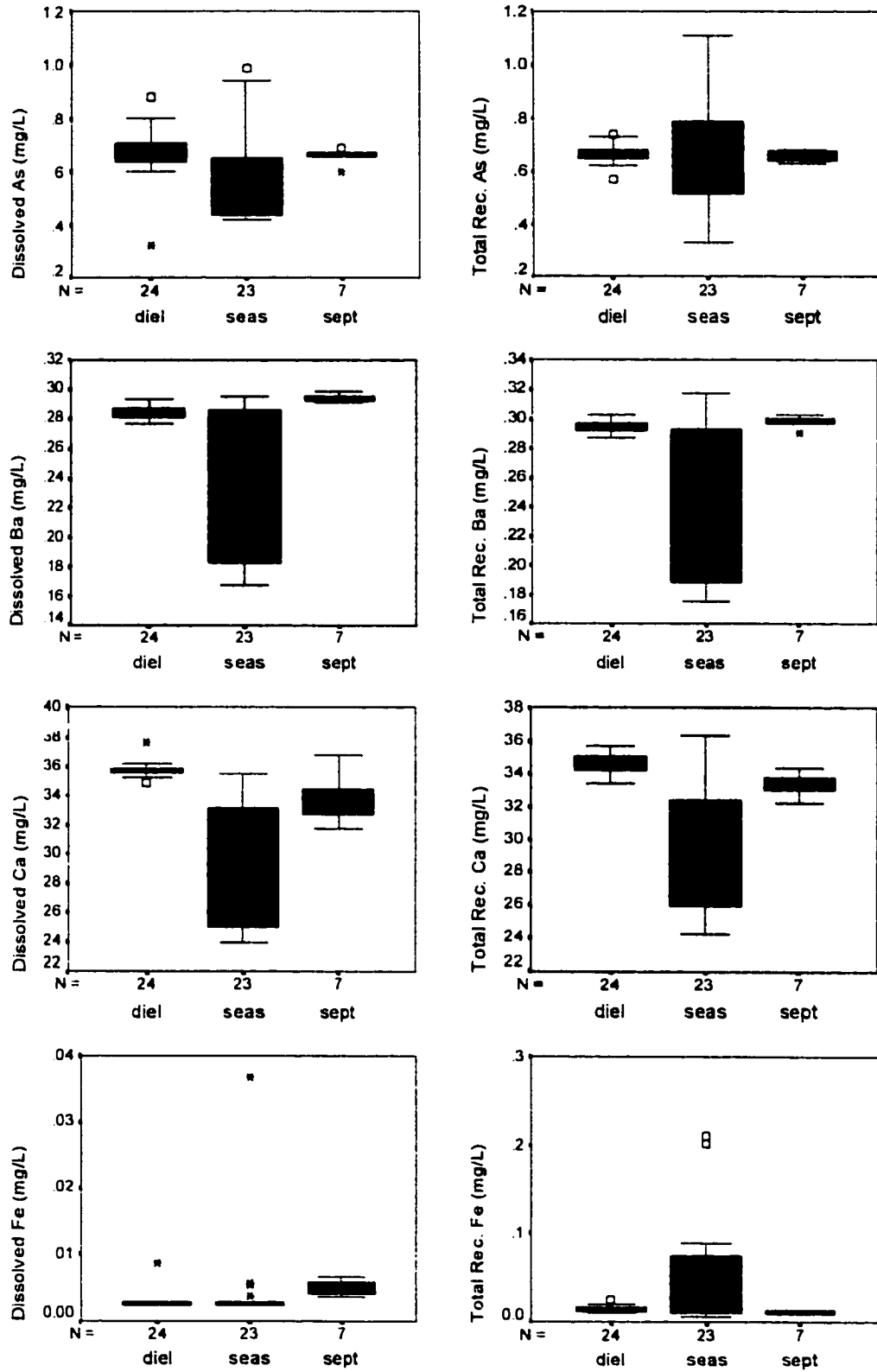


Figure 21, continued: Boxplots of diel, seasonal, and September rain event variability at site LF.

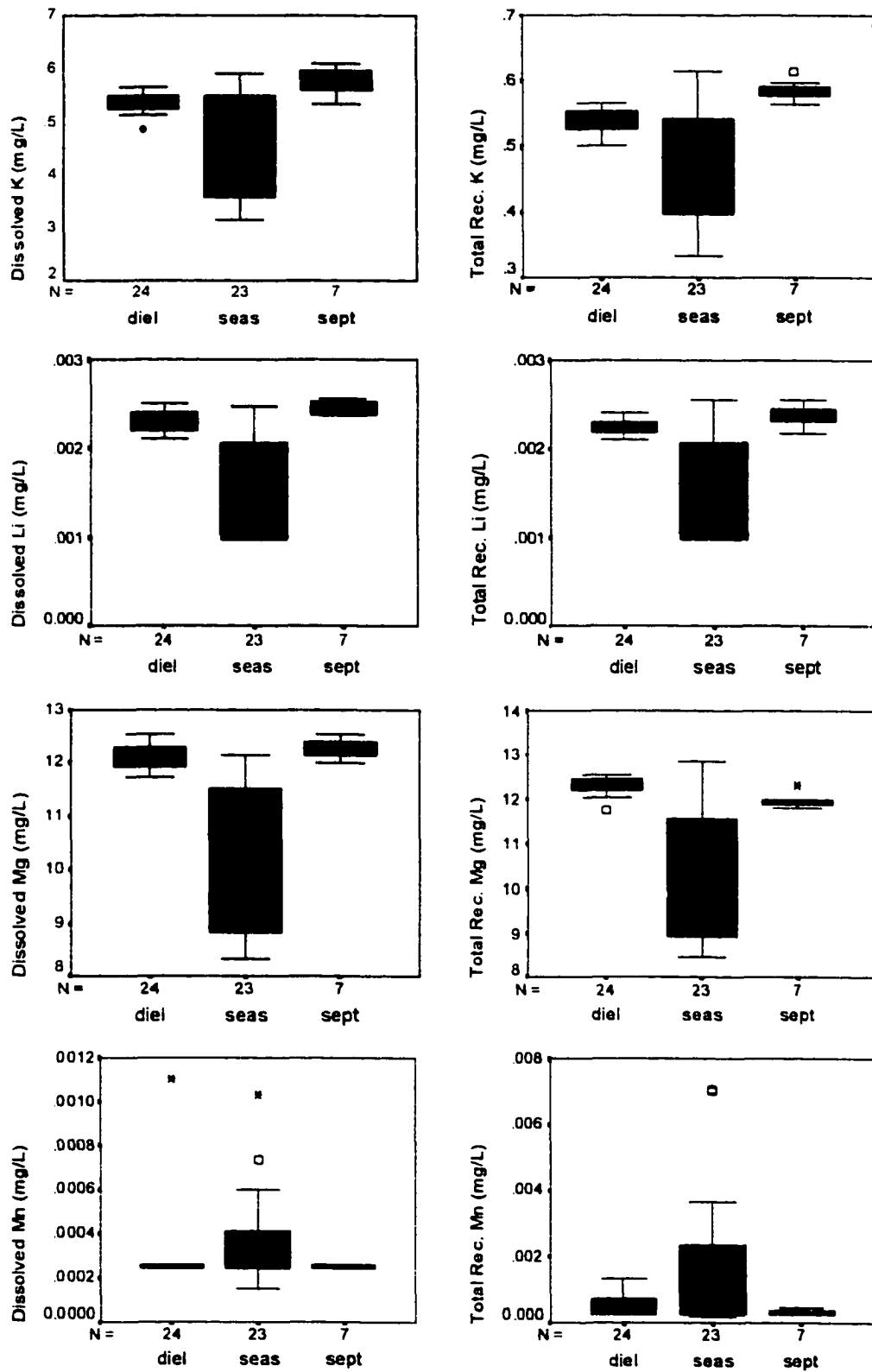


Figure 21, continued: Boxplots of diel, seasonal, and September rain event variability at site LF.

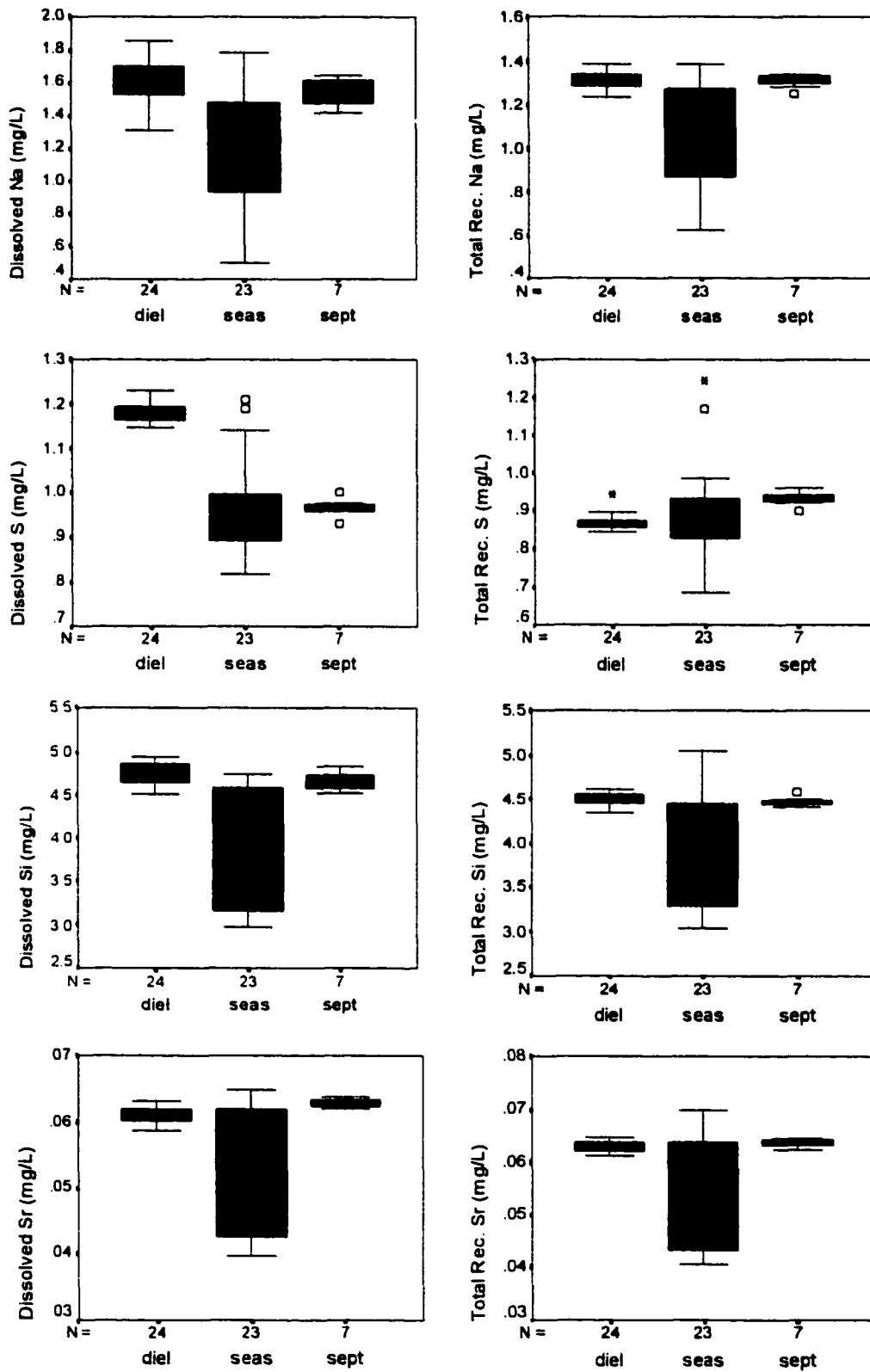


Figure 21, continued: Boxplots of diel, seasonal, and September rain event variability at site LF.

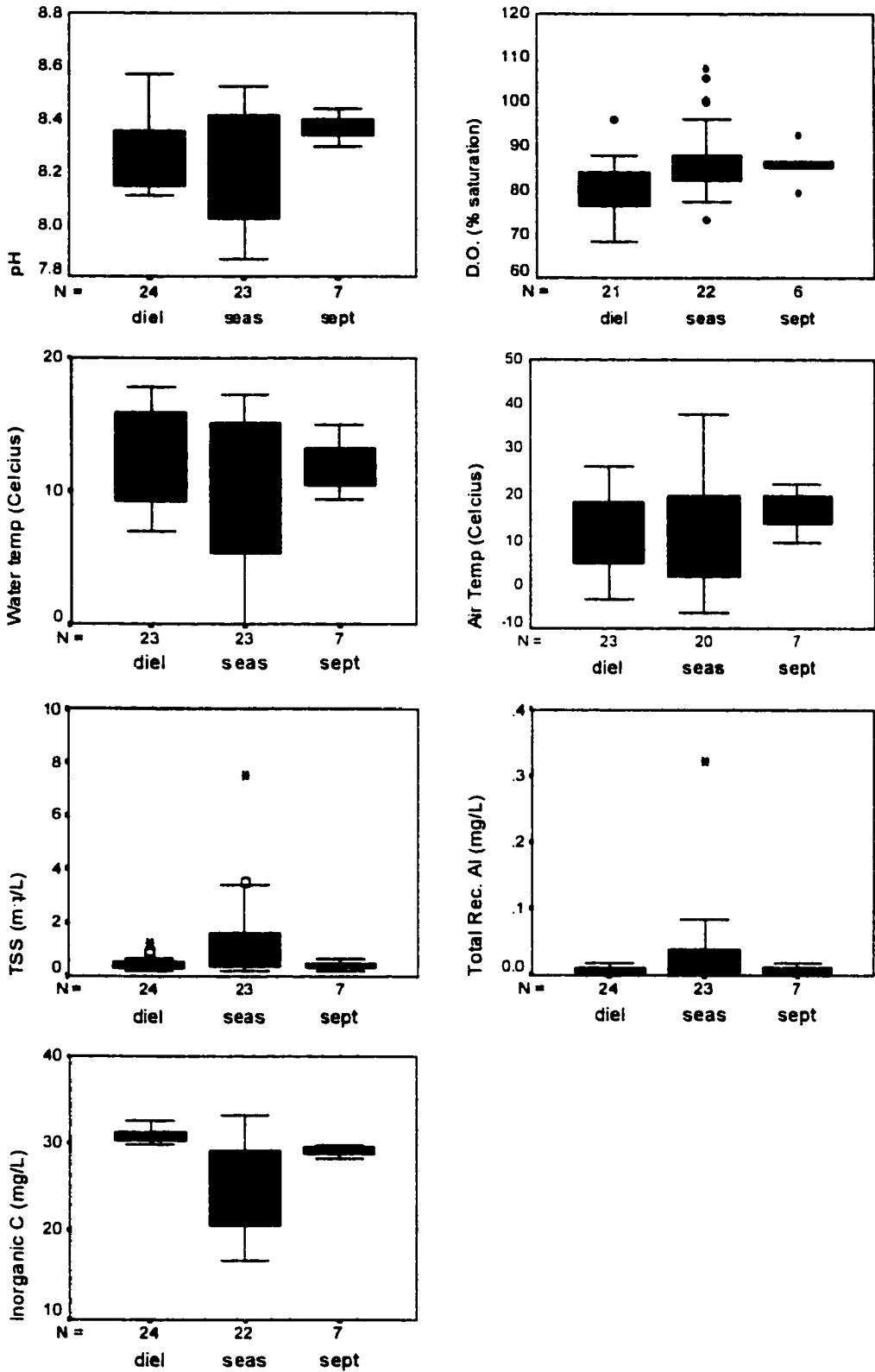


Figure 22: Boxplots of diel, seasonal, and September rain event variability at site BH.

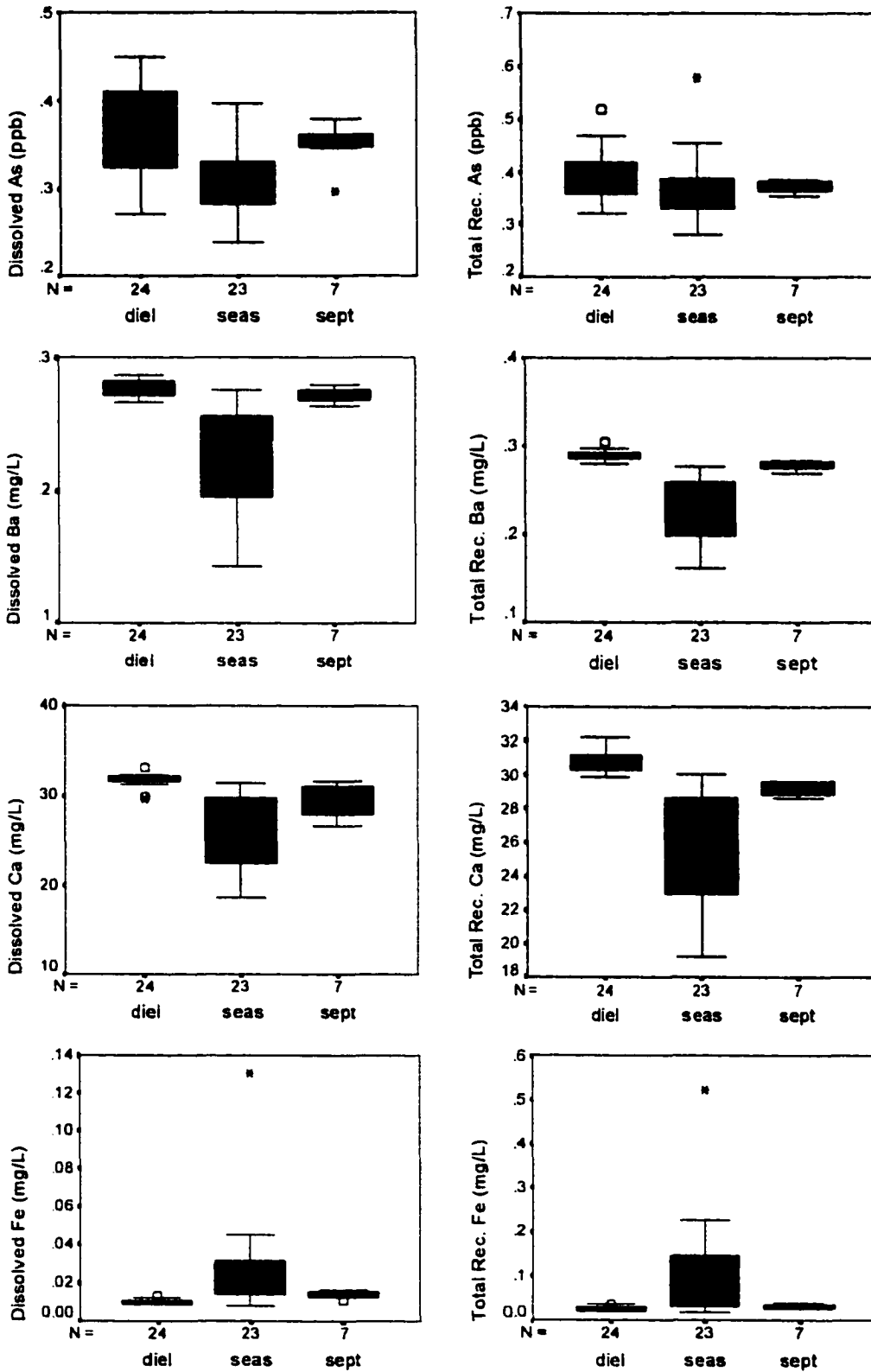


Figure 22, continued: Boxplots of diel, seasonal, and September rain event variability at site BH.

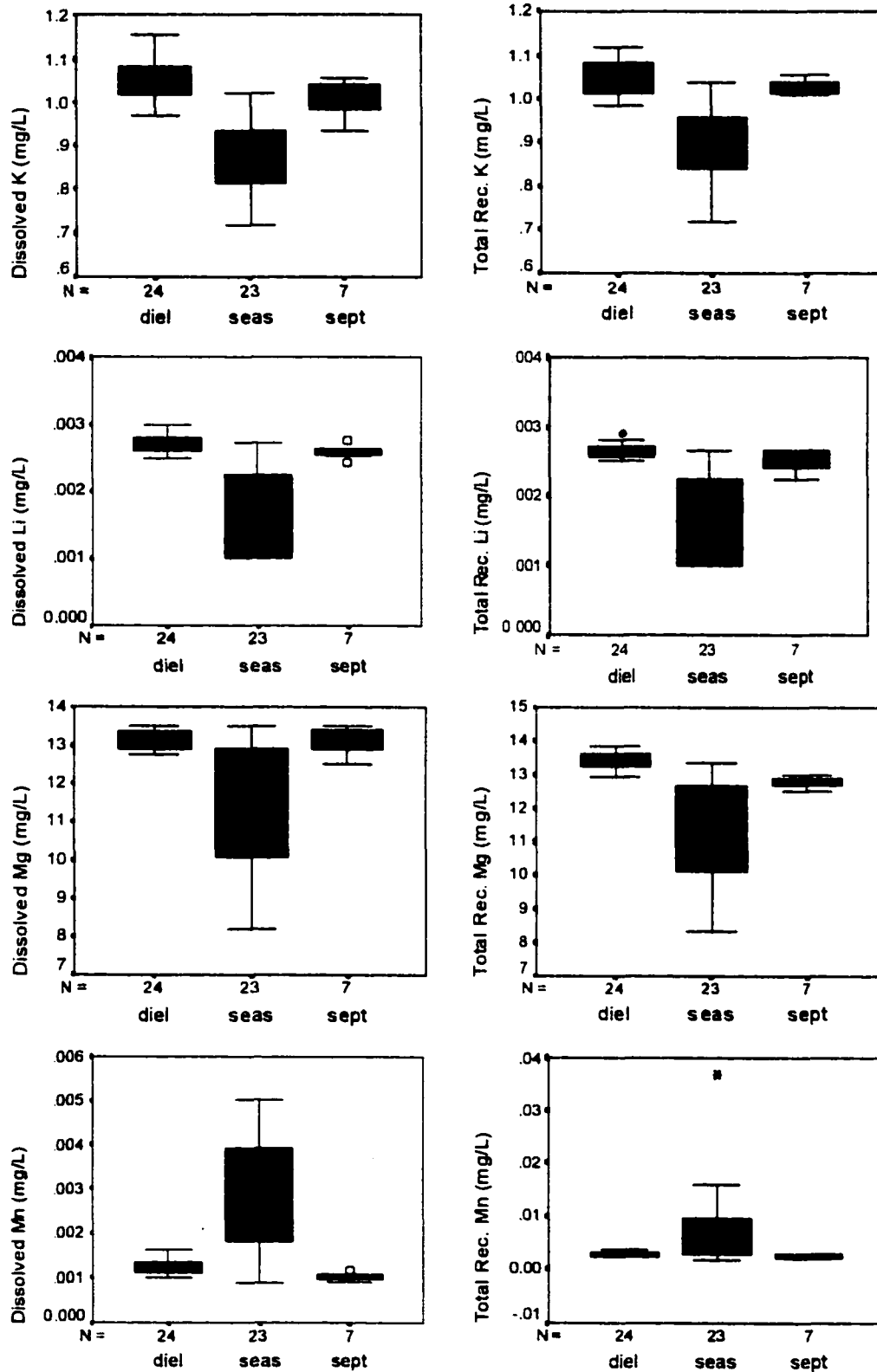


Figure 22, continued: Boxplots of diel, seasonal, and September rain event variability at site BH.

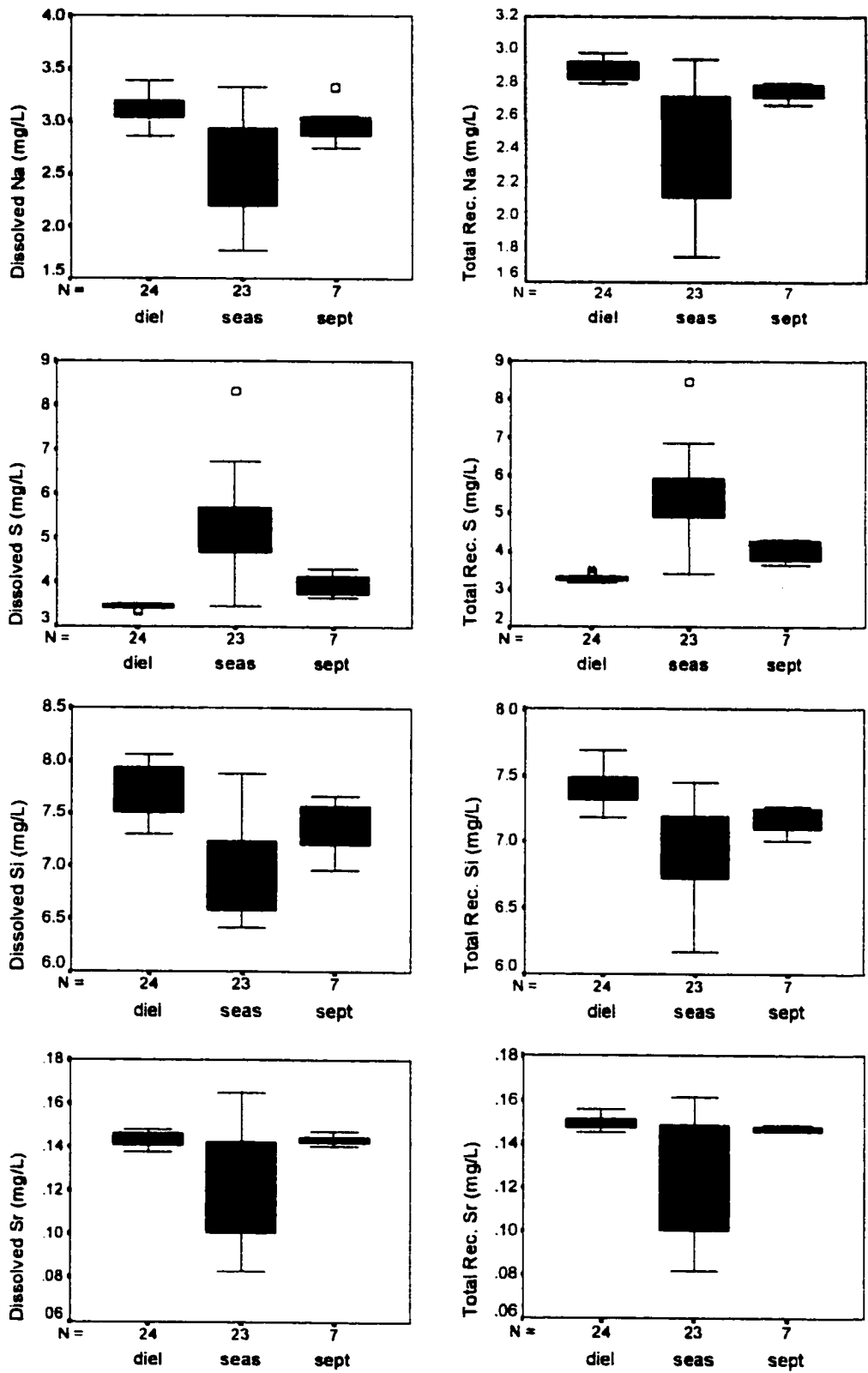


Figure 22, continued: Boxplots of diel, seasonal, and September rain event variability at site BH.



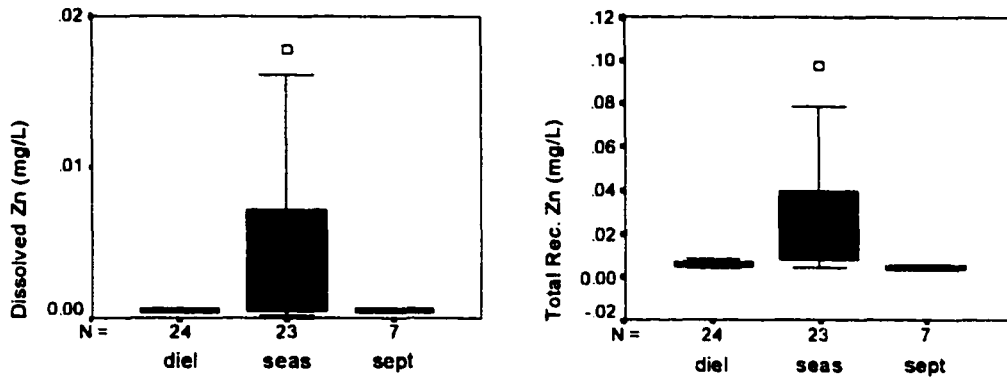


Figure 22, continued: Boxplots of diel, seasonal, and September rain event variability at site BH.





Chapter 4 Appendix All total recoverable samples collected for the diet studies at each site  
 All samples below PQL for Ag, Be, Cd, Co, Pb, Sn, and V. Element PQLs are listed under each element.  
 Note: Although Cr, Ni, P, and Zn values are listed, there were contamination problems with these elements, as revealed in the digest blanks.  
 All concentrations in mg/L, unless otherwise specified.

Site	Sampling Date	Time	As (µg/L)	Al	Ba	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	S	Si	Sr	Ti	Zn
			0.2	0.007	0.0005	0.070	0.005	0.003	0.005	0.200	0.002	0.100	0.001	0.003	0.180	0.001	0.010	0.007	0.020	0.001	0.005	0.001
LF	8/17/00	14:00	0.67	0.012	0.292	34.32	BPQL	BPQL	0.017	0.55	0.002	12.30	0.001	BPQL	1.3	BPQL	BPQL	0.87	4.45	0.062	BPQL	0.001
LF	8/17/00	16:00	0.67	0.008	0.297	35.72	BPQL	BPQL	0.018	0.55	0.002	11.75	0.001	BPQL	1.3	BPQL	BPQL	0.94	4.34	0.064	BPQL	0.001
LF	8/17/00	18:00	0.65	0.007	0.291	34.29	BPQL	BPQL	0.016	0.54	0.002	12.27	0.001	BPQL	1.3	BPQL	BPQL	0.86	4.48	0.062	BPQL	0.002
LF	8/17/00	20:00	0.63	0.012	0.299	34.72	BPQL	BPQL	0.014	0.56	0.002	12.50	0.001	BPQL	1.3	BPQL	BPQL	0.88	4.55	0.063	BPQL	0.001
LF	8/17/00	22:00	0.62	BPQL	0.290	34.68	BPQL	BPQL	0.014	0.52	0.002	12.19	BPQL	BPQL	1.3	BPQL	BPQL	0.85	4.45	0.061	BPQL	0.001
LF	8/18/00	0:00	0.65	0.012	0.302	35.39	BPQL	BPQL	0.014	0.57	0.002	12.52	0.001	BPQL	1.4	BPQL	BPQL	0.89	4.53	0.065	BPQL	0.001
LF	8/18/00	2:00	0.57	0.013	0.299	33.94	BPQL	BPQL	0.015	0.56	0.002	12.43	0.001	BPQL	1.3	BPQL	BPQL	0.89	4.35	0.063	BPQL	0.001
LF	8/18/00	4:00	0.64	0.010	0.297	35.57	BPQL	BPQL	0.012	0.54	0.002	12.48	BPQL	BPQL	1.4	BPQL	BPQL	0.87	4.44	0.064	BPQL	0.001
LF	8/18/00	6:00	0.73	BPQL	0.293	34.83	BPQL	BPQL	0.013	0.54	0.002	12.40	0.001	BPQL	1.3	BPQL	BPQL	0.87	4.50	0.063	BPQL	0.001
LF	8/18/00	8:00	0.68	BPQL	0.288	34.54	BPQL	BPQL	0.011	0.52	0.002	12.20	BPQL	BPQL	1.3	BPQL	BPQL	0.86	4.44	0.062	BPQL	0.001
LF	8/18/00	10:00	0.74	BPQL	0.292	34.76	BPQL	BPQL	0.012	0.54	0.002	12.36	BPQL	BPQL	1.3	BPQL	BPQL	0.85	4.50	0.063	BPQL	0.001
LF	8/18/00	12:00	0.69	0.014	0.291	33.55	BPQL	BPQL	0.014	0.54	0.002	12.11	BPQL	BPQL	1.3	BPQL	BPQL	0.85	4.44	0.062	BPQL	0.001
LF	8/20/00	14:00	1.68	0.014	0.295	33.42	BPQL	BPQL	0.016	0.56	0.002	12.02	BPQL	BPQL	1.2	BPQL	BPQL	0.87	4.47	0.064	BPQL	0.001
LF	8/20/00	16:00	0.70	0.008	0.297	34.71	BPQL	BPQL	0.019	0.56	0.002	12.34	0.001	BPQL	1.3	BPQL	BPQL	0.86	4.59	0.064	BPQL	0.002
LF	8/20/00	18:00	0.70	0.008	0.297	34.98	BPQL	BPQL	0.010	0.53	0.002	12.28	BPQL	BPQL	1.3	BPQL	BPQL	0.85	4.55	0.064	BPQL	0.001
LF	8/20/00	20:00	0.68	0.012	0.293	35.43	BPQL	BPQL	0.015	0.53	0.002	12.54	0.001	BPQL	1.3	BPQL	BPQL	0.86	4.58	0.062	BPQL	0.001
LF	8/20/00	22:00	0.69	0.009	0.296	33.87	BPQL	BPQL	0.015	0.57	0.002	12.13	0.001	BPQL	1.3	BPQL	BPQL	0.87	4.48	0.064	BPQL	0.002
LF	8/21/00	0:00	0.69	0.017	0.297	34.46	BPQL	BPQL	0.024	0.54	0.002	12.41	0.001	BPQL	1.3	BPQL	BPQL	0.87	4.56	0.063	BPQL	0.001
LF	8/21/00	2:00	0.65	0.020	0.263	35.25	BPQL	BPQL	0.017	0.52	0.002	12.38	0.001	BPQL	1.4	BPQL	BPQL	0.86	4.54	0.062	BPQL	0.001
LF	8/21/00	4:00	0.65	0.017	0.290	35.25	BPQL	BPQL	0.014	0.51	0.002	12.42	0.001	BPQL	1.4	BPQL	BPQL	0.85	4.54	0.062	BPQL	0.001
LF	8/21/00	6:00	0.64	0.019	0.292	34.41	BPQL	BPQL	0.014	0.53	0.002	12.28	0.001	BPQL	1.3	BPQL	BPQL	0.86	4.51	0.062	BPQL	0.001
LF	8/21/00	8:00	0.65	0.010	0.293	34.21	BPQL	BPQL	0.012	0.52	0.002	12.14	BPQL	BPQL	1.3	BPQL	BPQL	0.87	4.50	0.063	BPQL	0.001
LF	8/21/00	10:40	0.67	BPQL	0.287	34.22	BPQL	BPQL	0.010	0.50	0.002	12.28	BPQL	BPQL	1.3	BPQL	BPQL	0.84	4.49	0.061	BPQL	0.001
LF	8/21/00	12:00	0.62	0.008	0.297	34.97	BPQL	BPQL	0.012	0.53	0.002	12.47	BPQL	BPQL	1.3	BPQL	BPQL	0.86	4.61	0.064	BPQL	0.001
BH	8/17/00	15:00	0.36	0.014	0.286	29.93	BPQL	BPQL	0.027	1.02	0.003	13.17	0.003	BPQL	2.8	BPQL	BPQL	3.25	7.33	0.147	BPQL	0.005
BH	8/17/00	17:00	0.47	BPQL	0.286	30.66	BPQL	BPQL	0.026	1.04	0.003	12.93	0.003	BPQL	2.8	BPQL	BPQL	3.35	7.17	0.148	BPQL	0.005
BH	8/17/00	19:00	0.52	BPQL	0.287	30.41	BPQL	BPQL	0.034	1.08	0.003	13.41	0.003	BPQL	2.9	BPQL	BPQL	3.28	7.32	0.147	BPQL	0.005
BH	8/17/00	21:00	0.41	0.011	0.290	30.83	BPQL	BPQL	0.033	1.10	0.003	13.46	0.003	BPQL	2.9	BPQL	BPQL	3.27	7.31	0.148	BPQL	0.006
BH	8/17/00	23:00	0.43	BPQL	0.292	31.24	BPQL	BPQL	0.026	1.07	0.003	13.66	0.003	BPQL	3.0	BPQL	BPQL	3.29	7.52	0.147	BPQL	0.007
BH	8/18/00	1:00	0.37	0.008	0.305	32.25	BPQL	BPQL	0.026	1.12	0.003	13.80	0.003	BPQL	3.0	BPQL	BPQL	3.42	7.36	0.156	BPQL	0.007
BH	8/18/00	3:00	0.32	0.009	0.298	31.54	BPQL	BPQL	0.025	1.08	0.003	13.70	0.003	BPQL	3.0	BPQL	BPQL	3.27	7.34	0.152	BPQL	0.007
BH	8/18/00	5:00	0.36	BPQL	0.292	31.43	BPQL	BPQL	0.025	1.04	0.003	13.69	0.003	BPQL	3.0	BPQL	BPQL	3.29	7.43	0.149	BPQL	0.008
BH	8/18/00	7:00	0.41	0.014	0.283	30.63	BPQL	BPQL	0.027	1.00	0.003	13.57	0.002	BPQL	2.8	BPQL	BPQL	3.23	7.35	0.145	BPQL	0.008
BH	8/18/00	9:00	0.36	0.010	0.285	30.38	BPQL	BPQL	0.025	1.01	0.003	13.54	0.002	BPQL	2.9	BPQL	BPQL	3.26	7.36	0.146	BPQL	0.007
BH	8/18/00	11:00	0.40	0.009	0.283	30.28	BPQL	BPQL	0.025	0.99	0.003	13.22	0.002	BPQL	2.8	BPQL	BPQL	3.27	7.40	0.149	BPQL	0.006
BH	8/18/00	13:00	0.44	0.011	0.286	30.28	BPQL	BPQL	0.028	1.02	0.003	13.24	0.003	BPQL	2.8	BPQL	BPQL	3.50	7.69	0.150	BPQL	0.006
BH	8/20/00	15:00	0.41	0.012	0.290	29.95	BPQL	BPQL	0.029	1.04	0.003	13.17	0.003	BPQL	2.8	BPQL	BPQL	3.29	7.29	0.149	BPQL	0.005
BH	8/20/00	17:00	0.44	BPQL	0.292	30.80	BPQL	BPQL	0.034	1.08	0.003	13.58	0.004	BPQL	2.9	BPQL	BPQL	3.28	7.46	0.150	BPQL	0.006
BH	8/20/00	19:00	0.42	BPQL	0.289	30.12	BPQL	BPQL	0.025	1.07	0.003	13.13	0.003	BPQL	2.8	BPQL	BPQL	3.18	7.24	0.149	BPQL	0.005
BH	8/20/00	21:00	0.43	BPQL	0.291	30.58	BPQL	BPQL	0.033	1.09	0.003	13.40	0.003	BPQL	2.9	BPQL	BPQL	3.21	7.31	0.150	BPQL	0.006
BH	8/20/00	23:00	0.41	0.009	0.295	30.66	BPQL	BPQL	0.027	1.11	0.003	13.45	0.003	BPQL	2.9	BPQL	BPQL	3.25	7.33	0.151	BPQL	0.006
BH	8/21/00	1:00	0.39	BPQL	0.296	30.97	BPQL	BPQL	0.029	1.08	0.003	13.57	0.003	BPQL	2.9	BPQL	BPQL	3.30	7.47	0.152	BPQL	0.007
BH	8/21/00	3:00	0.35	0.018	0.293	31.36	BPQL	BPQL	0.023	1.07	0.003	13.86	0.003	BPQL	3.0	BPQL	BPQL	3.30	7.61	0.153	BPQL	0.007
BH	8/21/00	5:00	0.35	0.010	0.291	31.01	BPQL	BPQL	0.026	1.05	0.003	13.60	0.002	BPQL	2.9	BPQL	BPQL	3.21	7.55	0.152	BPQL	0.007
BH	8/21/00	7:00	0.32	BPQL	0.281	31.10	BPQL	BPQL	0.021	1.00	0.003	13.48	0.002	BPQL	2.9	BPQL	BPQL	3.21	7.47	0.147	BPQL	0.007
BH	8/21/00	9:00	0.34	0.010	0.281	30.31	BPQL	BPQL	0.020	1.01	0.003	13.46	0.002	BPQL	2.9	BPQL	BPQL	3.26	7.49	0.147	BPQL	0.007
BH	8/21/00	11:30	0.36	BPQL	0.287	31.43	BPQL	BPQL	0.025	1.00	0.003	13.64	0.002	BPQL	2.9	BPQL	BPQL	3.27	7.66	0.151	BPQL	0.006
BH	8/21/00	13:20	0.35	0.014	0.287	30.28	BPQL	BPQL	0.025	1.01	0.003	13.30	0.002	BPQL	2.8	BPQL	BPQL	3.25	7.49	0.149	BPQL	0.005















FA of	Sampling Date	Weather/ Intm. Comments	Total Q (Lb)	Water Temp (F)	Air Temp (F)	D.O. (mg/L)	D.O. (ppm)	DO Sat. (%)	DO Def. (%)	TSS (mg/L)	Amnity (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	K <sub>2</sub> O (mg/L)	N (mg/L)	P (mg/L)	S (mg/L)	Si (mg/L)	Sh (mg/L)	Si (mg/L)	Zn (mg/L)
FA BH-1	5/20/00	13.00 pt cloudy	81.74	8.33	11.8	6.06	1.1	100.8	20.61	25.56	20.61	25.56	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
FA BH-2	5/20/00	14.45 sunny	25.99	8.5	17.1	8.1	1.0	96.4	25.16	25.99	25.16	25.99	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022
FA BH-3	5/20/00	14.00 mostly sunny	20.11	8.5	17.1	8.1	1.0	96.4	25.16	20.11	25.16	20.11	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022
FA AVG BH	5/20/00		128.5	8.8	14.3	8.4	1.0	97.6	22.42	23.87	22.42	23.87	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018
FA BH-1	5/19/00	13.40 sneaky pt cloudy	10.08	8.41	15.5	8.2	0.1	170.0	30.0	31.53	30.0	31.53	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
FA BH-2	5/19/00	15.15 overcast	9.34	8.35	14.8	8.1	0.1	123.4	29.7	28.43	29.7	28.43	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
FA BH-3	5/19/00		9.34	8.34	14.8	8.1	0.1	123.3	29.7	28.32	29.7	28.32	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
FA AVG BH	5/19/00		28.76	8.37	15.4	8.1	0.1	113.9	29.7	30.00	29.7	30.00	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
FA BH-1	5/19/00	13.00 pt cloudy	81.74	8.33	11.8	6.06	1.1	100.8	20.61	25.56	20.61	25.56	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
FA BH-2	5/19/00	14.45 sunny	25.99	8.5	17.1	8.1	1.0	96.4	25.16	25.99	25.16	25.99	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022
FA BH-3	5/19/00	14.00 mostly sunny	20.11	8.5	17.1	8.1	1.0	96.4	25.16	20.11	25.16	20.11	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022
FA AVG BH	5/19/00		128.5	8.8	14.3	8.4	1.0	97.6	22.42	23.87	22.42	23.87	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018



























FA or FR?	SITE	Sampling Date	Sampling Time	As	Al	Ba	Ga	Ca	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	S	Si	Sr	Ti	Zn
TR	LC-1	9:5:00		0.56	0.009	0.236	0.00006	25.2	0.00119	0.0019	0.009	0.5	0.002	11.78	0.0025	0.0019	1.0	0.0006	0.00025	0.72	3.37	0.048	0.0025	0.001
TR	LC-2	9:6:00		0.62	0.011	0.285	0.00005	31.0	0.0025	0.0015	0.010	0.6	0.002	11.80	0.0025	0.0015	1.3	0.0005	0.0022	0.90	4.41	0.063	0.0025	0.0005
TR	LC-3	9:6:00		0.85	0.025	0.285	0.00005	33.1	0.0025	0.0015	0.010	0.6	0.002	11.96	0.0025	0.0015	1.3	0.0005	0.0033	0.87	4.47	0.062	0.0025	0.0005
TR	AVG LC	9:6:00		0.68	0.009	0.290	0.00005	32.7	0.0025	0.0015	0.010	0.6	0.002	11.87	0.0025	0.0015	1.3	0.0005	0.0020	0.90	4.42	0.062	0.0025	0.0005
TR	LC-1	9:8:00	14:00	0.65	0.005	0.297	0.00005	32.5	0.0025	0.0015	0.011	0.6	0.003	11.85	0.0025	0.0015	1.2	0.0005	0.0030	0.93	4.46	0.063	0.0025	0.0005
TR	LC-2	9:8:00		0.73	0.005	0.295	0.00005	33.0	0.0025	0.0015	0.011	0.6	0.002	11.83	0.0025	0.0015	1.3	0.0005	0.0030	0.92	4.42	0.063	0.0025	0.0005
TR	LC-3	9:8:00		0.62	0.012	0.302	0.00005	34.3	0.0025	0.0015	0.011	0.6	0.002	12.08	0.0025	0.0015	1.3	0.0005	0.005	0.94	4.49	0.064	0.0025	0.0005
TR	AVG LC	9:8:00		0.67	0.0074	0.298	0.00005	33.3	0.0025	0.0015	0.011	0.6	0.002	11.92	0.0025	0.0015	1.3	0.0005	0.0032	0.93	4.46	0.063	0.0025	0.0005
TR	LC-1	9:10:00	14:15	0.66	0.005	0.297	0.00005	32.2	0.0025	0.0015	0.009	0.6	0.003	11.92	0.0025	0.0015	1.3	0.0005	0.005	0.93	4.41	0.064	0.0025	0.0005
TR	LC-2	9:10:00		0.70	0.0329	0.298	0.00005	32.3	0.0025	0.0015	0.011	0.6	0.003	11.99	0.0025	0.0015	1.2	0.0005	0.028	0.93	4.47	0.064	0.0025	0.0005
TR	LC-3	9:10:00		0.68	0.019	0.298	0.00005	32.3	0.0025	0.0015	0.010	0.6	0.003	11.96	0.0025	0.0015	1.2	0.0005	0.017	0.93	4.44	0.064	0.0025	0.0005
TR	AVG LC	9:10:00		0.70	0.005	0.299	0.00005	32.9	0.0025	0.0015	0.009	0.6	0.002	11.93	0.0025	0.0015	1.3	0.0005	0.005	0.93	4.50	0.064	0.0025	0.0005
TR	LC-2	10:4:00		0.72	0.005	0.298	0.00005	32.8	0.0025	0.0015	0.010	0.6	0.002	11.87	0.0025	0.0015	1.3	0.0005	0.005	0.94	4.49	0.063	0.0025	0.0005
TR	LC-3	10:4:00		0.71	0.005	0.299	0.00005	32.2	0.0025	0.0015	0.010	0.6	0.003	12.02	0.0025	0.0015	1.2	0.0005	0.005	0.92	4.51	0.064	0.0025	0.0005
TR	AVG LC	10:4:00		0.71	0.005	0.299	0.00005	32.6	0.0025	0.0015	0.010	0.6	0.002	11.94	0.0025	0.0015	1.3	0.0005	0.005	0.93	4.50	0.064	0.0025	0.0005
TR	LC-1	11:5:00	15:20	0.71	0.005	0.293	0.00005	32.2	0.0025	0.0015	0.008	0.6	0.002	11.64	0.0025	0.0015	1.3	0.0005	0.005	0.92	4.42	0.064	0.0025	0.0005
TR	LC-2	11:5:00		1.04	0.0156	0.294	0.00005	32.9	0.0025	0.0015	0.007	0.6	0.002	11.63	0.0025	0.0015	1.3	0.0005	0.005	0.94	4.44	0.064	0.0025	0.0005
TR	LC-3	11:5:00		0.78	0.005	0.294	0.00005	32.4	0.0025	0.0015	0.015	0.6	0.003	11.81	0.0025	0.0015	1.3	0.0005	0.005	0.94	4.50	0.064	0.0025	0.0005
TR	AVG LC	11:5:00		0.82	0.012	0.294	0.00005	32.9	0.0025	0.0015	0.010	0.6	0.002	11.69	0.0025	0.0015	1.3	0.0005	0.005	0.93	4.45	0.064	0.0025	0.0005
TR	LC-1	12:3:00	13:50	0.84	0.005	0.292	0.00005	31.6	0.0025	0.0015	0.007	0.6	0.002	11.41	0.0025	0.0015	1.3	0.0005	0.005	0.95	4.45	0.063	0.0025	0.0005
TR	LC-2	12:3:00		0.86	0.005	0.288	0.00005	32.6	0.0025	0.0015	0.007	0.5	0.002	11.41	0.0025	0.0015	1.3	0.0005	0.005	0.87	4.44	0.063	0.0025	0.0005
TR	LC-3	12:3:00		0.83	0.005	0.304	0.00005	32.8	0.0025	0.0015	0.007	0.6	0.002	11.91	0.0025	0.0015	1.4	0.0005	0.005	0.96	4.63	0.066	0.0025	0.0005
TR	AVG LC	12:3:00		0.83	0.005	0.294	0.00005	32.4	0.0025	0.0015	0.007	0.6	0.002	11.58	0.0025	0.0015	1.3	0.0005	0.008	0.93	4.50	0.064	0.0025	0.0005
TR	LC-1	12:30:00		0.86	0.005	0.283	0.00005	31.9	0.0025	0.0015	0.008	0.5	0.002	11.04	0.0025	0.0015	1.4	0.002	0.005	0.80	4.29	0.062	0.0025	0.003
TR	LC-2	12:30:00		0.84	0.005	0.279	0.00005	31.6	0.0025	0.0015	0.007	0.5	0.002	11.02	0.0025	0.0015	1.3	0.002	0.0100	0.80	4.26	0.061	0.0025	0.003
TR	LC-3	12:30:00		0.85	0.005	0.294	0.00005	32.6	0.0025	0.0015	0.007	0.5	0.002	11.41	0.0025	0.0015	1.4	0.001	0.005	0.65	4.42	0.064	0.0025	0.003
TR	AVG LC	12:30:00		0.85	0.005	0.285	0.00005	32.0	0.0025	0.0015	0.007	0.5	0.002	11.16	0.0025	0.0015	1.3	0.002	0.007	0.82	4.32	0.062	0.0025	0.003
TR	LC-1	12:71:01	14:00	0.95	0.005	0.294	0.00005	32.5	0.0025	0.0015	0.008	0.5	0.002	11.39	0.0025	0.0015	1.4	0.002	0.005	0.85	4.43	0.065	0.0025	0.0005
TR	LC-2	12:71:01		0.96	0.005	0.294	0.00005	32.6	0.0025	0.0015	0.006	0.5	0.002	11.44	0.0025	0.0015	1.3	0.0005	0.005	0.86	4.47	0.065	0.0025	0.0005
TR	LC-3	12:71:01		0.92	0.005	0.293	0.00005	33.1	0.0025	0.0015	0.008	0.5	0.002	11.44	0.0025	0.0015	1.4	0.0005	0.005	0.84	4.43	0.064	0.0025	0.0005
TR	AVG LC	12:71:01		0.94	0.005	0.294	0.00005	32.7	0.0025	0.0015	0.008	0.5	0.002	11.42	0.0025	0.0015	1.4	0.0005	0.005	0.85	4.44	0.064	0.0025	0.0005



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