

Montana Bureau of Mines and Geology
Open-File Report 474
May, 2003

**Water-quality monitoring of the Butte Metro Storm Drain
during a storm event: June 26-27, 2002.**

Christopher H. Gammons¹, Chris Shope¹, and Ted Duaime²

Montana Tech of The University of Montana

¹*Dept. of Geological Engineering* ²*Montana Bureau of Mines and Geology*
Butte, MT 59701



Abstract

A detailed hydro-geochemical investigation was undertaken of the Butte Metro Storm Drain (MSD) during the 24-hour period between 6 a.m., June 26 and 6 a.m., June 27, 2002. On the afternoon of June 26, a heavy thunderstorm caused streamflow in the MSD to increase 100-fold, from 0.2 to more than 20 cfs (cubic feet per second). Field and chemical data were continuously collected before, during, and following the storm. These data included streamflow, water temperature, pH, specific conductivity, dissolved oxygen, alkalinity, filtered (0.45 μm) metals, and unfiltered (raw-acidified) metals.

The most significant finding in this study was that concentrations of copper increased during the storm surge, whereas the concentrations of most other elements decreased sharply. The calculated loadings (gram/hour) of both dissolved and particulate copper increased more than 100-fold in the first hour following the storm, and remained elevated over baseline conditions for the remainder of the study. Other metals, such as Zn, Cd, and Mn, showed a decrease in loading from pre-storm to post-storm conditions. The difference in behavior of copper with respect to the other heavy metals suggests the widespread presence of sources of soluble copper in the MSD watershed, or in the Metro Storm Drain itself. It is not possible to determine whether the storm flow became enriched in copper *before* or *after* it entered the storm drain. In addition to the large flush of copper, loadings of soluble P (most likely as orthophosphate) increased during the storm, whereas dissolved oxygen dropped to very low levels ($< 2 \text{ mg/L}$).

Geochemical modeling indicates that the pre-storm MSD waters were close to saturation with the minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), rhodochrosite (MnCO_3), otavite (CdCO_3), and hydrous Zn carbonate ($\text{ZnCO}_3 \cdot \text{H}_2\text{O}$), but were strongly

undersaturated with all Cu-bearing minerals. Unlike many polluted streams draining abandoned mine lands in Montana, the MSD waters showed no evidence of diel (24-hour) cycling of heavy metals in the 10-hour period prior to the thunderstorm.

Table of Contents

Abstract.....	i
Abbreviations and acronyms.....	iv
1. Introduction.....	1
1.1 Site background and previous investigations.....	2
2. Methods.....	5
3. Results.....	7
3.1 Field parameters.....	9
3.1.1 Streamflow.....	9
3.1.2 Temperature.....	10
3.1.3 pH.....	11
3.1.4 Specific Conductivity.....	11
3.1.5 Dissolved oxygen.....	12
3.1.6 Alkalinity.....	13
3.2 Major elements.....	13
3.3 Trace metals.....	14
3.3.1 Cu.....	14
3.3.2 Zn, Mn, Cd.....	15
3.3.3 Fe.....	17
3.3.4 Other elements.....	19
4. Discussion.....	20
4.1 Composition of storm flow.....	20
4.2 Metal loadings.	21
4.3 Geochemical modeling.....	23
4.4 Diel (24-hour) changes in water quality.....	25
5. Conclusions.....	27
6. Acknowledgements.....	28
7. References cited.....	29

Tables

1. Summary of QA/QC for ICP analyses.....	8
2. Calculated composition of storm water end-member	21
3. Saturation indices for selected minerals in pre-storm MSD water.....	25

Figures

1. Location map of the Butte Metro Storm Drain.....	3
2. Streamflow in the Metro Storm Drain from June 25 to June 28, 2002.....	10
3. Temperature and pH record from the Hydrolab.....	12
4. Specific conductivity (SC) and dissolved oxygen record from the Hydrolab.....	12
5. Results for major elements.....	14
6. Filtered and total copper vs. time.....	16
7. Filtered and total zinc vs. time.....	16
8. Filtered and total manganese vs. time.....	17
9. Filtered and total cadmium vs. time.....	17
10. Filtered and total iron vs. time.....	19
11. Changes in total loadings of Zn and Cu during the storm event.....	22

Appendices

A1. Streamflow data	32
A2. Hydrolab data	34
A3. Field measurements and observations.....	37
A4. ICP results.....	38

Abbreviations and acronyms used in this report

ARCO = The Atlantic Richfield Company (now owned by British Petroleum)
 DO = dissolved oxygen
 EPA = United States Environmental Protection Agency
 HDPE = high density poly-ethylene
 ICP-AES = inductively coupled plasma, argon emission spectroscopy
 MBMG = Montana Bureau of Mines and Geology
 MSD = Butte Metro Storm Drain
 PQL = practical quantification limit
 QA = quality assurance
 QC = quality control
 SC = specific conductivity
 SI = saturation index
 USGS = United States Geological Survey
 T = temperature

Units used in this study

$^{\circ}\text{C}$ = temperature in centigrade (celcius)¹
 cfs = streamflow, in cubic feet per second (ft^3/s)
 g = gram
 kg = kilogram
 mg = milligram
 mg/L = milligram per liter
 ppm = parts per million (equivalent to mg/L)
 μm = micrometer ($\text{m} \times 10^{-6}$)
 $\mu\text{g/L}$ = microgram per liter
 $\mu\text{S/cm}$ = micro-Siemens per centimeter

¹ Temperature in $^{\circ}\text{F} = 9/5\text{T}(^{\circ}\text{C}) + 32$

² Streamflow in cubic meters per second = $\text{cfs} \times 0.028317$

1. INTRODUCTION

The Butte Metro Storm Drain (MSD) is a man-made diversion ditch that collects ground water and urban runoff, draining a portion of Butte Hill in the extreme southeast corner of the Butte Summit Valley. The MSD runs more or less along the course of ancestral Silver Bow Creek. However, the entire drainage area has been disturbed by mining and urban development, with soil beneath and adjacent to the ditch consisting mainly of a combination of fill and buried tailings (Duaine and others, 1995). The MSD joins the much larger Blacktail Creek just upstream of Montana Street; below this point, the combined flow is referred to as Silver Bow Creek. At the time of this writing, MSD water flows directly into Silver Bow Creek with no treatment. The MSD is contaminated with heavy metals (Duaine and others, 1995), and therefore represents a significant source of metal loading into the upper Silver Bow Creek watershed.

As part of a larger investigation of diel (24-hour) changes in water chemistry in a number of Montana streams, a detailed monitoring study was undertaken of the MSD on June 26-27, 2002. A number of water-quality parameters were continuously monitored, including: streamflow, temperature, pH, specific conductivity (SC), dissolved oxygen (DO), alkalinity, filtered (0.45 μm) metals, and unfiltered (raw-acidified) metals. On the afternoon of June 26, a surprise thunderstorm brought more than an hour of hail and heavy rain, and increased the flow of the MSD from roughly 0.2 to greater than 20 cfs (cubic feet per second) in less than 15 minutes. Although this was quite problematic for the diel investigation, the fact that monitoring equipment was in place prior to, during, and after the thunderstorm afforded an opportunity to evaluate the chemistry of MSD waters during a storm event.

This Open-File Report summarizes the data collected during the 24-hour investigation. A discussion of changes in metal loading during the storm is followed by sections on diel behavior and geochemical modeling.

1.1. Site Background and Previous Investigations

The Metro Storm Drain (MSD) extends from the corner of Continental Drive and Texas Avenue on the northeast, to its confluence with Blacktail Creek, near the corner of Montana and George Streets (Fig. 1). It is a portion of the historic Silver Bow Creek that lies just below most of the underground and open-pit mining on Butte Hill. The term “Metro Storm Drain” was coined by investigators involved with the mid-1980's Silver Bow Creek Superfund Remedial Investigation, to more accurately convey the unnatural condition of this portion of the Silver Bow Creek watershed. Most recent investigators consider Silver Bow Creek proper to start at the confluence of Blacktail Creek and the Metro Storm Drain, near Montana Street.

The MSD has received waste water from mining operations – for example, mine dewatering, precipitation plant effluent, and historic mill and smelter discharges – that was very acidic and had high concentrations of heavy metals, including iron, aluminum, copper, and zinc (Spindler, 1977). The original stream bed has been straightened and lined with rip-rap. While mining operations in the 1960's intercepted water from the headwaters of Silver Bow Creek, other water was captured and routed around the mining operations in what the Anaconda Company called the “Clear Water Ditch.” This water – along with the treated water from the Weed Concentrator – was discharged into the MSD channel at Texas Avenue. According to Anaconda Company and Montana Bureau of

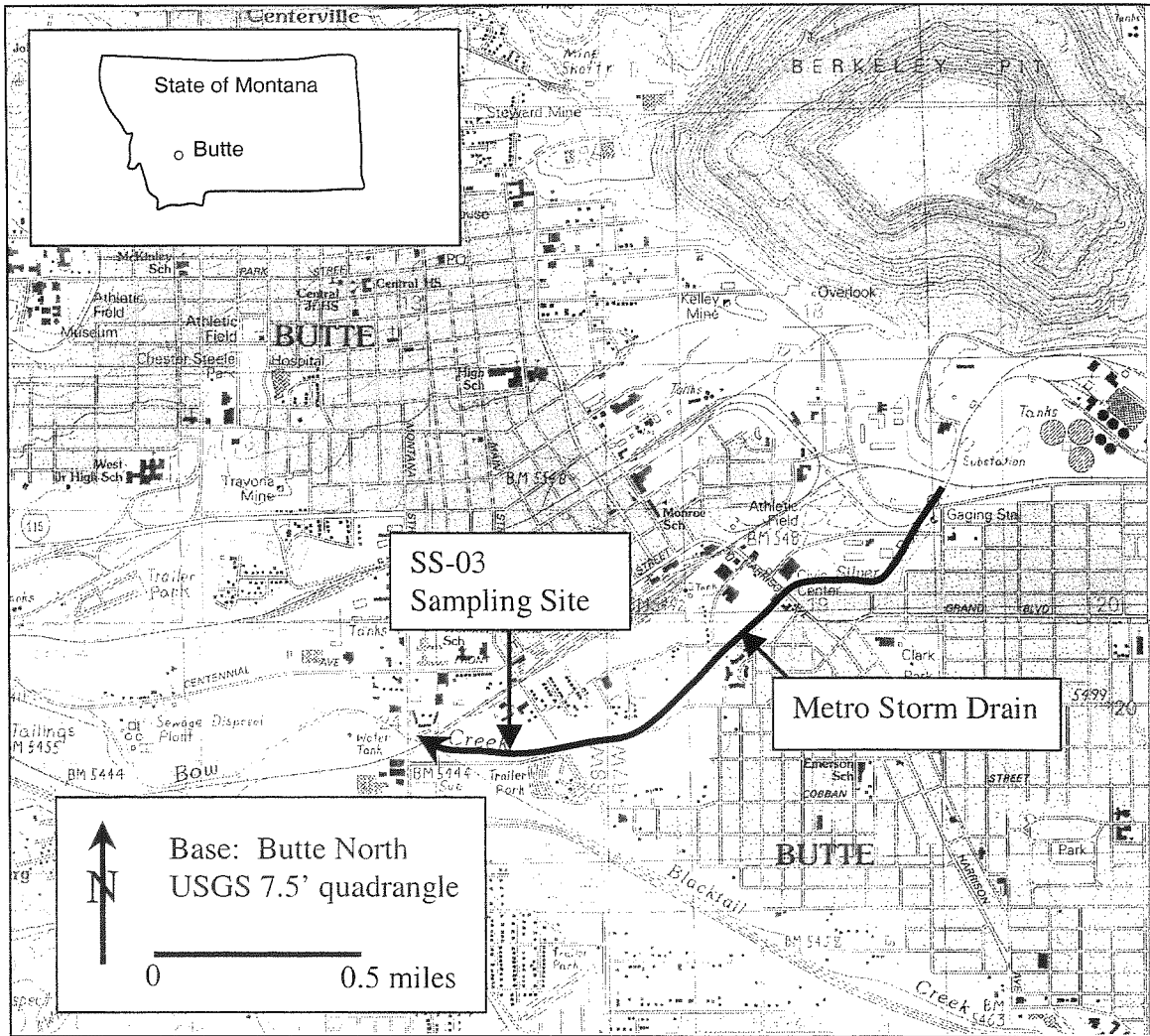


Figure 1. Location of the Butte Metro Storm Drain.

Mines and Geology (MBMG) records, historic flow rates were in the range of 14-30 cubic feet per second (cfs) during this time. Shortly after Anaconda's 1982 decision to flood the underground mines and suspend mining in the Berkeley Pit, the company went to a zero-discharge policy. Instead of releasing water to Silver Bow Creek, water from the concentrator was pumped to the Yankee Doodle Tailings Dam for reuse as make-up water in the concentrator. This had two major consequences: 1) it reduced the amount of

fresh make-up water brought in through the Silver Lake pipeline; and 2) it dramatically reduced the flow of water in the MSD and Silver Bow Creek. The Anaconda Company suspended all its mining operations in July 1983 and as a result diverted water from the "Clear Water Ditch" into the Berkeley Pit. Since that time, the only flow of water in the MSD has come from ground-water discharge, storm-water runoff, and storm-sewer discharge. Despite the fact that discharges of water from the mining operations have ceased, the quality of water in the Metro Storm Drain remains poor.

The major flow of water in the MSD occurs during precipitation and snowmelt events. Along with the increase in flows is an increase in both dissolved and total recoverable metals, e.g., iron, copper, zinc, and arsenic (MBMG unpublished data; CH2M Hill and Chen-Northern, 1990). CH2M Hill and Chen-Northern's work documented increased metal concentrations during a March snowmelt event. Flows ranged from 1 cfs to 20 cfs, while dissolved copper, zinc and arsenic concentrations ranged from 400 $\mu\text{g/L}$ to 6200 $\mu\text{g/L}$; 1300 $\mu\text{g/L}$ to 12,000 $\mu\text{g/L}$; and 1 $\mu\text{g/L}$ to 5 $\mu\text{g/L}$, respectively. Total recoverable concentrations were considerably higher in most samples, with the exception of zinc. Similarly, Duaime and Appleman (1990) documented increased metal concentrations in Silver Bow Creek just below the confluence of the MSD and Blacktail Creek during spring and summer rainfall events.

In the 12 years since the last monitoring studies of the MSD were conducted, considerable reclamation has occurred on Butte Hill, including backfilling and capping of the Alice Open Pit, and installation of a storm water collection system. Concurrently, the State of Montana has begun reclamation of the upper reaches of Silver Bow Creek. Results of the present study therefore provide an up-to-date assessment of metal loading

and water quality of the MSD, which may be useful to agencies overseeing the overall reclamation process.

2. METHODS

The 24-hour diel study began at 6:30 a.m. on June 26 2002, and ended at 5:30 a.m. of the following day. All field data were collected on the MSD at the SS-03 monitoring station, downstream from Kaw Avenue, and directly across from the Butte Visitor's Center. A Hydrolab Datasonde 3 multimeter was used to continuously monitor changes in water temperature (T), pH, dissolved oxygen (DO), and specific conductivity (SC). The Hydrolab was set up to record data for a 2-day period at half-hour intervals. Manual measurements of T, pH, DO and SC were taken periodically during the diel investigation. This provided an independent quality-control check on the accuracy of the Hydrolab measurements. A hand-held Orion 1230 multimeter was used with T-compensated pH, SC, and DO electrodes. Field pH was calibrated using pH 7 and pH 4 buffers. The DO electrode was calibrated to air saturation at 100% humidity immediately before each field measurement. This unit automatically adjusts for changes in barometric pressure corresponding to changes in elevation or weather. In addition, alkalinity was determined 3 times during the 24-hour study. Filtered (0.45 μ m) samples were titrated to a pH 4.5 endpoint, using a HACH digital titrator and 0.16N H₂SO₄ solution.

Streamflow measurements at SS-03 for the period of interest were provided by Trec Corporation (Bozeman, MT), with permission from ARCO. ARCO maintains the SS-03 station to closely monitor streamflow in the MSD, and records data at 15-minute intervals. In addition to collection of the remote data, manual streamflow measurements

were performed below the SS-03 station at 7:15 a.m. (June 26), 6:00 p.m. (June 26), and 6:30 a.m. (June 27). These times corresponded to pre-storm baseflow, post-storm high flow, and post-storm baseflow periods, respectively. Manual measurements were performed using a Marsh-McBirney Flo-Mate velocity meter, a top-setting wading rod, and a measuring tape. At least 10 velocity measurements were made across the stream.

Water samples were collected using an ISCO automatic sampler, set up to collect 500mL of raw sample on the hour (beginning at 6:30 a.m., June 26), from the same location in the creek. A 25-foot vinyl sampling tube was completely flushed with creek water before collection of each sample into acid-washed ISCO bottles. Each sample was filtered in the field into 60 mL, acid-washed HDPE bottles, using a syringe and a 0.45 μm cellulose-acetate syringe filter. The initial 10 to 15 mL of water passed through each filter was used to rinse the sample bottle, and was then discarded. Raw (unfiltered) samples were also collected every other hour. For the raw samples, the ISCO bottles were capped and shaken to re-suspend particles in the water immediately before filling a 60 mL sample bottle. All of the water samples were transported back to the laboratory on ice, and were acidified in a fume hood to a matrix of 1% HNO_3 (Trace Metal grade). The samples were stored in the refrigerator for 2 months, and were then analyzed by ICP-ES at the Murdock Environmental Laboratory, Univ. of Montana, using a Thermo Jarrel Ash IRIS Inductively Coupled Plasma Emission Spectrophotometer. No specific digestion procedure was used for the raw (non-filtered) water samples, other than addition of 1% HNO_3 , and the 2-month holding time. To prevent clogging of the tubing and nebulizer, the raw-acidified samples were filtered before ICP analysis. The following elements were quantified, using EPA Method 200.7: Al, As, B, Ba, Be, Ca, Cd,

Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, and Zn. Of these, As, Be, Cr, Hg, Pb, Sb, Se, Sn, Ti, Tl, and V were below their respective Practical Quantification Limits (PQLs) for all MSD water samples.

Strict QA/QC procedures were followed during the ICP analyses, as required by EPA Method 200.7. Laboratory duplicate, laboratory spike, Instrument Performance Calibration (IPC), and laboratory blanks were run every 10 samples. A summary of QA/QC results relevant to this study is given in Table 1. The elements B, Mg, Na, P, S, and Sr had at least one QA/QC violation during the analytical session, which was either a high blank, a low spike recovery, or an IPC sample that exceeded 10% deviation from the true value. All other analytes passed all QA/QC checks. Field blanks (filtered and non-filtered) were below the PQL for most analytes, with the exception of B, Ba, Na, Si, and Zn. Of these, the only element of potential concern to this study is Zn. However, the field blanks had concentrations of Zn that were still less than 10% of the lowest concentration of Zn measured in any of the MSD water samples, and less than 1% of most of the samples.

3. RESULTS

Results for field parameters and chemical analysis of water samples are summarized in the Appendices. Selected data are discussed in more detail as follows.

Table 1: Summary of QA/QC for ICP analyses.

Element	Al	B	Ba	Ca	Cd	Co	Cu	Fe	K	Li
PQL	0.04	0.01	0.003	0.2	0.005	0.005	0.03	0.08	0.40	0.005
LDR	1000	100	50	2000	100	100	500	1500	100	30
IPC %	1.3%	1.4%	1.2%	2.3%	2.6%	5.0%	3.7%	0.9%	2.1%	8.0%
% LBLANK	100%	50%	100%	100%	100%	100%	100%	100%	100%	100%
FBANK (raw)	< 0.04	0.04	0.012	0.23	< 0.0050	< 0.0050	< 0.3	< 0.800	< 40	< 0.0050
FBANK (filt)	< 0.04	0.04	0.018	< 0.2	< 0.0050	< 0.0050	< 0.3	< 0.800	< 40	< 0.0050
RSD of LDUP	1.5%	2.5%	1.2%	1.5%	3.8%	3.8%	5.6%	2.5%	2.5%	2.4%
% spike recov.	101%	77.4%	99.0%	96.9%	97.8%	78.6%	97.2%	94.5%	98.8%	93.6%
% QC viol.	0%	50%	0%	0%	0%	0%	0%	0%	0%	0%
Element	Mg	Mn	Mo	Na	Ni	P	S	Si	Sr	Zn
PQL	0.40	0.04	0.01	0.1	0.01	0.05	0.5	0.02	0.01	0.008
LDR	2000	400	100	50	100	250	1000	100	25	50
IPC %	3.9%	9.8%	1.8%	2.0%	4.7%	6.8%	21.9%	2.3%	4.7%	1.6%
% LBLANK	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
FBANK (raw)	< 4000	< 0.400	< 0.100	0.74	< 0.100	< 0.500	< 0.5	0.061	< 0.100	0.026
FBANK (filt)	< 4000	< 0.400	< 0.100	0.72	< 0.100	< 0.500	< 0.5	0.046	< 0.100	0.032
RSD of LDUP	1.6%	0.8%	3.3%	1.8%	2.7%	7.1%	1.5%	1.1%	1.6%	1.0%
% spike recov.	94.1%	96.0%	103.4%	-30.9%	94.0%	102.2%		81.5%	72.4%	95.0%
% QC viol.	50%	0%	0%	75%	0%	25%	100%	0%	50%	0%

EXPLANATION

PQL = practical quantification limit, mg/L; LDR = linear detection range (upper limit), mg/L

IPC % = average deviation (%) of Internal Performance Calibration samples from true values (should be less than 10%)

% LBLANK = % of laboratory blanks with concentration below the PQL

FBANK (raw) = concentration (ppm) of raw (unfiltered) field blank

FBANK (filt) = concentration (ppm) of filtered field blank

RSD of LDUP = average rsd (rsd = standard deviation/mean) of laboratory duplicates

% spike recov. = average % spike recovery for all spiked samples (should be within 30% of 100%)

% QC viol. = total % of samples with QC violations

3.1 Field parameters

3.1.1 *Streamflow*

The results of streamflow measurements recorded by ARCO at the SS-03 station for the 72-hour period from June 25 to 27 are given in Fig. 2. The raw data are in Appendix 1. Weather was stable prior to the storm of June 26, with baseflow in the MSD varying slightly, between 0.18 and 0.20 cubic feet per second (cfs). Shortly before 3:30 p.m. on June 26, hail began to fall at the site, turning to heavy rain by 3:45. A surge of storm water swept down the MSD sometime between 4:30 and 4:45, increasing flows 100-fold, from 0.2 to 20 cfs. The increase in flow was extremely rapid, attaining peak discharge in less than 15 minutes. Following this sharp peak, flow decreased more gradually, returning to near-baseflow conditions of 0.23 cfs within 12 hours.

Also shown in Fig. 2 are manual streamflow measurements collected near SS-03, using a Marsh-McBirney flow meter, a wading rod, and measuring tape. Whereas the manual and remote data agreed well during the high-flow period, the manual estimates were significantly lower during the low-flow periods, both before and after the storm. The estimated uncertainty in the manual flow measurements is $\pm 20\%$, which is contained within the size of the symbols in Fig. 2. These results suggest that either the ARCO gage was not calibrated properly for the period in question, or the measurements contain an unknown systematic error (such as meter malfunction). It is worth pointing out that the current velocities were quite low before and after the storm event, averaging less than 0.1 ft/second. At such low velocities, accurate stream gaging is difficult.

3.1.2 Temperature

Changes in water temperature and pH recorded by the Hydrolab are given in Fig.

3. Manual water temperature readings are also shown, and are in close agreement. The morning and early afternoon of June 26, 2002 were sunny. Consequently, water temperatures warmed from an early morning low of 13.9°C, to a mid-afternoon high of 21.4°C, for a 7.5°C difference. Despite the fact that much of the storm precipitation fell as hail, the storm surge between 4:00 p.m. and 4:30 p.m. did not significantly drop water temperatures. Perhaps overland flow was warmed by the ground before reaching the MSD.

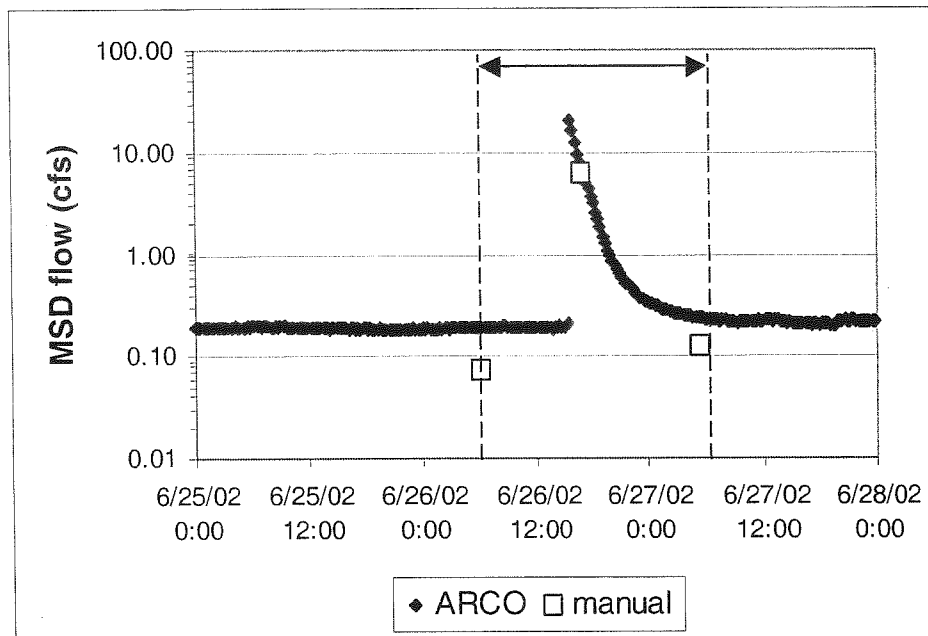


Figure 2. Streamflow in the Metro Storm Drain from June 25 to June 28, 2002. The period of the 24-hour investigation is shown by the arrow. Manual flow measurements are shown by open squares. Uncertainty in the manual measurements falls within the height of the data symbols.

3.1.3 *pH*

In the 24 hours prior to the storm, pH was relatively stable, varying less than 0.2 log units, between 6.6 and 6.8 (Fig. 3). The storm surge raised pH to a high of 7.4, after which it slowly declined back to 6.8. The lack of any acidic inflow associated with the storm surge is notable. It should also be realized that the rise in pH cannot be attributed to dilution by rain water, since unpolluted rain is naturally slightly acidic (pH 5.7). There appears to be a weak diel pattern of slightly higher pH at night, and lower during the day. This pattern is the opposite of what is typically observed in healthy Montana creeks, in which day-time photosynthesis raises pH, followed by a drop in pH during the night (Gammons and others, 2001). Manual pH measurements agreed within 0.3 log units with the Hydrolab data, but were somewhat scattered compared to the continuous data, and were therefore omitted from Fig. 3.

3.1.4 *SC*

Changes in specific conductivity (SC) and dissolved oxygen (DO) recorded by the Hydrolab are given in Fig. 4. Before the storm of June 26, the SC of the MSD was roughly 1600 $\mu\text{S}/\text{cm}$. Dilution with storm water quickly lowered SC to 150 $\mu\text{S}/\text{cm}$, after which it slowly climbed back above 700 $\mu\text{S}/\text{cm}$. These results are consistent with the observation that the concentration of most dissolved solutes in post-storm MSD water never returned to their pre-storm values during the monitoring period (see section 3.2), despite the fact that streamflow dropped to near-baseline conditions. Manual SC measurements showed very similar trends, but were displaced to SC values that were about 20% higher than those of the Hydrolab. Manual SC data are not plotted here, but are given in Appendix 3.

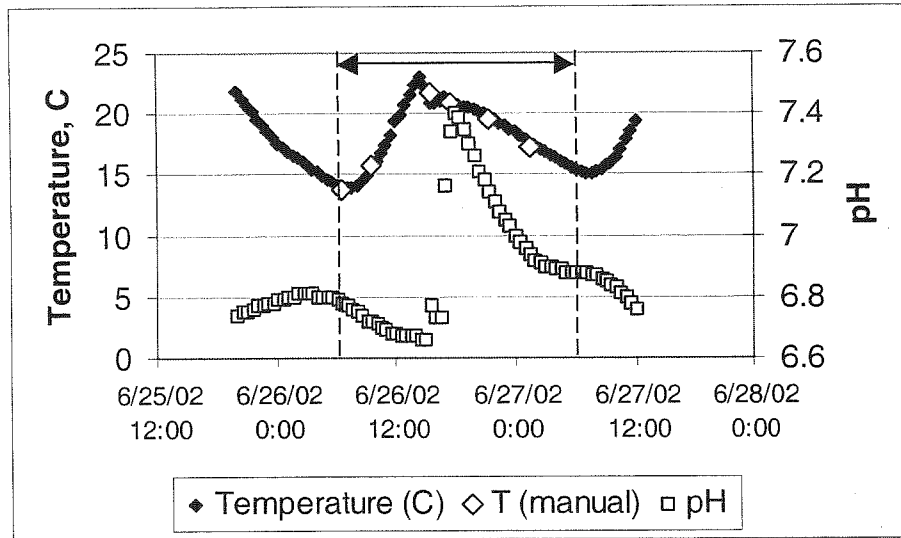


Figure 3. Temperature and pH record from the Hydrolab. The period of the diel investigation is shown by the arrow. Manual temperature readings are given by the open diamonds.

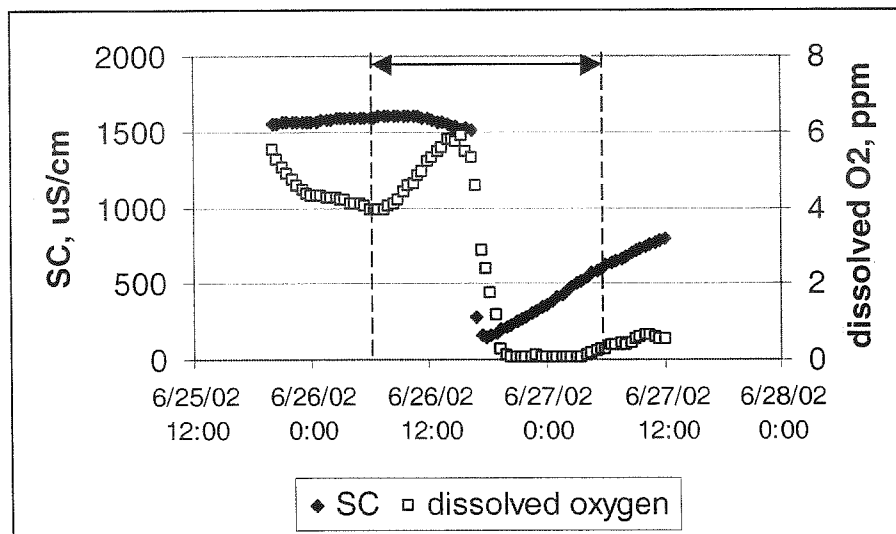


Figure 4. Specific conductivity (SC) and dissolved oxygen record from the Hydrolab. The period of the diel investigation is shown by the arrow.

3.1.5 Dissolved oxygen.

Results for DO (Fig. 4) showed a dramatic drop in this parameter associated with the storm surge. Pre-storm DO levels were between 4 and 6 ppm O_2 . After the storm, DO dropped to less than 1 ppm, and remained low for the rest of the monitoring period.

There is a possible problem with the Hydrolab DO readings, in that the electrode was partly clogged with silt and vegetation left over from the storm surge. However, manual DO measurements (Appendix 3) also indicated a drop in DO, to values between 1 and 2 ppm. The drop in DO must reflect a flushing of water with high biological or chemical oxygen demand into the MSD. It is somewhat surprising that DO levels did not rebound faster than observed. As discussed below, the drop in DO also coincided with an increase in filtered Fe concentration. It is not known to what extent these two observations are related.

3.1.6 *Alkalinity*

The alkalinity of MSD water was measured in the field at 6:40 a.m. of June 26, 5:30 p.m. of June 26, and 6:00 a.m. of June 27. The results were 144, 58, and 76 ppm CaCO_3/L , respectively. The rather high alkalinity of baseflow to the MSD is consistent with its near-neutral pH, and is mainly due to the presence of HCO_3^- ion.

3.2 Major elements

Results for selected major elements (Ca, K, Mg, Na, SO_4) are given in Fig. 5. As expected, all of the major ions showed a sharp decrease in concentration corresponding to the sudden increase in flow down the MSD. There were subtle differences in the way each element behaved during the decrease in flow back to baseline conditions. Concentrations of Mg^{2+} and SO_4^{2-} increased faster than the other ions (Ca^{2+} , K^+ , Na^+). However, none of the elements rebounded to their pre-storm concentrations, despite the fact that streamflow returned to near-baseline conditions.

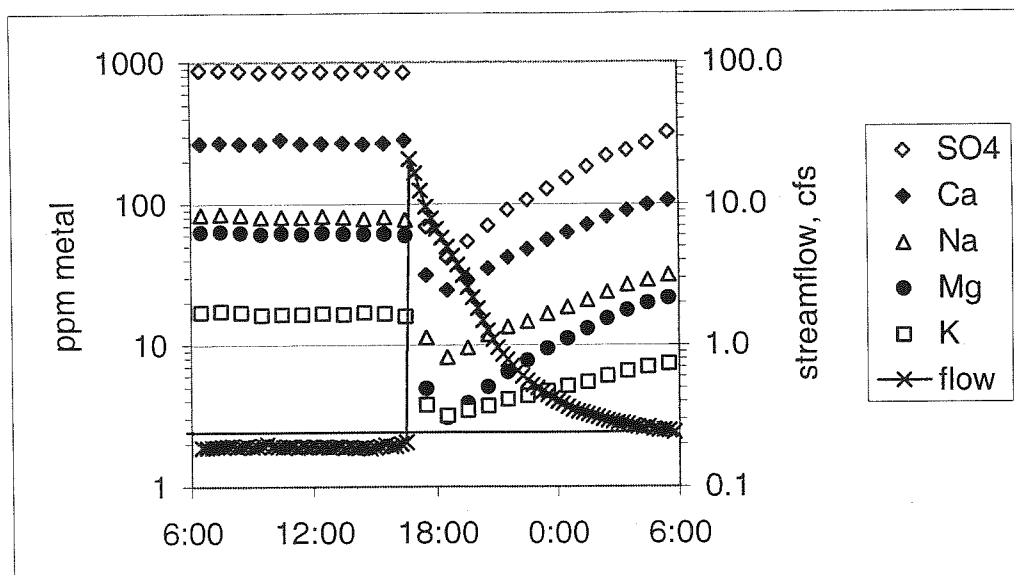


Figure 5. Results for major elements.

3.3 Trace elements

3.3.1 Copper

Graphs showing changes in filtered (0.45 μm) and total (raw-acidified) Cu with time are given in Fig. 6. Average dissolved and total Cu concentrations for the 10 hours prior to the storm were 0.49 and 0.94 ppm, respectively, indicating that roughly 50% of the total Cu was present in particulate (filterable to 0.45 μm) form. It is possible that some or most of this particulate Cu was adsorbed onto hydrous oxides of iron or aluminum. Unlike most analytes, the concentration of Cu *increased* (dissolved Cu doubled, total Cu tripled) upon arrival of the storm surge, and continued to remain elevated over baseline conditions for the remainder of the study period. The fact that Cu levels increased despite a 100-fold increase in flow means that Cu concentrations in the storm runoff had to be higher than in the MSD baseflow itself. This is discussed in more detail in Sections 4.1 and 4.2 of this report.

3.3.2 Zinc, Cadmium, Manganese

Graphs showing changes in filtered (0.45 μm) and total (raw-acidified) Zn, Mn, and Cd with time are given in Figures 7, 8 and 9. These three elements are discussed together, because they show very similar trends. Prior to the storm event, the concentrations of Zn, Cd, and Mn were 9.54, 0.025, and 9.89 ppm, respectively. Close agreement between filtered and raw samples indicates that each metal was mainly present in non-particulate (dissolved) form. During the thunderstorm, concentrations of Zn and Mn fell rapidly to a minimum 1 hour after the initial storm surge, and then rose slowly over the remainder of the monitoring period. The concentrations of Cd fell below the method detection limit of the ICP (5 ppb) for a period of 10 hours. During peak flow, a significant amount of Zn and Mn was present in particulate form (up to 50% of total Zn, up to 30% of total Mn). However, within 6 hours, particle abundances for both metals diminished to levels below detection.

If one compares the graphs for Cu and Zn, one sees major differences in the hydro-geochemical behavior of the two heavy metals. Whereas the storm runoff diluted the concentrations of Zn (and Mn, Cd), the concentration of Cu increased. This is discussed in greater detail in Sections 4.1 and 4.2.

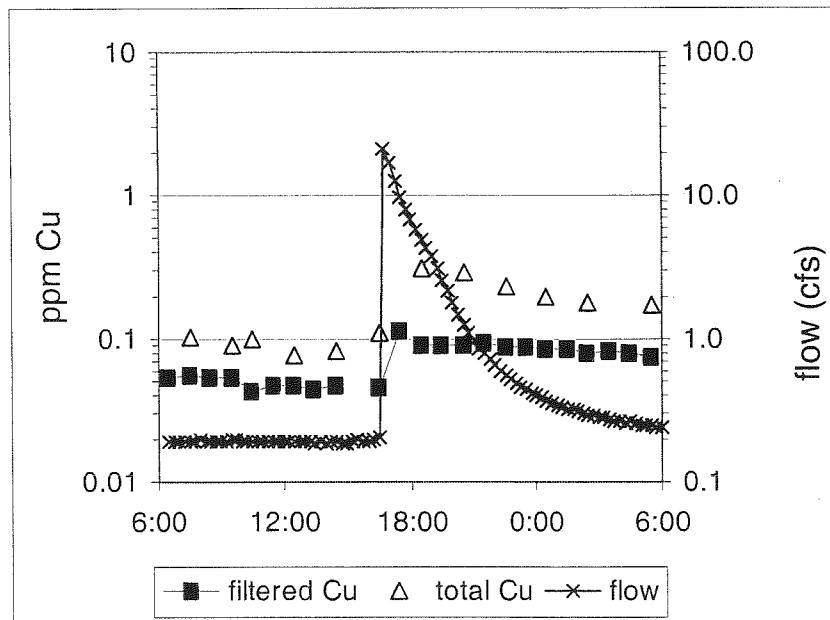


Figure 6. Filtered and total copper vs. time.

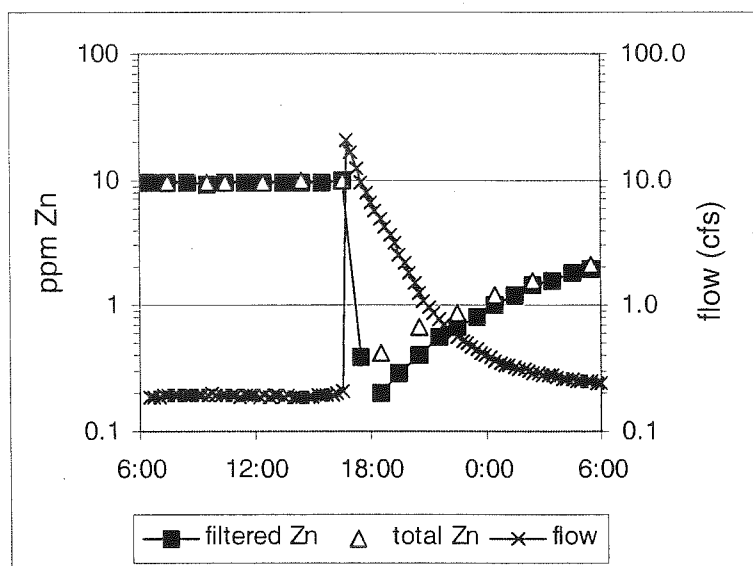


Figure 7. Filtered and total zinc vs. time.

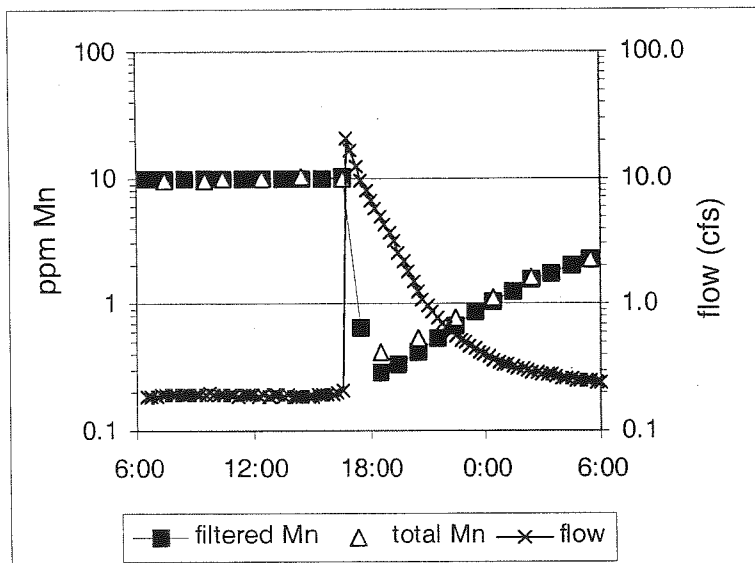


Figure 8. Filtered and total manganese vs. time.

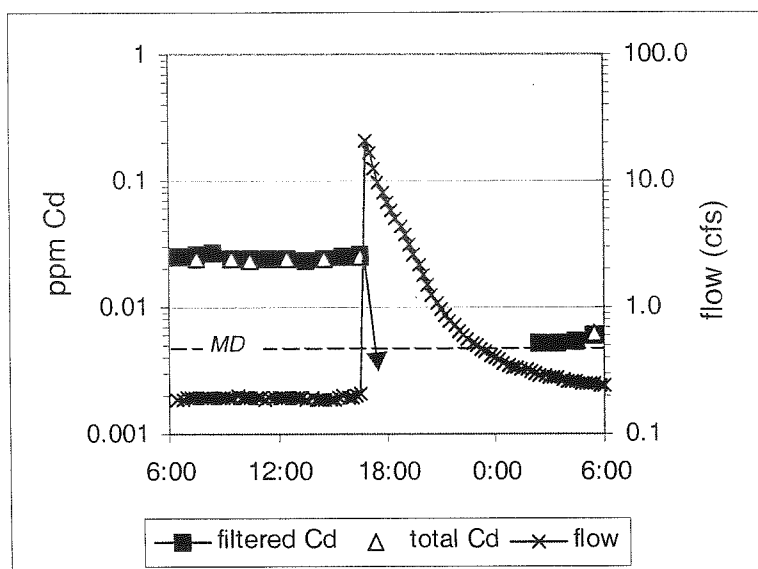


Figure 9. Filtered and total cadmium vs. time.

3.3.3. Iron

Changes in filtered ($0.45 \mu\text{m}$) and total (raw-acidified) Fe with time are given in Figure 10. Prior to the storm event, there was no detectable Fe in the filtered fraction (PQL = 0.08 ppm), and 1 to 3 ppm in the total (particulate) fraction. Iron concentrations

did not change much during the peak storm flow period. Given the neutral pH and aerobic nature of the MSD, it is likely that most of this particulate iron was present as ferric hydroxide, also known as ferrihydrite, or hydrous ferric oxide (HFO). This is the substance that is responsible for the turbid, reddish-brown color of the MSD water (see cover photograph). After the initial storm surge subsided, concentrations of dissolved Fe increased to detectable levels, reaching a peak of 0.3 ppm at the end of the monitoring period. Un-complexed Fe^{3+} is insoluble at the pH's of the MSD waters (Drever, 1997; Langmuir, 1997). The rise in filtered Fe concentration is attributed to one or more of the following: 1) an influx of more soluble Fe^{2+} ; 2) an influx of organically-complexed Fe^{3+} ; or 3) an influx of colloidal Fe particles that had diameters sufficiently small to pass through the 0.45 μm filters. The former hypothesis is consistent with the observation that dissolved oxygen was extremely low during the period when filtered Fe concentrations increased. The second hypothesis is plausible, as dissolved organic acids (e.g., acetate, oxalate, or more complex humic or fulvic acids) can increase the solubility of otherwise insoluble Fe^{3+} and Al^{3+} by forming strong chelate complexes (Drever, 1997). It would not be surprising to find elevated dissolved organic carbon in urban runoff, given a multitude of possible sources (e.g., oil, gasoline, garbage, chemical spills). The last hypothesis is the simplest explanation, although it is somewhat difficult to reconcile an increase in colloidal Fe with a decrease in streamflow. For future reference, all of these hypotheses are testable: 1) Fe^{2+} concentrations can be directly measured using a portable spectrophotometer; 2) dissolved organic carbon could be monitored to test for an influx of organic acids; and 3) the presence of colloidal Fe particles could be tested by using a range in filter diameters (e.g., 0.45 μm , 0.2 μm , 0.1 μm , 0.02 μm).

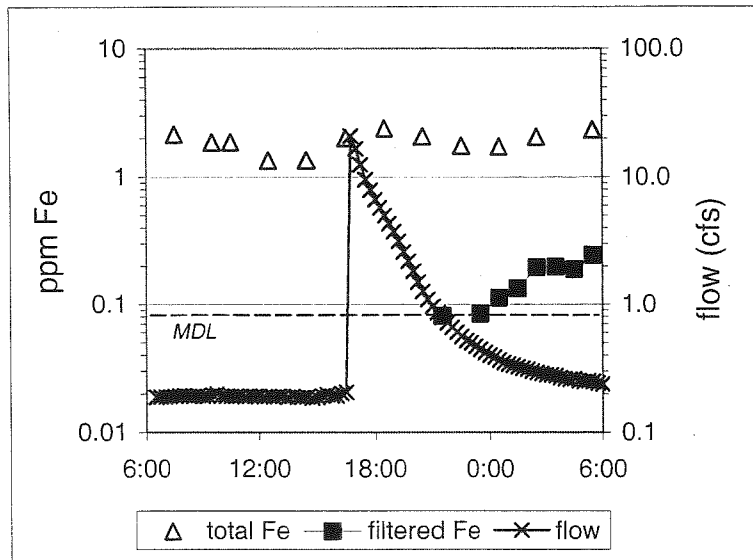


Figure 10. Filtered and total iron vs. time.

3.3.3 Other elements.

Prior to the storm event, aluminum was only detectable in the particulate fraction, presumably as suspended clays, or as hydrous Al oxide (HAO). After the storm, filtered Al values rose to detectable levels, in a manner similar to filtered Fe. The rise in filtered Al may be due to the presence of organically-complexed Al^{3+} , or colloidal (less than 0.45 μm) particles (see preceding section).

Before the storm, phosphorous was mainly present in dissolved form, presumably as orthophosphate (H_2PO_4^- and HPO_4^{2-}). After the storm, a significant particulate fraction was present. Phosphorous is known to co-precipitate with HFO in mine waters, possibly as an Fe-phosphate compound (strengite) (Tate and others, 1995). However, it is also possible that the particulate form of P is some sort of fine-grained organic substance, such as pollen, algae, bacteria, or urban waste, washed into the creek by the storm. Based on this study, the baseline concentration of phosphorous in the MSD was rather high (0.1

ppm as P, 0.4 ppm as PO₄), and could be a significant source of nutrient loading for upper Silver Bow Creek.

The elements Li, Ni, and Sr were dominantly in the dissolved phase, and showed similar dilution trends to Zn, Mn and Cd during the storm event.

Concentrations of dissolved and total As and Pb were below the method detection limits of the ICP for most of the samples collected in this study. Therefore, trends for these metals cannot be evaluated.

4. DISCUSSION

4.1 Composition of storm flow

Because the flow in the MSD increased by a factor of 100 during the thunderstorm of June 26, the water composition at peak flow should have been dominated by runoff (storm flow) entering the MSD. A more quantitative estimate of the concentration of each element in the storm flow can be derived mathematically, from re-arrangement of the following mass balance equation:

$$Q_b \cdot C_b + Q_s \cdot C_s = Q_T \cdot C_T$$

where Q is flow (cfs), C is concentration (ppm), and the subscripts b, s, and T stand for baseflow, storm flow, and total flow, respectively. Q_b and Q_T are simply the flows measured before and immediately after the storm, respectively, and Q_s is the difference in these values. C_b and C_T are also known, making it possible to solve for C_s , the

concentration of each analyte in the storm flow. Following this model, the composition (filtered ppm) of the storm flow based on the peak discharge period is given in Table 2.

Table 2. Calculated composition of the storm water end-member.

	SC	Ca	Cu	K	Mg	Mn	Na	P	SO ₄	Si	Zn
Storm flow	129	27	0.12	3.5	3.8	0.47	9.9	0.09	53	2.6	0.20
% of baseflow	8.4%	10%	250%	21%	6.1%	4.7%	12%	120%	6.1%	24%	2.1%

All data in ppm, except SC ($\mu\text{S}/\text{cm}$).

The most significant thing to note from Table 2 is the fact that the end-member storm water had a significantly higher filtered Cu concentration than the MSD baseflow itself (Cu in the storm water was 250% of the baseflow concentration). In contrast, the storm waters had a much lower concentration of Zn (only 2% of baseflow levels). With the exception of phosphorous, all of the other analytes were also much more diluted in the storm flow compared to MSD baseflow.

There are two possible explanations for the elevated Cu concentration of storm water during the thunderstorm of June 26, 2002: 1) runoff from the heavy precipitation event leached Cu from unknown sources upgradient of the MSD, and attained its elevated Cu concentration before it entered the drain itself; or 2) storm runoff entering the drain had relatively low Cu concentrations, but the Cu levels rapidly rose after it entered the MSD. With the data in hand, it is not possible to discriminate between these two hypotheses. In both cases, it is somewhat difficult to explain the fact that concentrations of Cu in the storm flow were so high relative to other metals of concern (e.g., Zn, Mn).

4.2 Metal loadings

Chemical analyses were combined with flow measurements to calculate the total hourly loading of Cu and Zn for the monitoring period. The results are summarized in Fig. 11.

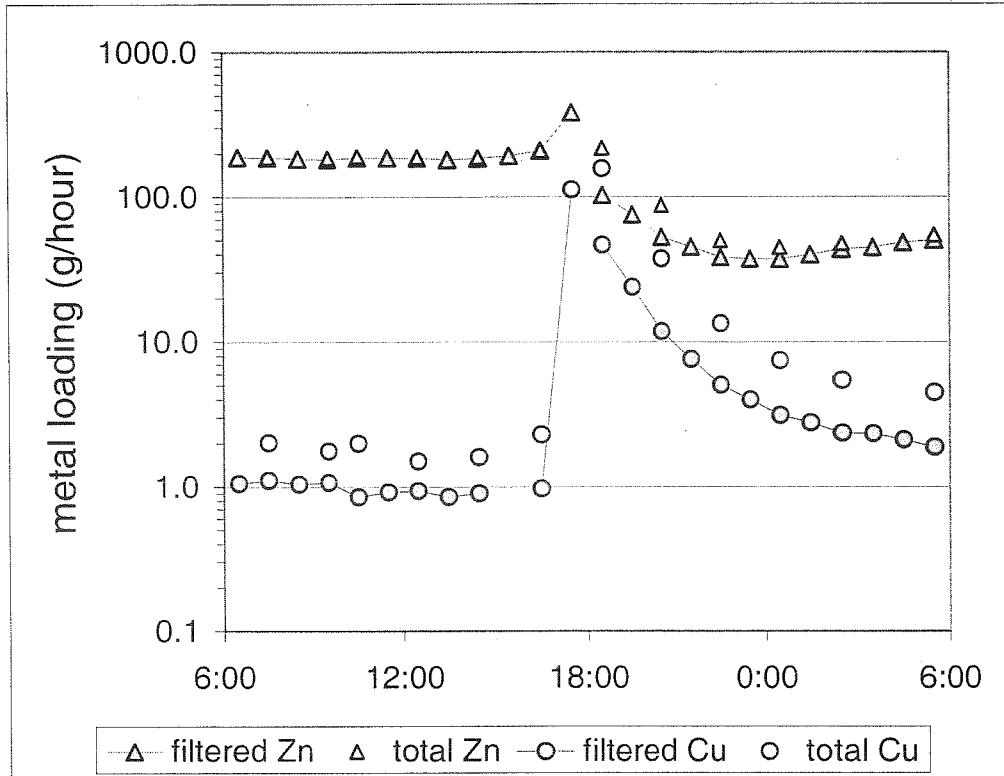


Figure 11. Changes in total loadings of Zn and Cu during the storm event.

During pre-storm baseflow conditions, the loadings of filtered and total Zn were similar, at roughly 200 g/hour (roughly 5 kg/day). Immediately after the storm surge, Zn loadings increased slightly for 1 hour, but then *decreased* over the rest of the monitoring period. This decrease in Zn loading cannot be explained by dilution (since dilution by itself does not affect loading). Also, it would be incorrect to jump to the conclusion that the storm “flushed” Zn out of the system, since there was not a significant increase in Zn loading at any time during the storm. Instead, it implies that the storm changed the hydro-

geochemical character of the MSD, such that less Zn was released, even 12 hours later when flows had returned to baseline conditions. It is worth noting that the pH of the MSD waters was slightly higher in post-storm vs. pre-storm time periods. Recent research has shown that the concentration of Zn in non-acidic streams polluted by mining is highly sensitive to small pH changes, decreasing roughly 10-fold for each unit increase in pH (Xie, 2002). However, this hypothesis does not explain the fact that most other analytes (including the majors, Ca, Mg, K, and Na) also did not return to their pre-storm loading values. A more likely explanation is that rapid infiltration of fresh rain water in the MSD catchment temporarily displaced contaminated ground water to greater depths, making it more difficult for the normally “dirty” ground water to return to the MSD as baseflow seepage. Although this hypothesis is somewhat awkward, there seems no other plausible explanation.

The situation for copper is completely different than that of zinc. As shown in Fig. 11, copper loadings increased 100-fold immediately after the storm surge, and remained elevated relative to baseline conditions for the remainder of the monitoring period. During the 1-hour period after the initial storm surge, roughly the same amount of copper was washed down the MSD as would happen in 4 days of normal baseflow conditions. This is true for both filtered and raw (total) Cu. These results underscore the importance of storm events in flushing copper from the MSD into the recently reclaimed upper Silver Bow Creek.

4.3 Geochemical modeling

The average chemical composition of MSD water prior to the storm was input into the geochemical modeling program MINTEQA2 (Allison and others, 1991). The purpose of this exercise was to see if the chemistry of the MSD waters under normal baseflow conditions is buffered by equilibrium with minerals in the stream bed, or in adjacent soil and sediment. The computed saturation indices for selected minerals and amorphous solids are given in Table 3. Significant findings include the following:

- MSD water is very close to saturation with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum is probably present in the bank sediment and soils, and is most likely a major factor in buffering the specific conductivity of MSD water to fairly high levels during baseflow conditions.
- The water is slightly undersaturated with calcite (CaCO_3) and $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$, and is very close to equilibrium with rhodochrosite (MnCO_3) and otavite (CdCO_3). All of these carbonate minerals are probably present in bank sediment and soil, at least locally (e.g., in micro-environments of higher pH or alkalinity).
- MSD water is undersaturated with all Cu-bearing solids in the MINTEQA2 database by at least 1 order of magnitude. The Cu mineral with the highest saturation index is tenorite (CuO) ($\text{SI} = -1.42$). These results suggest that the Cu concentrations of MSD waters are not controlled by solubility constraints, but are more likely limited by adsorption or co-precipitation onto suspended sediment. This is consistent with the

fact that a large percentage of the total Cu is consistently in the particulate (suspended sediment) fraction.

Table 3. Saturation indices for selected minerals in pre-storm MSD water.

MINERAL	FORMULA	S.I.	MINERAL	FORMULA	S.I.
HYDROXYAPATITE	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	2.23	$\text{SiO}_2(\text{A,PT})$	SiO_2	-0.65
BARITE	BaSO_4	1.05	ARAGONITE	CaCO_3	-0.67
QUARTZ	SiO_2	0.71	SMITHSONITE	ZnCO_3	-0.77
CRISTOBALITE	SiO_2	0.27	CERRUSITE	PbCO_3	-0.84
OTAVITE	CdCO_3	0.25	CELESTITE	SrSO_4	-1.01
CHALCEDONY	SiO_2	0.19	WILLEMITE	Zn_2SiO_4	-1.35
RHODOCHROSITE	MnCO_3	-0.12	TENORITE	CuO	-1.42
GYPSUM	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-0.19	DOLOMITE	$\text{CaMg}(\text{CO}_3)_2$	-1.45
$\text{SiO}_2(\text{A,GL})$	SiO_2	-0.32	MAGNESITE	MgCO_3	-1.45
$\text{ZnCO}_3 \cdot \text{H}_2\text{O}$	$\text{ZnCO}_3 \cdot \text{H}_2\text{O}$	-0.39	MALACHITE	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	-1.84
CALCITE	CaCO_3	-0.49	STRONTIANITE	SrCO_3	-2.09
ANHYDRITE	CaSO_4	-0.51	ZNO(ACTIVE)	ZnO	-2.11

4.4 Diel (24-hour) changes in water quality

The results of this study were disappointing in terms of the original objective, to document diel (24-hour) changes in water chemistry in a highly polluted water body. Recent work – much of it in Montana – has documented large and reproducible variations in the concentration of trace metals in non-acidic streams polluted by mine drainage (Brick and Moore, 1996; Nimick and others, 1998, 2000, 2003). In most of the systems investigated, the concentrations of Fe and As tend to increase during the day and decrease at night, whereas the reverse pattern is witnessed for the divalent cations (Zn^{2+} , Mn^{2+} , Cd^{2+}). Similar diel changes were expected in the case of the Metro Storm Drain. However, in the 12 hours prior to the thunderstorm, no significant change in the

concentration of any parameter was observed, despite a cool, clear morning followed by a sunny, warm mid-day (weather conditions that are known to produce diel fluctuations in other creeks). Because filtered metal concentrations of Fe and As were below analytical detection limits in this study, further discussion is moot. The absence of a diel pattern for the divalent cations (for which data are available) is tentatively explained as follows.

Field and laboratory studies have shown that Zn, Mn, and Cd concentrations are sensitive to small changes in both pH and temperature, decreasing with an increase in either field parameter (Xie and Gammons, 2001; Shope and others, 2002; Nimick and others, 2003). In all of the streams in which diel Zn cycling has been observed (Nimick and others, 2003), pH rose during the day (due to photosynthetic consumption of CO_2), and decreased at night (due to respiration and increase in CO_2). At the same time, daytime warming and nighttime cooling occurred. In this scenario, the two variables that influence Zn concentration vary in a way that is mutually reinforcing, resulting in the observed 24-hour fluctuations in dissolved Zn. In the case of the MSD, pH actually decreased slightly (0.2 log units) during the day, at the same time that water temperature increased. Thus, the effects of pH change and temperature change would have been working against each other, and may have cancelled each other out.

A different hypothesis to explain the fact that metal concentrations in the MSD did not show diel variations is that Mn, Cd, and Zn levels may have been buffered by mineral solubility controls (see preceding section). In contrast, aqueous transport of metals in streams with lower metal concentrations is most likely influenced by sorption-desorption reactions. Although mineral solubility reactions are also sensitive to temperature and pH changes, dissolution and precipitation of minerals is a relatively slow process. This is

particularly true for carbonate minerals, which often require substantial degrees of supersaturation before precipitation can occur at a measurable rate (Drever, 1997; Langmuir, 1997).

5. CONCLUSIONS

The following is a list of some of the more important conclusions reached in this study:

- 1) During the storm event of June 26, 2002, MSD flows increased 100-fold over a 15-minute period, and then slowly relaxed back to baseline conditions.
- 2) The storm surge brought an increase in pH and decrease in dissolved oxygen to the MSD waters.
- 3) Prior to the storm, average concentrations of filtered Cd, Cu, Zn, and Mn were 0.025, 0.49, 9.54, and 9.89 ppm, respectively. No evidence for particulate Cd, Mn, or Zn was noted prior to the storm. In contrast, roughly the same amount of Cu was present in filtered and suspended particle form.
- 4) After the storm surge, the concentrations of filtered and unfiltered Cd, Zn, and Mn dropped precipitously, whereas the concentration of filtered and unfiltered Cu both increased. For 6 hours after the initial storm surge, there was a small but significant fraction of Zn and Mn in the particulate phase. After this high-flow period, no Zn or Mn particles were observed.

- 5) Fe and Al existed predominantly in the particulate fraction throughout the study period. Filtered Fe and filtered Al were below detection limits before the storm, but increased slightly after the storm passed. It is not known whether the filtered Fe and Al were truly dissolved, or were present as colloids with diameters less than the filters used ($0.45\ \mu\text{m}$).
- 6) Cu loadings (g/hour) increased by a factor of 100 during the storm surge, and remained elevated above baseline conditions over the remainder of the study period.
- 7) Zn loadings (g/hour) increased slightly in the first hour of the storm surge, but then decreased to values less than baseline for the remainder of the monitoring period.
- 8) The concentration of Cu in storm flow rushing into the MSD after the thunderstorm was 2.5 times greater than Cu levels in the MSD prior to the storm. In contrast, Zn concentrations in the storm flow were very low compared to pre-storm baseline conditions. Based on this study alone, it is not possible to determine whether the storm flow attained its high Cu concentration *before* or *after* entering into the MSD.
- 9) Geochemical modeling suggests that the pre-storm MSD waters were very close to saturation with the minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), rhodochrosite (MnCO_3), and otavite (CdCO_3), and slightly undersaturated with calcite (CaCO_3) and hydrous Zn-carbonate ($\text{ZnCO}_3 \cdot \text{H}_2\text{O}$). It is highly probable that these minerals are present in bank soil and sediment, and influence the chemistry of MSD waters. In contrast, MSD water is highly undersaturated with all Cu-bearing minerals in the MINTEQ database. Consequently, Cu concentrations are more likely controlled by adsorption or co-precipitation onto suspended particles.

- 10) In the 10-hour period (6:30 a.m. to 4:30 p.m.) prior to the storm, no diel changes in the concentration of any dissolved metals were observed.

Acknowledgements This research was supported under EPA-EPSCOR contract to CHG. Graduate student Adam Wenz assisted with the field work. Thanks Adam! Heiko Langner and Johnnie Moore (Univ. of Montana, Missoula) are also thanked for their cooperation in the ICP laboratory analyses, as are Craig Deeney (Trec Corp.) and the Atlantic Richfield Company for providing valuable streamflow information.

References cited

- Allison, J. D., Brown, D. S., and Novo-Gradac K. J., 1991, MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 users manual. Environ. Res. Lab., U.S. Environmental Protection Agency.
- Brick, C. M. and Moore, J. N., 1996, Diel variation of trace metals in the upper Clark Fork River, Montana: Environmental Science & Technology, vol. 30, p. 1953-1960.
- CH2M Hill, Inc., and Chen-Northern, Inc., 1990, Draft Silver Bow Creek CERCLA Phase II Remedial Investigation Data Summary, Area I Operable Unit, Vol 1, March 1990.
- Drever, J. I., 1997, The Geochemistry of Natural Waters: 3rd ed. Prentice-Hall, Upper Saddle River, N.J., 436 p.
- Duaime, T.E., and Appleman, R. A., 1990, Storm-event monitoring and the Upper Clark Fork River Basin, Silver Bow and Deer Lodge Counties: Montana Bureau of Mines and Geology Open-File Report No. 228.

- Duaine, T.E., Metesh, J.J., Bergantino, R.N., Burns, G., Yovich, M.J., Lee-Roark, C.L., Smart, E.W., and Ford, J.F., 1995, Hydrogeologic aspects of remediation of metal mine impacts on Upper Clark Fork Superfund sites, Butte-Warm Springs, MT: Northwest Geology, vol. 24, p. 99-158
- Gammons, C. H., Ridenour, R. and Wenz, A., 2001, Diurnal and longitudinal variations in water quality along the Big Hole River and tributaries during the drought of August, 2000: Montana Bureau of Mines and Geology, Open-File Report 424, 39 p.
- Langmuir, D., 1997, Aqueous Environmental Geochemistry: Prentice-Hall, Upper Saddle River, N.J., 600 p.
- Nimick, D. A., Moore, J. N., Dalby, C. E., and Savka, M. W., 1998, The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming: Water Resources Research, vol. 34, p. 3051-3067.
- Nimick, D.A., Cleasby, T.E., and Lambing, J.H., 2000, Diel variation in dissolved metal concentrations in streams draining abandoned mine lands: abstract, 17th Annual Montana Water Conference, Amer. Water Resources Assoc., West Yellowstone, Montana, October 5-6, 2000.
- Nimick, D.A., Gammons, C. H., Cleasby, T. E., Madison, J. M., Skaar, D., and Brick, C. M., 2003, Diel variations in dissolved metal concentrations in streams: occurrence and possible causes: Water Resources Research, in press.
- Shope, C. L., Xie Ying, and Gammons, C. H., 2002, Groundwater-surface water interactions and diel zinc cycling in non acidic streams draining abandoned mines: abstract, Proc. 2002 Annual Meeting of the National Groundwater Association, Las Vegas, NV, Dec., 2002.

Spindler, John C., 1977, The Clean Up of Silver Bow Creek: Mining Congress Journal, June 1977.

Tate, C. M., Broshears, R. E., and McKnight, D. M., 1995, Phosphate dynamics in an acidic mountain stream: interactions involving algal uptake, sorption by iron oxide, and photoreduction: Limnol. Oceanogr., vol. 40, p. 938-946.

Xie, Y., 2002, Experimental investigation of the causes of diel cycling of zinc in streams contaminated with acid mine drainage. M.S. Thesis, Montana Tech of The University of Montana, Butte, MT.

Xie, Y. and Gammons, C. H., 2001, Experimental investigation of the causes of diurnal cycling of zinc in a stream impacted by mine drainage: abstract, 18th Annual Montana Water Conference, Amer. Water Resources Assoc., Missoula, MT, Oct. 2001.

Appendix A1. Streamflow data

The table on the following page gives streamflow data (cfs) for the SS-03 monitoring station at the Butte Metro Storm Drain. All times were recalculated from the raw data supplied from ARCO by adding 1 hour (to take into account Daylight Savings Time).

date/time	flow (cfs)	date/time	flow (cfs)	date/time	flow (cfs)	date/time	flow (cfs)
6/26/02 0:00	0.187	6/26/02 12:00	0.193	6/27/02 0:00	0.399	6/27/02 12:00	0.220
6/26/02 0:15	0.184	6/26/02 12:15	0.190	6/27/02 0:15	0.385	6/27/02 12:15	0.218
6/26/02 0:30	0.186	6/26/02 12:30	0.192	6/27/02 0:30	0.365	6/27/02 12:30	0.225
6/26/02 0:45	0.186	6/26/02 12:45	0.190	6/27/02 0:45	0.350	6/27/02 12:45	0.223
6/26/02 1:00	0.187	6/26/02 13:00	0.191	6/27/02 1:00	0.339	6/27/02 13:00	0.223
6/26/02 1:15	0.184	6/26/02 13:15	0.192	6/27/02 1:15	0.333	6/27/02 13:15	0.227
6/26/02 1:30	0.187	6/26/02 13:30	0.188	6/27/02 1:30	0.324	6/27/02 13:30	0.227
6/26/02 1:45	0.185	6/26/02 13:45	0.191	6/27/02 1:45	0.316	6/27/02 13:45	0.226
6/26/02 2:00	0.186	6/26/02 14:00	0.188	6/27/02 2:00	0.310	6/27/02 14:00	0.224
6/26/02 2:15	0.186	6/26/02 14:15	0.189	6/27/02 2:15	0.300	6/27/02 14:15	0.226
6/26/02 2:30	0.185	6/26/02 14:30	0.189	6/27/02 2:30	0.293	6/27/02 14:30	0.224
6/26/02 2:45	0.190	6/26/02 14:45	0.186	6/27/02 2:45	0.288	6/27/02 14:45	0.221
6/26/02 3:00	0.186	6/26/02 15:00	0.187	6/27/02 3:00	0.282	6/27/02 15:00	0.217
6/26/02 3:15	0.188	6/26/02 15:15	0.193	6/27/02 3:15	0.280	6/27/02 15:15	0.216
6/26/02 3:30	0.187	6/26/02 15:30	0.197	6/27/02 3:30	0.276	6/27/02 15:30	0.209
6/26/02 3:45	0.186	6/26/02 15:45	0.193	6/27/02 3:45	0.268	6/27/02 15:45	0.217
6/26/02 4:00	0.189	6/26/02 16:00	0.193	6/27/02 4:00	0.262	6/27/02 16:00	0.212
6/26/02 4:15	0.189	6/26/02 16:15	0.200	6/27/02 4:15	0.259	6/27/02 16:15	0.212
6/26/02 4:30	0.191	6/26/02 16:30	0.205	6/27/02 4:30	0.262	6/27/02 16:30	0.210
6/26/02 4:45	0.187	6/26/02 16:45	20.86	6/27/02 4:45	0.253	6/27/02 16:45	0.210
6/26/02 5:00	0.189	6/26/02 17:00	16.58	6/27/02 5:00	0.250	6/27/02 17:00	0.209
6/26/02 5:15	0.188	6/26/02 17:15	12.49	6/27/02 5:15	0.251	6/27/02 17:15	0.210
6/26/02 5:30	0.188	6/26/02 17:30	9.570	6/27/02 5:30	0.249	6/27/02 17:30	0.211
6/26/02 5:45	0.189	6/26/02 17:45	7.912	6/27/02 5:45	0.242	6/27/02 17:45	0.208
6/26/02 6:00	0.190	6/26/02 18:00	6.675	6/27/02 6:00	0.238	6/27/02 18:00	0.204
6/26/02 6:15	0.194	6/26/02 18:15	5.765	6/27/02 6:15	0.244	6/27/02 18:15	0.207
6/26/02 6:30	0.189	6/26/02 18:30	4.978	6/27/02 6:30	0.237	6/27/02 18:30	0.205
6/26/02 6:45	0.189	6/26/02 18:45	4.299	6/27/02 6:45	0.238	6/27/02 18:45	0.203
6/26/02 7:00	0.190	6/26/02 19:00	3.725	6/27/02 7:00	0.232	6/27/02 19:00	0.207
6/26/02 7:15	0.191	6/26/02 19:15	3.122	6/27/02 7:15	0.233	6/27/02 19:15	0.206
6/26/02 7:30	0.193	6/26/02 19:30	2.582	6/27/02 7:30	0.230	6/27/02 19:30	0.205
6/26/02 7:45	0.194	6/26/02 19:45	2.178	6/27/02 7:45	0.227	6/27/02 19:45	0.209
6/26/02 8:00	0.195	6/26/02 20:00	1.820	6/27/02 8:00	0.230	6/27/02 20:00	0.203
6/26/02 8:15	0.191	6/26/02 20:15	1.490	6/27/02 8:15	0.226	6/27/02 20:15	0.202
6/26/02 8:30	0.192	6/26/02 20:30	1.265	6/27/02 8:30	0.223	6/27/02 20:30	0.204
6/26/02 8:45	0.194	6/26/02 20:45	1.093	6/27/02 8:45	0.228	6/27/02 20:45	0.216
6/26/02 9:00	0.191	6/26/02 21:00	0.960	6/27/02 9:00	0.227	6/27/02 21:00	0.214
6/26/02 9:15	0.192	6/26/02 21:15	0.860	6/27/02 9:15	0.220	6/27/02 21:15	0.218
6/26/02 9:30	0.196	6/26/02 21:30	0.788	6/27/02 9:30	0.219	6/27/02 21:30	0.227
6/26/02 9:45	0.200	6/26/02 21:45	0.713	6/27/02 9:45	0.218	6/27/02 21:45	0.222
6/26/02 10:00	0.193	6/26/02 22:00	0.656	6/27/02 10:00	0.218	6/27/02 22:00	0.220
6/26/02 10:15	0.191	6/26/02 22:15	0.602	6/27/02 10:15	0.209	6/27/02 22:15	0.224
6/26/02 10:30	0.191	6/26/02 22:30	0.559	6/27/02 10:30	0.218	6/27/02 22:30	0.224
6/26/02 10:45	0.192	6/26/02 22:45	0.520	6/27/02 10:45	0.217	6/27/02 22:45	0.221
6/26/02 11:00	0.193	6/26/02 23:00	0.498	6/27/02 11:00	0.219	6/27/02 23:00	0.221
6/26/02 11:15	0.189	6/26/02 23:15	0.466	6/27/02 11:15	0.216	6/27/02 23:15	0.220
6/26/02 11:30	0.193	6/26/02 23:30	0.443	6/27/02 11:30	0.219	6/27/02 23:30	0.221
6/26/02 11:45	0.191	6/26/02 23:45	0.419	6/27/02 11:45	0.223	6/27/02 23:45	0.215

Appendix A2. Hydrolab data.

Data on the following 2 pages were collected by a Hydrolab Datasonde 3, at the SS-03 monitoring station. Specific conductivity is in $\mu\text{S}/\text{cm}$. DO is dissolved oxygen in ppm.

Date and Time	Temp	pH	SC	DO
6/25/02 20:00	21.82	6.74	1553	5.52
6/25/02 20:30	21.23	6.75	1553	5.24
6/25/02 21:00	20.70	6.75	1557	5.01
6/25/02 21:30	20.14	6.76	1561	4.87
6/25/02 22:00	19.56	6.77	1561	4.71
6/25/02 22:30	19.01	6.77	1564	4.56
6/25/02 23:00	18.50	6.78	1567	4.47
6/25/02 23:30	18.02	6.78	1567	4.37
6/26/02 0:00	17.61	6.79	1568	4.30
6/26/02 0:30	17.25	6.79	1569	4.30
6/26/02 1:00	16.92	6.80	1576	4.27
6/26/02 1:30	16.62	6.80	1577	4.23
6/26/02 2:00	16.32	6.81	1579	4.26
6/26/02 2:30	16.02	6.81	1585	4.23
6/26/02 3:00	15.75	6.81	1588	4.19
6/26/02 3:30	15.46	6.81	1589	4.19
6/26/02 4:00	15.18	6.80	1592	4.10
6/26/02 4:30	14.90	6.80	1592	4.08
6/26/02 5:00	14.65	6.80	1594	4.07
6/26/02 5:30	14.37	6.80	1595	4.04
6/26/02 6:00	14.14	6.79	1595	3.93
6/26/02 6:30	13.95	6.78	1596	3.90
6/26/02 7:00	13.86	6.77	1597	3.93
6/26/02 7:30	13.90	6.76	1598	3.93
6/26/02 8:00	14.08	6.75	1602	4.03
6/26/02 8:30	14.41	6.74	1603	4.09
6/26/02 9:00	14.87	6.72	1603	4.20
6/26/02 9:30	15.44	6.72	1602	4.39
6/26/02 10:00	16.13	6.71	1599	4.56
6/26/02 10:30	16.78	6.70	1597	4.61
6/26/02 11:00	17.43	6.69	1598	4.84
6/26/02 11:30	18.16	6.68	1590	4.94
6/26/02 12:00	19.30	6.68	1586	5.17
6/26/02 12:30	19.92	6.67	1577	5.29
6/26/02 13:00	20.75	6.67	1568	5.44
6/26/02 13:30	21.57	6.67	1562	5.55
6/26/02 14:00	22.39	6.67	1552	5.76
6/26/02 14:30	22.99	6.66	1543	5.80
6/26/02 15:00	22.22	6.66	1539	5.70
6/26/02 15:30	20.86	6.77	1509	5.90

Date and Time	Temp	pH	SC	DO
6/26/02 16:00	20.84	6.73	1520	5.45
6/26/02 16:30	21.10	6.73	1511	5.31
6/26/02 17:00	21.43	7.16	283	4.54
6/26/02 17:30	21.03	7.34	157	2.86
6/26/02 18:00	20.76	7.40	150	2.36
6/26/02 18:30	20.62	7.39	161	1.76
6/26/02 19:00	20.57	7.35	177	1.17
6/26/02 19:30	20.50	7.30	195	0.28
6/26/02 20:00	20.40	7.26	213	0.09
6/26/02 20:30	20.22	7.21	231	0.07
6/26/02 21:00	19.99	7.18	248	0.07
6/26/02 21:30	19.74	7.14	266	0.05
6/26/02 22:00	19.48	7.11	284	0.05
6/26/02 22:30	19.22	7.08	301	0.07
6/26/02 23:00	18.97	7.05	321	0.11
6/26/02 23:30	18.74	7.03	343	0.07
6/27/02 0:00	18.49	7.00	362	0.05
6/27/02 0:30	18.22	6.98	382	0.04
6/27/02 1:00	17.83	6.96	407	0.05
6/27/02 1:30	17.58	6.94	426	0.05
6/27/02 2:00	17.31	6.92	451	0.04
6/27/02 2:30	17.08	6.91	475	0.04
6/27/02 3:00	16.87	6.90	499	0.05
6/27/02 3:30	16.61	6.90	521	0.06
6/27/02 4:00	16.34	6.89	541	0.11
6/27/02 4:30	16.07	6.89	563	0.17
6/27/02 5:00	15.83	6.88	581	0.23
6/27/02 5:30	15.60	6.88	598	0.25
6/27/02 6:00	15.36	6.88	617	0.29
6/27/02 6:30	15.20	6.88	634	0.35
6/27/02 7:00	15.13	6.88	650	0.37
6/27/02 7:30	15.08	6.87	667	0.43
6/27/02 8:00	15.19	6.87	682	0.39
6/27/02 8:30	15.45	6.86	697	0.42
6/27/02 9:00	15.68	6.85	712	0.53
6/27/02 9:30	15.91	6.84	727	0.60
6/27/02 10:00	16.41	6.83	744	0.63
6/27/02 10:30	17.10	6.81	758	0.63
6/27/02 11:00	17.87	6.80	773	0.58
6/27/02 11:30	18.58	6.78	782	0.54
6/27/02 12:00	19.34	6.76	792	0.53

Appendix A3. Field measurements and observations.

The following table summarizes field measurements obtained manually in the field for pH, water temperature (T), specific conductivity (SC), dissolved oxygen (DO), alkalinity, and streamflow. Notes on the weather are also given.

Date	time	pH	water T °C	SC μS/cm	DO mg/L	alkalinity mgCaCO ₃ /L	Flow cfs
6-25-02	19:00	6.79	22.2	2040	4.85		
6-26-02	6:00	6.68	13.8	2040	3.45		
6-26-02	6:20	sunrise ... sunny, cool AM but warmed quickly towards noon					
6-26-02	6:40					144	
6-26-02	7:15						.072
6-26-02	9:50	6.95	15.8	2050	4.03		
6-26-02	15:00	6.45	21.7	2070	5.10		
6-26-02	15:20	hail begins					
6-26-02	15:45	hail turns to rain – heavy rain for 1 hour					
6-26-02	17:30	7.21	20.9	226	3.62	61.4	
6-26-02	18:00						6.4
6-26-02	21:10	7.00	19.5	391	1.93		
6-27-02	1:40	6.97	17.2	678	1.92		
6-27-02	5:40	6.85		947	2.02	76.4	
		sunrise					
6-27-02	6:30						0.126

The following table gives SC measurements of each of the 24 ISCO samples collected. These measurements were taken back in the laboratory, with all water samples at the same temperature.

date	time collected	SC, lab	date	time collected	SC, lab
6-26-02	6:30	2010	6-26-02	18:30	241
6-26-02	7:30	2020	6-26-02	19:30	284
6-26-02	8:30	2000	6-26-02	20:30	339
6-26-02	9:30	-	6-26-02	21:30	395
6-26-02	10:30	2020	6-26-02	22:30	450
6-26-02	11:30	2020	6-26-02	23:30	514
6-26-02	12:30	2030	6-27-02	0:30	578
6-26-02	13:30	2030	6-27-02	1:30	653
6-26-02	14:30	2040	6-27-02	2:30	728
6-26-02	15:30	2020	6-27-02	3:30	789
6-26-02	16:30	2020	6-27-02	4:30	854
6-26-02	17:30	317	6-27-02	5:30	906

Appendix A4. ICP results.

The following tables summarize results for ICP-AES analysis of filtered and non-filtered (raw) samples, using EPA Method SED 5 5S. PQL = practical quantification limit.

Filtered-acidified samples.

	Al3082	As1890	B2497	Ba2335	Be2348	Ca3158	Cd2265	Cd2288	Co2286	Cr2677	Cu3247
PQL	0.0400	0.0500	0.010	0.0030	0.0010	0.2	0.0050	0.0050	0.0050	0.0500	0.0300
6/26/02 6:30	<.0400	<.0500	1.319	0.0604	<.00100	269.3	0.0245	0.0260	0.0093	<.0500	0.0537
6/26/02 7:30	<.0400	<.0500	1.332	0.0584	<.00100	271.4	0.0260	0.0275	0.0098	<.0500	0.0562
6/26/02 8:30	<.0400	<.0500	1.298	0.0673	<.00100	267.3	0.0270	0.0292	0.0093	<.0500	0.0533
6/26/02 9:30	<.0400	<.0500	1.276	0.0620	<.00100	265.2	0.0237	0.0256	0.0078	<.0500	0.0548
6/26/02 10:30	<.0400	<.0500	1.315	0.0649	<.00100	286.1	0.0238	0.0252	0.0089	<.0500	0.0431
6/26/02 11:30	<.0400	<.0500	1.296	0.0666	<.00100	267.7	0.0239	0.0246	0.0089	<.0500	0.0467
6/26/02 12:30	<.0400	<.0500	1.313	0.0735	<.00100	268.1	0.0243	0.0252	0.0094	<.0500	0.0478
6/26/02 13:30	<.0400	<.0500	1.319	0.0790	<.00100	269.5	0.0235	0.0247	0.0088	<.0500	0.0442
6/26/02 14:30	<.0400	<.0500	1.386	0.0906	<.00100	266.0	0.0242	0.0257	0.0100	<.0500	0.0467
6/26/02 15:30	<.0400	<.0500	1.342	0.0682	<.00100	268.8	0.0250	0.0255	0.0097	<.0500	<.0300
6/26/02 16:30	0.0668	<.0500	1.415	0.0678	<.00100	283.8	0.0257	0.0263	0.0099	<.0500	0.0464
6/26/02 17:30	0.0526	<.0500	0.191	0.0474	<.00100	31.5	<.0050	<.0050	<.0050	<.0500	0.1147
6/26/02 18:30	0.0472	<.0500	0.152	0.0492	<.00100	24.5	<.0050	<.0050	<.0050	<.0500	0.0913
6/26/02 19:30	0.0862	<.0500	0.176	0.0396	<.00100	29.2	<.0050	<.0050	<.0050	<.0500	0.0903
6/26/02 20:30	0.0667	<.0500	0.223	0.0484	<.00100	35.0	<.0050	<.0050	<.0050	<.0500	0.0910
6/26/02 21:30	0.0806	<.0500	0.245	0.0765	<.00100	42.0	<.0050	<.0050	<.0050	<.0500	0.0946
6/26/02 22:30	0.0500	<.0500	0.240	0.0494	<.00100	48.0	<.0050	<.0050	<.0050	<.0500	0.0884
6/26/02 23:30	0.0416	<.0500	0.260	0.0584	<.00100	55.7	<.0050	<.0050	<.0050	<.0500	0.0883
6/27/02 0:30	0.0722	<.0500	0.280	0.0472	<.00100	62.9	<.0050	<.0050	<.0050	<.0500	0.0837
6/27/02 1:30	0.0500	<.0500	0.317	0.0690	<.00100	71.4	<.0050	<.0050	<.0050	<.0500	0.0840
6/27/02 2:30	0.0834	<.0500	0.347	0.0507	<.00100	81.0	0.0051	0.0056	<.0050	<.0500	0.0785
6/27/02 3:30	<.0400	<.0500	0.368	0.0704	<.00100	89.9	0.0052	<.0050	<.0050	<.0500	0.0825
6/27/02 4:30	<.0400	<.0500	0.382	0.0534	<.00100	98.8	0.0054	0.0063	<.0050	<.0500	0.0792
6/27/02 5:30	<.0400	<.0500	0.411	0.0678	<.00100	105.7	0.0061	0.0068	<.0050	<.0500	0.0738

Filtered-acidified samples (cont.)

	Fe2327	Hg1942	K_7698	Li6707	Mg2936	Mn2933	Mo2020	Na5889	Ni2316	P 1782	Pb2203
PQL	0.0800	0.0500	0.40	0.0050	0.40	0.040	0.0100	0.1	0.0100	0.050	0.040
6/26/02 6:30	<.0800	<.0500	17.14	0.1090	63.21	9.936	0.0110	84.2	0.0134	0.100	0.041
6/26/02 7:30	<.0800	<.0500	17.38	0.1125	63.47	9.907	0.0113	85.0	0.0130	0.105	0.046
6/26/02 8:30	<.0800	<.0500	16.99	0.1096	62.61	9.759	0.0126	83.7	0.0152	0.116	0.061
6/26/02 9:30	0.1803	<.0500	16.27	0.1048	61.11	9.621	0.0110	80.6	0.0137	0.108	<.040
6/26/02 10:30	<.0800	<.0500	16.44	0.1042	61.95	9.925	<.0100	81.0	0.0149	0.103	<.040
6/26/02 11:30	<.0800	<.0500	16.47	0.1038	61.12	9.881	0.0105	80.6	0.0127	0.101	<.040
6/26/02 12:30	<.0800	<.0500	16.74	0.1044	62.30	9.963	0.0113	82.0	0.0142	0.103	<.040
6/26/02 13:30	<.0800	<.0500	16.50	0.1024	61.28	9.976	0.0113	80.5	0.0128	0.107	<.040
6/26/02 14:30	<.0800	<.0500	16.99	0.1055	61.15	9.901	<.0100	82.1	0.0121	0.122	<.040
6/26/02 15:30	<.0800	<.0500	16.67	0.1032	61.43	9.924	0.0107	80.5	0.0133	0.091	<.040
6/26/02 16:30	<.0800	<.0500	15.96	0.1002	59.82	9.890	0.0115	77.3	0.0135	0.098	<.040
6/26/02 17:30	<.0800	<.0500	3.76	0.0110	4.91	0.654	<.0100	11.3	<.0100	0.094	<.040
6/26/02 18:30	<.0800	<.0500	3.16	0.0067	3.06	0.272	<.0100	8.2	<.0100	0.111	<.040
6/26/02 19:30	<.0800	<.0500	3.43	0.0080	3.87	0.332	<.0100	9.6	<.0100	0.104	<.040
6/26/02 20:30	<.0800	<.0500	3.70	0.0103	5.05	0.398	<.0100	11.9	<.0100	0.095	<.040
6/26/02 21:30	0.0812	<.0500	4.14	0.0126	6.43	0.530	<.0100	13.5	<.0100	0.089	<.040
6/26/02 22:30	<.0800	<.0500	4.35	0.0156	7.77	0.658	<.0100	14.6	<.0100	0.052	<.040
6/26/02 23:30	0.0841	<.0500	4.72	0.0192	9.42	0.826	<.0100	16.6	<.0100	0.063	<.040
6/27/02 0:30	0.1121	<.0500	5.13	0.0222	11.10	1.016	<.0100	18.6	<.0100	<.050	<.040
6/27/02 1:30	0.1326	<.0500	5.47	0.0257	13.10	1.216	<.0100	20.9	<.0100	0.058	<.040
6/27/02 2:30	0.1952	<.0500	6.05	0.0307	15.41	1.501	<.0100	23.8	<.0100	0.057	<.040
6/27/02 3:30	0.1980	<.0500	6.54	0.0356	17.65	1.733	<.0100	26.9	<.0100	0.076	<.040
6/27/02 4:30	0.1887	<.0500	7.00	0.0394	19.79	1.973	<.0100	28.9	<.0100	0.065	<.040
6/27/02 5:30	0.2428	<.0500	7.39	0.0426	21.57	2.180	<.0100	31.4	<.0100	0.092	<.040

Filtered-acidified samples (cont.).

	S_1807	Sb2068	Se1960	Si2124	Sn1899	Sr4215	Ti3234	Ti1908	Zn2025
PQL	0.5	0.0800	0.0800	0.02	0.0300	0.010	0.1000	0.0800	0.008
6/26/02 6:30	292.8	<.0800	<.0800	11.26	<.0300	1.683	<.1000	<.0800	9.626
6/26/02 7:30	290.2	<.0800	<.0800	11.21	<.0300	1.706	<.1000	<.0800	9.538
6/26/02 8:30	287.5	<.0800	<.0800	11.01	<.0300	1.655	<.1000	<.0800	9.397
6/26/02 9:30	281.5	<.0800	<.0800	10.76	<.0300	1.595	<.1000	<.0800	9.321
6/26/02 10:30	286.5	<.0800	<.0800	10.90	<.0300	1.631	<.1000	<.0800	9.497
6/26/02 11:30	282.9	<.0800	<.0800	10.74	<.0300	1.609	<.1000	<.0800	9.466
6/26/02 12:30	285.1	<.0800	<.0800	10.80	<.0300	1.619	<.1000	<.0800	9.481
6/26/02 13:30	282.2	<.0800	<.0800	10.69	<.0300	1.611	<.1000	<.0800	9.431
6/26/02 14:30	288.9	<.0800	<.0800	10.72	<.0300	1.615	<.1000	<.0800	9.572
6/26/02 15:30	286.4	<.0800	<.0800	10.68	<.0300	1.620	<.1000	<.0800	9.589
6/26/02 16:30	281.0	<.0800	<.0800	10.59	0.0308	1.617	<.1000	<.0800	9.987
6/26/02 17:30	23.1	<.0800	<.0800	2.79	<.0300	0.146	<.1000	<.0800	0.391
6/26/02 18:30	13.9	<.0800	<.0800	2.63	<.0300	0.100	<.1000	<.0800	0.202
6/26/02 19:30	18.1	<.0800	<.0800	3.05	<.0300	0.128	<.1000	<.0800	0.287
6/26/02 20:30	23.4	<.0800	<.0800	3.43	<.0300	0.159	<.1000	<.0800	0.409
6/26/02 21:30	30.3	<.0800	<.0800	3.89	<.0300	0.196	<.1000	<.0800	0.560
6/26/02 22:30	35.6	<.0800	<.0800	4.21	<.0300	0.231	<.1000	<.0800	0.670
6/26/02 23:30	42.7	<.0800	<.0800	4.64	<.0300	0.276	<.1000	<.0800	0.827
6/27/02 0:30	51.1	<.0800	<.0800	5.04	<.0300	0.318	<.1000	<.0800	0.997
6/27/02 1:30	61.4	<.0800	<.0800	5.50	<.0300	0.372	<.1000	<.0800	1.204
6/27/02 2:30	73.4	<.0800	<.0800	6.02	<.0300	0.431	<.1000	<.0800	1.451
6/27/02 3:30	80.4	<.0800	<.0800	6.23	<.0300	0.484	<.1000	<.0800	1.589
6/27/02 4:30	90.0	<.0800	<.0800	6.62	<.0300	0.569	<.1000	<.0800	1.807
6/27/02 5:30	106.9	<.0800	<.0800	6.87	<.0300	0.608	<.1000	<.0800	1.973

Raw-acidified samples.

	Al3082	As1890	B2497	Ba2335	Be2348	Ca3158	Cd2265	Cd2288	Co2286	Cr2677	Cu3247
PQL	0.0400	0.0500	0.010	0.0030	0.0010	0.2	0.0050	0.0050	0.0050	0.0500	0.0300
6/26/02 7:30	0.0612	<.0500	1.248	0.0713	<.0010	266.8	0.0237	0.0246	0.0082	<.0500	0.1023
6/26/02 9:30	<.0400	<.0500	1.271	0.0855	<.0010	265.4	0.0237	0.0249	0.0078	<.0500	0.0906
6/26/02 10:30	0.1085	<.0500	1.291	0.0725	<.0010	268.4	0.0236	0.0255	0.0100	<.0500	0.1015
6/26/02 12:30	<.0400	<.0500	1.302	0.0812	<.0010	269.2	0.0242	0.0252	0.0092	<.0500	0.0767
6/26/02 14:30	<.0400	<.0500	1.316	0.0456	<.0010	286.7	0.0242	0.0262	0.0093	<.0500	0.0833
6/26/02 16:30	0.0975	<.0500	1.360	0.0823	<.0010	266.9	0.0251	0.0271	0.0091	<.0500	0.1096
6/26/02 18:30	2.0550	<.0500	0.097	0.0564	<.0010	26.2	<.0050	<.0050	<.0050	<.0500	0.3098
6/26/02 20:30	1.7610	<.0500	0.193	0.0855	<.0010	37.4	<.0050	<.0050	<.0050	<.0500	0.2895
6/26/02 22:30	1.2790	<.0500	0.237	0.0859	<.0010	49.1	<.0050	<.0050	<.0050	<.0500	0.2332
6/27/02 0:30	0.9499	<.0500	0.291	0.0757	<.0010	63.9	<.0050	0.0055	<.0050	<.0500	0.1996
6/27/02 2:30	0.8243	<.0500	0.351	0.0789	<.0010	81.1	<.0050	0.0057	<.0050	<.0500	0.1820
6/27/02 5:30	0.5095	<.0500	0.424	0.0849	<.0010	107.1	0.0063	0.0071	<.0050	<.0500	0.1761

Raw-acidified samples (cont.).

	Fe2327	Hg1942	K_7698	Li6707	Mg2936	Mn2933	Mo2020	Na5889	Ni2316	P 1782	Pb2203
PQL	0.080	0.0500	0.40	0.0050	0.40	0.040	0.0100	0.1	0.0100	0.0500	0.0400
6/26/02 7:30	2.149	<.0500	15.87	0.1009	59.80	9.619	<.0100	77.4	0.0134	0.0975	<.0400
6/26/02 9:30	1.861	<.0500	16.22	0.1020	59.96	9.645	0.0102	78.7	0.0136	0.0915	<.0400
6/26/02 10:30	1.871	<.0500	16.66	0.1029	61.38	9.871	<.0100	80.4	0.0131	0.0982	<.0400
6/26/02 12:30	1.344	<.0500	16.50	0.1023	60.59	9.910	0.0107	79.5	0.0125	0.1160	<.0400
6/26/02 14:30	1.355	<.0500	16.21	0.1011	60.87	10.060	0.0118	78.7	0.0126	0.0781	<.0400
6/26/02 16:30	2.008	<.0500	16.57	0.1029	60.22	9.818	0.0100	79.1	0.0120	0.0917	<.0400
6/26/02 18:30	2.389	<.0500	4.73	0.0096	4.02	0.417	<.0100	8.7	<.0100	0.2274	<.0400
6/26/02 20:30	2.068	<.0500	4.57	0.0124	5.96	0.530	<.0100	12.0	<.0100	0.2186	<.0400
6/26/02 22:30	1.744	<.0500	5.04	0.0177	8.49	0.735	<.0100	15.3	<.0100	0.1948	<.0400
6/27/02 0:30	1.730	<.0500	5.74	0.0239	11.7	1.082	<.0100	19.4	<.0100	0.1712	<.0400
6/27/02 2:30	2.062	<.0500	6.46	0.0318	15.8	1.538	<.0100	24.4	<.0100	0.1699	<.0400
6/27/02 5:30	2.332	<.0500	7.66	0.0442	21.9	2.233	<.0100	31.8	<.0100	0.1478	<.0400

Raw-acidified samples (cont.)

	S_1807	Sb2068	Se1960	Si2124	Sn1899	Sr4215	Ti3234	Ti1908	Zn2025
PQL	0.5	0.0800	0.0800	0.02	0.0300	0.010	0.1000	0.0800	0.008
6/26/02 7:30	282.3	<.0800	<.0800	10.99	<.0300	1.579	<.1000	<.0800	9.594
6/26/02 9:30	283.4	<.0800	<.0800	10.87	<.0300	1.581	<.1000	<.0800	9.588
6/26/02 10:30	290.5	<.0800	<.0800	11.17	<.0300	1.605	<.1000	<.0800	9.660
6/26/02 12:30	287.7	<.0800	<.0800	10.88	<.0300	1.606	<.1000	<.0800	9.640
6/26/02 14:30	284.5	<.0800	<.0800	10.87	<.0300	1.619	<.1000	<.0800	9.788
6/26/02 16:30	285.7	<.0800	<.0800	10.92	<.0300	1.611	<.1000	<.0800	10.040
6/26/02 18:30	14.2	<.0800	<.0800	6.96	<.0300	0.115	0.1132	<.0800	0.430
6/26/02 20:30	24.4	<.0800	<.0800	7.00	<.0300	0.174	<.1000	<.0800	0.677
6/26/02 22:30	36.9	<.0800	<.0800	6.88	<.0300	0.245	<.1000	<.0800	0.874
6/27/02 0:30	52.9	<.0800	<.0800	7.13	<.0300	0.329	<.1000	<.0800	1.203
6/27/02 2:30	73.1	<.0800	<.0800	7.68	<.0300	0.438	<.1000	<.0800	1.596
6/27/02 5:30	106.7	<.0800	<.0800	8.04	<.0300	0.624	<.1000	<.0800	2.141