

Basin reactivity: Determination of solute fate on a basin scale

Temple McKinnon, Department of Geology, University of Montana, Missoula, MT 59812

ABSTRACT

A basin-wide sampling of the surface water of the Upper Clark Fork Basin from Silver Bow Creek at Opportunity to Turah Bridge was conducted during the summer of 1998. This assessment of the Clark Fork was to determine the transport processes of dissolved-phase metals and attempt to quantify the impacts to the river. Tributaries of the primary drainages to the basin having varied mining histories were included in the sampling event. The headwaters region (immediately above and below the Warm Springs Ponds) produced elevated concentrations of As, Cu, Fe, and Mn in surface waters with relatively high pH values (8.5 to 9.2). Most trace element concentrations decrease through the pond system, with the exception of As. On a basin-wide scale, the concentration trends for trace elements in the system vary from reactivity to domination by dilution with the surface water discharge of the Clark Fork and its tributaries. Major cations appear to have downstream sources associated with tributaries or groundwater. Calculated background concentrations indicate that all cations analyzed have excess loads at some point in the study area with the exceptions of Fe and Mn. The reactive nature of Mn may account for its trend while Fe appears to be originating from a primary headwater source. These preliminary excess loads in the system identify segments of basin where remediation resources and efforts should be focused.

Purpose

- To identify stream reaches that may be source areas of metal and arsenic contributions to the dissolved phase of the Clark Fork River.
- To quantify impacts to the upper basin by identifying excess loads.
- To identify suitable sites for a more detailed temporal study of the basin's surface water. Results from this study are still being compiled.

Site Description

- Flood plain deposits along the upper Clark Fork contain As, Cd, Cu, Pb, and Zn 10 to 100 times greater than estimated background concentrations (Andrews, 1987).
- These flood plain deposits provide a continual source to the Clark Fork River ecosystem (Nimick and Moore, 1991).
- The area of study extends approximately 200 river Km from Silver Bow Creek at Opportunity (above the Warm Springs Ponds) to Turah Bridge (Figure 1).
- Ten mainstem and 6 tributary sites were sampled in September 1998.

Methods

Field Methods

- At least 4 samples were collected at each site. Ten samples were collected at the sites CF below Ponds and CF at Drummond to better define within-site variability.

- Ultra-clean sampling techniques were utilized during sample collection, preparation, and analysis (Windom et al., 1991; Benoit, 1994; Taylor and Shiller, 1995).
- Water temperature and pH were measured in-situ.
- Five sites were gaged using a Price AA current meter and discharge at the Gold Creek site was visually estimated. The remaining sites are equipped with USGS gaging stations (Figure 1).
- Discharge measurement error for all sites is conservatively rounded to 10% with the exception of Turah Bridge and Jens, which were assigned errors of 15%.

Analytical Methods

- Dissolved phase is defined as < 0.2-mm.
- Cations were analyzed by ICAPES.

Quality Control Results:

- Mean (n = 40) USGS T-143 during ICAPES fell within the reported range for all elements.
- Mean percent differences on ICAPES duplicates were < 5% except Ag (17.9%) and Zn (7.1%).
- Mean ICAPES spike recoveries were 88.9% to 102.5% except Ag (128.2%).

Results

Dissolved Concentration Trends

- Dissolved As immediately below the ponds is twice the As above the ponds (35mg/l vs. 15 mg/l).
- Major cations (Ca, K, Mg, Na) exhibit downstream trends similar to each other (concentrations increase near Deer Lodge and again near Bearmouth).
- Concentrations of S and Sr increase sharply around Bearmouth, perhaps corresponding to geothermal inputs.
- As and Fe decrease with distance downstream (Figure 2).
- Mn concentrations decrease significantly below the ponds.

Dissolved Load Trends

- Dissolved loads (concentration*Q) were calculated for elements above the PQL at each of the mainstem sampling sites.
- Dilution curves were developed for the study area to calculate basin background loads. The calculated background concentration for each mainstem site (MS_{bkg}) was converted to load as Kg/day.

$$MS_{bkg} = Fsb_{MS}*[SB@WS] + Fcf_{MS}*[nearest\ upstream\ tributary]$$

Where:

Fsb_{MS} = The volume of water at the mainstem site measured which originated from the Silver Bow @ Warm Springs site immediately below the Warm Springs Ponds.

[SB@WS] = The measured dissolved concentration at the Silver Bow @ Warm Springs site.

$F_{cf_{MS}}$ = The volume of water at the mainstem site measured which is not attributed to the Silver Bow @ Warm Springs site (i.e.: $1 - F_{sbMS}$).

[nearest upstream tributary] = the measured dissolved concentration from the sampled tributary immediately upstream of the mainstem site of interest.

- Excess or deficient loads relative to the calculated background are determined by: measured load – modeled load
- An excess load of Cu exists throughout the study area (Figure 3).
- Notable increases in excess loads at the CF @ Turah Bridge site were seen for As, Ca, K, Mg, and Na.
- Increases downstream from CF @ Drummond were seen for S and Sr, a pattern possibly attributed to geothermal waters in the area.
- The load of Mn fluctuates throughout the study area and is always at or below the calculated background, indicating reactive behavior in the system.
- Increased loads at Turah Bridge similar to that seen for As exist for Ba, Ca, K, Mg, Mo, Na, and Si.

Conclusions

- The As concentration below the ponds is more than double that above the ponds.
- There is a notable increase in excess As, Ca, K, Mg, Mo, Na, and Si loads at the Turah Bridge site – one possible source could be shallow groundwater from the flood plain.
- There is a continual source of Cu throughout the upper reach of the basin.
- Fe appears to originate from a primary upstream source.
- Downstream additions of Ca, Mg, S, and Sr seem to coincide with geothermal areas in the basin.
- The reactive nature of Mn prevents any prediction of its geochemical behavior on a basin scale.

Acknowledgements

Partial funding for this project was provided by the USGS-WRD. Analyses were conducted at the University of Montana's Murdock Biogeochemistry Lab. Johnnie Moore, Sonia Nagorski, and Mick Wilson assisted with field work. Johnnie Moore, Sonia Nagorski, and Anna Breuninger provided helpful suggestions and reviews.

References

Andrews, E.D., Longitudinal dispersion of trace metals in the Clark Fork River, Montana. In Averett, R.C. and D.M. McKnight, eds., *The Chemical Quality of Water and the Hydrologic Cycle* Chapter 13, Lewis Publishers, 1-13, 1987.

Benoit, G., Clean technique measurement of Pb, Ag, and Cd in freshwater: A redefinition of metal pollution. *Environ. Sci. Technol.*, 28(11): 1987-1991, 1994.

Nimick, D.A. and J.N. Moore, Prediction of water-soluble metal concentrations in fluvially deposited tailings sediments, Upper Clark Fork Valley, Montana, U.S.A. *Appl. Geochem.*, 6: 635-646, 1991.

Taylor, H.E. and A.M. Shiller, Mississippi River methods comparison study: Implications for water quality monitoring of dissolved trace elements. *Environ. Sci. Technol.* 29(5): 1313-1317, 1995.

Windom, H.L., J.T. Byrd, R.G. Smith, and F. Huan, Inadequacy of NASQAN data for assessing metal trends in the nation's rivers. *Environ. Sci. Technol.* 25(6): 1137-1142, 1991.