Appendix E. Trace Metals and Ionic Composition in the Blackfoot River[1]

In addition to selenium, within the Meade Peak formation the "waste shale" that has to be removed to access the phosphatic shale is exceptionally enriched with other trace elements that are readily leached from freshly exposed rock, including cadmium, copper, chromium, and zinc (Herring, 2004; Herring and Grauch, 2004). Accordingly, these elements as well as arsenic and vanadium have been included in the U.S. Geological Survey water-chemistry monitoring. Except for cadmium, all results of trace element sampling were consistently low, and less than regulatory or recommended guidelines to protect the environment. For zinc, the maximum measured value of 17µg/L was well below the Idaho chronic criterion value of 252 µg/L, calculated for an ambient water hardness of 244 mg/L (Idaho Department of Environmental Quality, 2011). For copper, the recommended U.S. Environmental Protection Agency water-quality criteria are functions of pH, major ion concentrations, and dissolved organic carbon (U.S. Environmental Protection Agency, 2007). Dissolved organic carbon was not measured, but copper concentrations were generally low, with a maximum concentration of 4.5 µg/L measured in May 2006. Although not measured here, dissolved organic carbon is typically elevated during spring runoff, relative to low flow times of the year.

Cadmium concentrations are puzzling, because although the great majority of the concentration data were low (<0.1 µg/L), occasional high values were obtained, with a maximum concentration of 2.3 µg/L obtained from an autosampler sample on April 21, 2012. This value is the same as the acute criterion for maximum concentrations intended to avoid unacceptable adverse effects to aquatic life in short-term exposures to cadmium at a water hardness of 193 mg/L, and is considerably higher than the corresponding chronic criterion concentration of 0.8 µg/L intended to protect aquatic communities from long-term exposures to cadmium (Mebane, 2006; Idaho Department of Environmental Quality, 2011). Recalling that 1 out of 21 ambient blank samples exposed to the open atmosphere within the autosampler showed a high level of cadmium contamination (0.8 µg/L) (Table C1), it is possible to discount this anomalous cadmium result as the possible result of contamination within the autosampler. However, infrequent elevated cadmium concentrations also were obtained at other times from samples that were independent of the autosampler. For instance, cadmium concentrations of 0.36 and 0.21µg/L resulted from equal-width increment samples collected on April 30, 2010, and September 16, 2010, respectively, and a value of 0.26 µg/L resulted from a grab sample on May 18, 2006. These results indicate that the occasional elevated cadmium concentrations obtained from the autosampler are likely real (for example, March 22, 2007 at 1.0 µg/L and March 31, 2006 at 0.74 µg/L), and should not be summarily dismissed.

In a limited review of other trace metal data from the upper Blackfoot River watershed, high concentrations have been reported from springs, seeps, and shallow groundwater in close proximity to waste dumps (Amacher and others, 1995; Myers, 2013). However, most samples from second-order or larger streams tended to be low, well below their aquatic life criteria (Millennium Science & Engineering, 2011; Whetstone Associates, 2012). High trace metals concentrations have been sporadically detected in surface water, including a cadmium concentration of 299 µg/L in a small tributary to Dry Valley Creek in May 2009 and a zinc concentration of 630 µg/L in lower Dry Valley Creek just above its confluence with the Blackfoot River in May 2011 (Whetstone Associates, 2012). These results are congruent with our results from the intensive monitoring at streamgage 13063000 on the main stem Blackfoot River. That is, there is potential for, and some evidence of elevated trace metals in the watershed as result of mining disturbance. However, most data indicate that trace metals concentrations in the larger streams and main stem Blackfoot River usually are lower than concentrations at risk to aquatic life, and that the focus on selenium is warranted.

Ionic Composition

Relations Between Selenium Concentrations and Major Ions

The ionic composition of streams reflects the geology of the watershed, can be used to infer the origins of stream water, and can influence the mobility of and bioavailability of selenium and other trace elements (McNeal and Balistrieri, 1989; Hem, 1992). Anions such as phosphate, sulfate, and carbonate tend to increase the mobility of selenate (Balistrieri and Chao, 1990; Sandy and DiSanti, 2010). Sulfate has been shown to decrease the bioavailability of selenate, through reduced uptake in plants (Bailey and others, 1995).

Temporal patterns between sulfate, selenium, and streamflow also were examined because sulfur and selenium have chemical similarities (McNeal and Balistrieri, 1989). Sulfate primarily originates from groundwater; therefore, sulfate and selenium concentrations tracking together over time would suggest a generalized groundwater source of selenium. If not tracking, then the discontinuity between streamflow and selenium would imply differing selenium contributions from different tributaries. In 2009, a relatively high-flow year, sulfate and selenium mostly tracked together, suggesting a common groundwater source (*fig. E1*). However, in 2010, sulfate and selenium showed distinctly different patterns over time. Discharge and selenium showed three distinct peaks, although the timing of the peaks differed. Sulfate showed only two peaks, both occurring at about the same time as the streamflow peaks. At the same time that selenium reached its annual peak, sulfate decreased to near its annual minimum (*fig. E1*). This suggests that the largest selenium sources in the Blackfoot River watershed are discreet, and are not closely coupled to watershed sulfate sources.
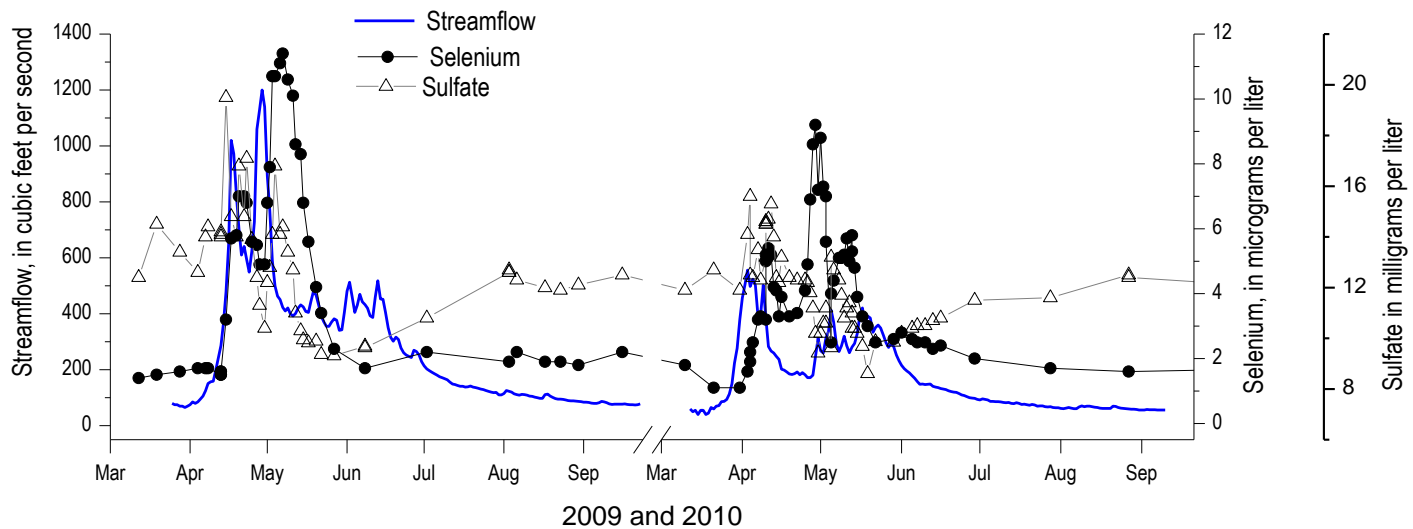

Figure E1. Patterns between selenium, sulfate, and streamflow, Blackfoot River watershed, southeastern Idaho, 2009 and 2010. Selenium and sulfate concentrations are from 0.45 micrometer filtered samples; streamflow is daily mean streamflow.

One reason for monitoring major ions was to evaluate whether the water characteristics in the Blackfoot River changed appreciably during the peak runoff and post-peak runoff. Because in the

Blackfoot River near the outlet, the annual peaks in selenium concentrations consistently lag the annual peak flows (main report, section "Temporal Patterns and Trends in Selenium Concentrations and Loads"), we considered whether the ionic composition changed as well. In 2009, particular attention was made to sampling the ionic composition prior to, and immediately after the peak discharge. The hypothesis was that if the ionic composition shifted along with the annual peaks, different groundwater and surface-water inputs of selenium could be reflected. The results of the pre- and post-snowmelt flush analyses did not support that hypothesis. Hydrogeochemically, waters in the Blackfoot River would be classified as a calcium-bicarbonate water type, based on the relative concentrations of major ions (*fig. E2*). During snowmelt runoff flush, the relative concentrations of major ions were little changed, indicating a simple dilution with low ionic strength snowmelt.
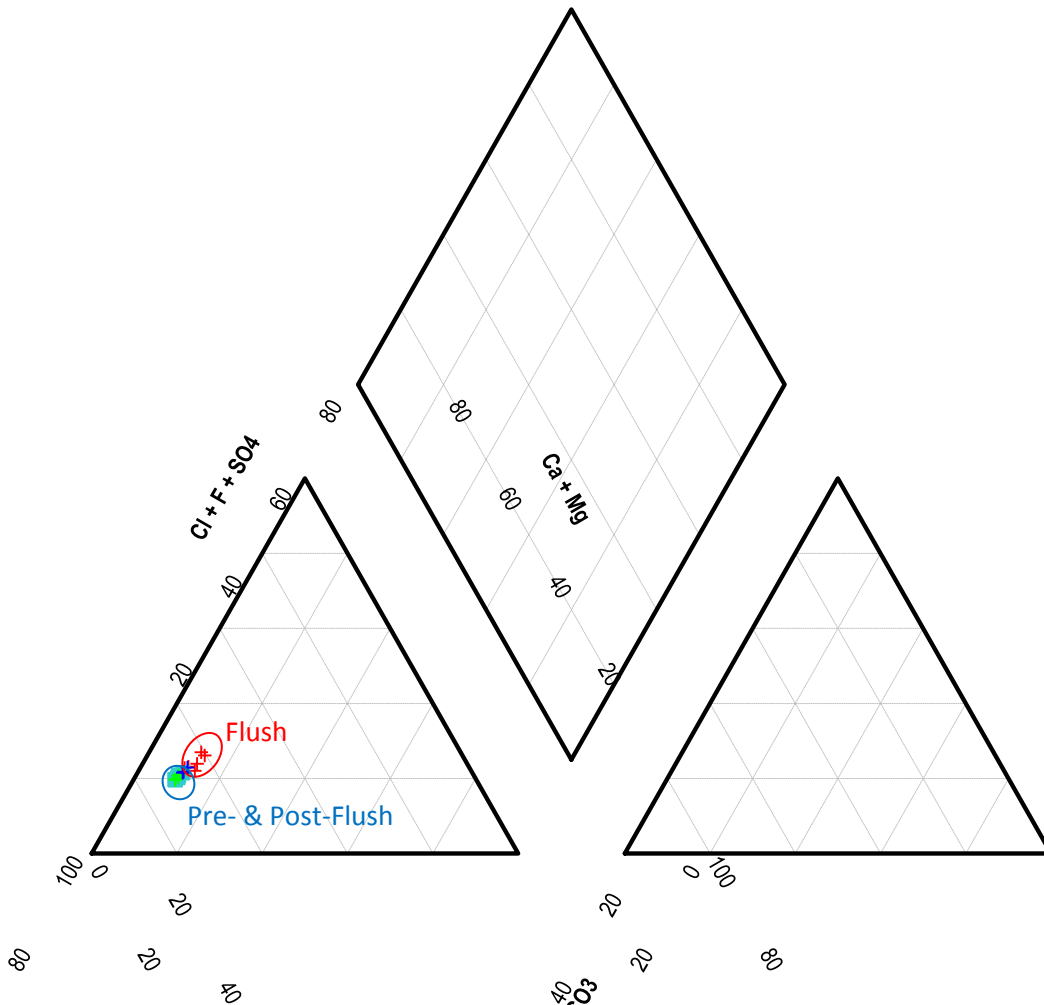

Figure E2. Piper diagram showing major ion composition in different flow conditions in the Blackfoot River, southeastern Idaho, 2009-10. Appreciable separation of the relative ion composition under different flow conditions (spring snowmelt flush, compared to pre- and post-snowmelt flush ion composition) indicates different water sources at different times of the year.

E-3
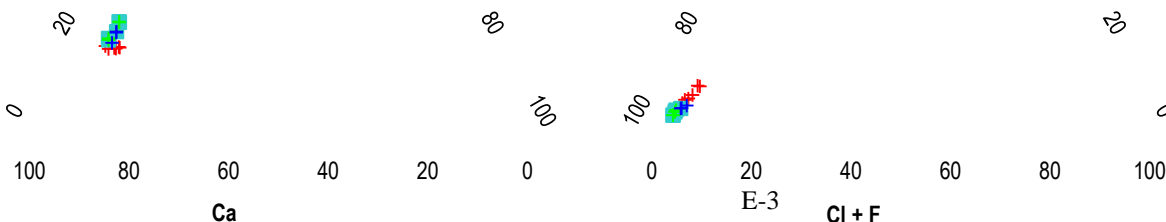
Another relation from the major ion data could be of value for interpreting risks to aquatic life from elevated trace metals such as cadmium and zinc. Water hardness and alkalinity can be estimated well from specific conductance, which may be useful because conductivity is easily and reliably measured in the field, as opposed to titrations or laboratory analyses required for alkalinity or hardness. Water hardness can be estimated within about ± 12 percent with 90 percent confidence, for a given specific conductance (*fig. E3*).
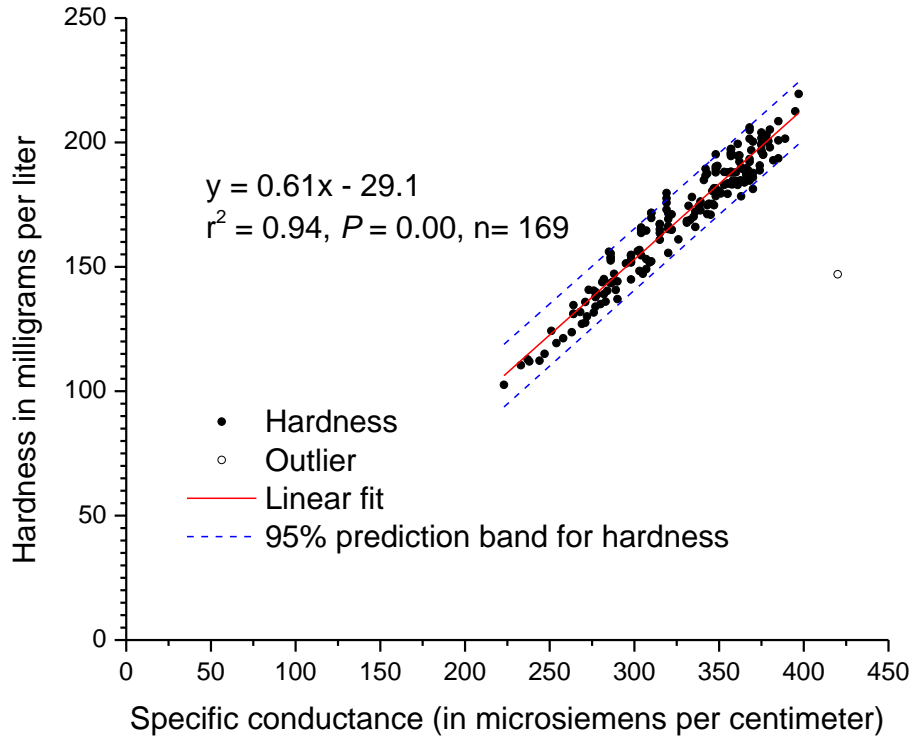

Figure E3. Water hardness (in milligrams per liter as calcium carbonate) can be estimated reliably from field measurements of specific conductance [in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C)]

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