

## APPROACH FOR ENVIRONMENTAL BASELINE WATER SAMPLING

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### ABSTRACT

Samples collected during the exploration phase of mining represent baseline conditions at the site. As such, they can be very important in forecasting potential environmental impacts should mining proceed, and can become measurements against which future changes are compared. Constituents in stream water draining mined and mineralized areas tend to be geochemically, spatially, and temporally variable, which presents challenges in collecting both exploration and baseline water-quality samples. Because short-term (daily) variations can complicate long-term trends, it is important to consider recent findings concerning geochemical variability of stream-water constituents at short-term timescales in designing sampling plans. Also, adequate water-quality information is key to forecasting potential ecological impacts from mining. Therefore, it is useful to collect baseline water samples adequate for geochemical and toxicological modeling. This requires complete chemical analyses of dissolved constituents that include major and minor chemical elements as well as physicochemical properties (including pH, specific conductance, dissolved oxygen) and dissolved organic carbon. Applying chemical-equilibrium and appropriate toxicological models to water-quality information leads to an understanding of the speciation, transport, sequestration, bioavailability, and aquatic toxicity of potential contaminants. Insights gained from geochemical and toxicological modeling of water-quality data can be used to design appropriate mitigation and for economic planning for future mining activities.

### INTRODUCTION

Explorationists are very aware that metal concentrations are highly variable over space in mineralized and mined areas depending on location, climate, underlying geology, geochemistry, and weathering of ore deposits (e.g., Nimick et al., 2003; Church et al., 2007). Researchers also are learning that constituents can be highly variable in time, and that short-term (daily) variations can complicate long-term trends. An example of this short-term variability is demonstrated by Gammons et al. (2007). In this one-day study in a mining influenced stream, one sampler consecutively collected samples going upstream, and another sampler consecutively collected samples going downstream. The sampler who moved downstream concluded that the zinc load steadily decreased downstream, and the sampler moving upstream concluded that the zinc load increased downstream (and that zinc sources existed along the stream). In reality, the average zinc load over the 24-hour period was relatively constant and the differences observed by the samplers were due to diel (24-hour cycle) variations.

When collecting water samples for exploration purposes it is important to keep in mind that the data could later be used to determine pre-mining baseline conditions. As such, it is important to collect, preserve, and analyze water samples so that they can be used to establish an historical framework for comparing future data. This paper covers (1) recent advances in understanding variation in solute concentrations as a function of temporal, spatial, and hydrologic conditions, (2) approaches for water-sampling protocols, and (3) geochemical and toxicological modeling needs. All of these topics are

important in designing and refining sampling plans for both exploration and environmental purposes. Most of the information in this paper applies to sampling surface water, but some of the information also pertains to sampling groundwater.

### SPATIAL AND TEMPORAL VARIATION CONSIDERATIONS

Spatial and temporal variation of metal concentrations can be significant in streams draining mineralized and mined areas. Caruso and Bishop (2009) studied seasonal and spatial variation of metal loads in a mining impacted mountain watershed. They found large variations in metal concentrations and loads between spring snowmelt high flow and summer low flow. They attributed their observed spatial variations to the spatial distribution of mine-waste sources in the watershed and to complex watershed and biogeochemical processes including sorption reactions (see Smith, 1999), surface-water/groundwater interactions, attenuation in the hyporheic zone at the surface-water/groundwater interface, and diel influences. Their study and others illustrate that the variation of solutes, especially trace elements, is extremely complicated and related to a number of processes and to the properties of the trace elements (see Smith, 2007). Underlying geology and mineral-deposit characteristics also can influence spatial variation in metal loads in watersheds (e.g., Plumlee et al., 1999; Church et al., 2007). It is essential to consider this complexity when choosing sampling locations and designing sampling plans to collect water-quality samples.

Nagorski et al. (2003) conducted a year-long study of four Montana streams. They found that monthly changes were dominated by snowmelt and precipitation dynamics, which tend to follow an annual cycle. Daily-scale changes were dominated by episodic events, such as thunderstorms, that resulted in short-term solute and particulate concentrations similar in magnitude to those during the early spring flush. They also observed diel cycles for several constituents and noted that short-term (daily) variations of some geochemical parameters were similar in magnitude to much longer (monthly) timescales.

### Diel (24-Hour) Cycles

In their review of biogeochemical diel cycles in streams, Nimick et al. (2010) state that the amplitude of diel changes for some water constituents can be as large as changes occurring on annual timescales. Nimick et al. (2003) report substantial diel cycles in dissolved metal concentrations (e.g., arsenic, cadmium, manganese, nickel, and zinc) during low-flow conditions for 18 sampling episodes at 14 sites along 12 neutral and alkaline streams draining historical mining areas in Montana and Idaho. They documented variations in zinc concentrations as much as 500% between the maximum concentration just after sunrise and the mid-afternoon minimum concentration. They attribute these diel variations to in-stream geochemical processes, especially sorption processes responding to diel changes in pH and temperature. In a study of the seasonality of diel cycles, Nimick et al. (2005) state that "Diel cycles of dissolved metal concentrations should be assumed to occur at any time of year in any stream with dissolved metals and neutral to alkaline pH." Diel cycles also have been documented in acidic streams and appear to be

related to photoreduction of iron oxyhydroxides (e.g., McKnight et al., 1988; Sullivan and Drever 2001).

Diel variations have serious implications for the evaluation of historical water-quality data, collection of baseline water-quality data, and collection of mineral-exploration data. Nagorski et al. (2003) point out that short-term (daily) variations of constituent concentrations in streams can be similar in magnitude to variations reported for seasonal timescales. It is therefore necessary to consider these short-term variations when designing water-quality sampling plans, and it cannot be assumed that a single water sample accurately represents water-quality conditions for a given stream. Current U.S. Environmental Protection Agency (EPA) acute freshwater aquatic-life standards for metals refer to 24-hour average concentrations. As such, it might be useful to consider a sampling program that involves collecting samples throughout the day and night to obtain actual 24-hour average concentrations (see Nimick et al., 2010). Also, consistently collecting periodic samples at a particular site at a specific time of day minimizes the influence of diel variations (Nagorski et al., 2003). However, this approach is problematic for comparisons between sites unless all sites are sampled at the same time under similar hydrologic conditions, as shown by the example given in the Introduction.

### **Flow Considerations**

In mineralized and mined areas it is common to see relationships between solute concentrations and flow. Predominant causes of changes in hydrologic conditions include evapotranspiration, snowmelt, rain storms, and loss or gain due to infiltration through the streambed. In their evaluation of historical surface-water quality data for the Red River Valley, New Mexico, Maest et al. (2004) found that the time of year has a major effect on water quality, due to changes in hydrologic conditions. They also report that episodic events, such as thunderstorms, caused flushing of sulfide oxidation products from altered areas, and they note that alkalinity values decrease during storm events, which indicates that there can be short-term changes in buffering capacity. Jambor et al. (2000) also reported elevated metal concentrations in streams draining mined areas with increasing flow due to flushing of stored acid and metals from soils and mining wastes by melting snow and rain events. McKnight and Bencala (1990) and Boyer et al. (1997) reported flushing of dissolved organic carbon and other constituents from soil during spring snowmelt. Generally, non-episodic increase in flow over longer time periods tends to have a dilution effect.

When collecting stream-water samples it is important to know where the samples fall on the annual stream hydrograph. Maest et al. (2004) define five different hydrologic conditions on the hydrograph: rising limb, peak, falling limb, storm event, and low flow. They define rising limb as starting when flows first increase as a result of snowmelt and ending when flows reach 50% of peak flow for that water year. Peak flow is defined as starting and ending at 50% of peak flow on either side of the peak. Falling limb starts after the peak when flows fall to 50% of peak values and ends when flows fall to 25% of peak values. Low flow starts at 25% of peak flow after the peak and continues to the start of the rising limb the following water year. Storm events are defined as increases in flow superimposed on the hydrograph.

Understanding interactions between groundwater and surface water is an important, often overlooked consideration in water management. Winter et al. (1998) provide an overview of groundwater/surface-water interactions. Interactions at the surface-water/groundwater interface (the "hyporheic zone") can play an important role in the concentration and load of constituents and can have significant environmental influences on biogeochemical processes (Bencala, 2005). Hyporheic exchange flows are one of several mechanisms that influence the interaction between surface water and groundwater (Winter et al., 1998). The direction of this exchange varies depending on the time of year and the hydrologic

conditions. The geological, hydrological, and vegetation properties of the catchment and streambed topography generally determine the degree of surface-water/groundwater exchange. Gandy et al. (2007) provide a review of information about attenuation of mining-derived pollutants in the hyporheic zone, and Ibrahim et al. (2010) have developed a conceptual framework for this interface. Important processes include sorption, precipitation, redox reactions, and reductive dissolution of iron and manganese oxyhydroxides. Researchers continue to study and model the hyporheic zone in various environments (e.g., Bencala, 2000; Runkel et al., 2003; Zaramella et al., 2006).

### **SAMPLING PROTOCOLS**

There have been major advances made in developing "clean" sampling procedures and extremely sensitive analytical techniques for trace elements. However, sampling procedures that address and capture the natural variability of constituents in water need some further development. It is critical to use current, relevant, documented sampling protocols and to record how, when, and where samples were collected, preserved, and analyzed. There are numerous protocols that describe sampling, preservation, and analytical procedures (e.g., U.S. Geological Survey, variously dated). Great care must be taken to ensure that water-quality sampling procedures, sampling devices, and preservatives do not contaminate the sample, react with the sample, or interfere with the analytical method. Experienced personnel should be chosen to collect water-quality samples. Collection of QA/QC samples, such as replicates and blanks, is very useful to determine if any contamination has occurred and whether variation in constituents between samples is due to contamination or to actual variation. It is important to document such things as frequency of sampling, whether samples were composited, where in the stream samples were collected, whether samples were collected using a pump or by a grab method, the existence of QA/QC samples, and whether samples were filtered (and filter size and type). Field parameters (i.e., temperature, pH, specific conductance, dissolved oxygen) should be measured in the field, and samples should be filtered in the field. Documentation of calibration should be included for all field instruments.

Federal and state regulations for water-quality criteria have changed over time regarding total recoverable metals and total dissolved metals. Federal regulations began to recommend use of dissolved metals in 1995 (U.S. Environmental Protection Agency, 1995); prior to 1995 federal water-quality criteria were based on total recoverable metals. It is important to collect samples in a manner that addresses current regulations and also meets the needs of geochemical or toxicological modeling (i.e., dissolved concentrations). When collecting stream-water samples below confluences or inflows it is important to ensure that the stream water is well mixed or that sampling procedures are chosen that account for poorly-mixed conditions. Measuring specific conductance across the stream at the sampling location can help determine whether the stream water is well mixed. When choosing analytical methods it is key to consider analytical limits of detection and interferences with solutes common in mineralized and mined areas. QA/QC samples, such as standard reference materials, should be submitted to the laboratory along with the samples so that analytical performance can be evaluated. The National Environmental Methods Index (NEMI, <http://www.nemi.gov/>) is an online methods database that can be used to search for and compare regulatory and non-regulatory analytical methods.

It can be quite useful to compile meteorological information (e.g., temperature min/max, precipitation, and snowfall) at the time of sample collection and to retain that information with the analytical information. Photographs also can be useful to document sampling sites and conditions for future consideration. Detailed field notes should include date, time, recent and current weather conditions, field conditions, water color, and any other relevant information.

Stream-water flow/discharge measurements can be quite valuable when comparing solute concentrations between different sampling events because concentration variations and flow variations generally are linked. There are a number of traditional techniques to obtain stream-water flow or discharge measurements (e.g., U.S. Geological Survey, variously dated (b)). An approach using a tracer-dilution method to quantify stream-water discharge and synoptic sampling to quantify solute concentrations has been developed to determine metal loading in streams located in mined and mineralized areas (Kimball, 1997; Kimball et al., 2007). Using this approach it is possible to identify and quantify the principle inflows of metals, the presence of non-point source, dispersed inflows of metals, and the amount of attenuation of metals in a stream.

#### **GEOCHEMICAL AND TOXICOLOGICAL MODELING NEEDS**

For geochemical modeling it is necessary to have complete dissolved water analyses including major, minor, and trace elements, and both anions and cations. Additional important determinations include pH, temperature, specific conductance, alkalinity, and dissolved oxygen. Potentially useful determinations in mineralized and mined areas include ferrous iron, total iron, and acidity. In water with low dissolved oxygen concentration, it also may be useful to directly measure redox couples of interest. Current analytical techniques, such as ICP-AES and ICP-MS, offer analysis of a number of chemical elements. Therefore, it is relatively simple to obtain complete water analyses. Also, complete water analyses can serve as a guide to unanticipated environmental concerns or to potential by-products that may be recovered. Nordstrom and Munoz (2006) discuss information needs for various applications of geochemical modeling. For transport modeling it is necessary to have water flow or discharge measurements. For inverse modeling it is necessary to have mineralogical information about the geologic material in contact with the water.

Toxicological modeling of water quality is beginning to have a presence in federal regulations. For example, the EPA incorporated the biotic ligand model (BLM) into its recently revised aquatic life ambient freshwater quality criteria for copper (U.S. Environmental Protection Agency, 2007). The BLM is a computational model that predicts metal toxicity to biota in aqueous systems for one metal and one organism at a time (Di Toro et al., 2001; Santore et al., 2001). Required input for the BLM includes temperature, pH, dissolved organic carbon (DOC), percent DOC as humic acid (default is 10%), alkalinity, and dissolved concentrations for calcium, magnesium, sodium, potassium, sulfate, and chloride. Although DOC samples are rarely collected, DOC is a required input parameter for the BLM and can have a significant influence on predicted toxicity of some metals such as copper. Therefore, it is important to include DOC in water sampling plans. A research version of the BLM is available at [http://www.hydroqual.com/wr\\_blm.html](http://www.hydroqual.com/wr_blm.html) and allows for computations for copper, silver, cadmium, and zinc. In addition to determining site-specific water-quality criteria, the BLM can be used to determine the time of year when the water chemistry is most toxic, which often is difficult to determine without a rigorous and expensive toxicity-testing program.

#### **SUGGESTIONS**

It is suggested that the following steps be taken when developing a water-quality sampling plan.

- Follow current, relevant sampling, preservation, and analytical protocols. Use consistent methodologies employing best-practice techniques and equipment, and appropriate QA/QC. Use experienced personnel to collect water samples. Avoid sample contamination. Measure field parameters (i.e., temperature, pH, specific conductance, dissolved oxygen) in the field, and filter

samples in the field. Ensure that stream water is well mixed at sampling locations.

- Collect samples for complete dissolved chemical analyses, including major, minor, and trace cations and anions, and dissolved organic carbon.
- Communicate with the laboratory to ensure that adequate sample volumes are collected and that proper sample preservation is performed.
- Be consistent in sampling procedures, locations, and time of day.
- Conduct stream-water flow or discharge measurements.
- Collect meteorological information.
- Account for natural variability by nesting short-term studies within long-term studies that encompass variable climatic and hydrologic conditions (see Nagorski et al., 2003).
- Obtain samples throughout the day and night for an actual 24-hour average of constituent concentrations at a given site (see Nimick et al., 2010).
- For comparison between sites, collect samples simultaneously under similar hydrologic conditions.
- Sample high-flow and transient hydrologic events to obtain an estimate of flushing of constituents from soils, mining wastes, hyporheic zones, etc. in a watershed.

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