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High-frequency, long-duration water sampling in acid mine drainage studies: A short review of current methods and recent advances in automated water samplers



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ABSTRACT

Hand-collected grab samples are the most common water sampling method but using grab sampling to monitor temporally variable aquatic processes such as diel metal cycling or episodic events is rarely feasible or cost-effective. Currently available automated water samplers are a proven, widely used technology and typically collect as many as 24 samples during a deployment. However, these automated water samplers are not well suited for long-term sampling in remote areas or in freezing conditions. There is a critical need for low-cost, long-duration, high-frequency water sampling technology to improve our understanding of the geochemical response to temporally variable processes. This review article will examine recent developments in automated water sampler technology and utilize selected field data from acid mine drainage studies to illustrate the utility of high-frequency, long-duration water sampling.

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1. Introduction

Hand-collected water samples, also known as “grab”, “spot” or “discrete” samples, are the most common type of water sample collected and well-developed protocols have been established to avoid sampling error and contamination (USGS, 2006). Grab sampling can be very labor intensive and expensive, with significant costs for salary, field vehicles and sampling equipment. For example, the U.S. Geological Survey (USGS) estimated that a single grab sample collected from the Mississippi River costs 4000–6000 USD before analytical costs are added in Horowitz (2013). If study sites are in areas that are difficult to access (remote, snowbound, large river, etc.) or dangerous (abandoned mines, flash flood or high current areas, etc.) then sampling costs can increase significantly due to specialized vehicles and safety procedures.

The goal of water sampling is to collect a ‘representative’ water sample while maintaining sample integrity and sample accuracy. One of the greatest challenges in collecting a ‘representative’ water sample is addressing the issue of temporal changes in water chemistry (Madrid and Zayas, 2007). Long-term, high-frequency monitoring of more easily measured water quality parameters such as streamflow and conductivity clearly demonstrate that water chemistry changes can occur on timescales ranging from seconds to years. However, documenting temporally variable processes such as diel cycles or episodic events with traditional grab sampling is often very difficult, expensive and rarely feasible in remote areas.

Efforts to monitor high-frequency biogeochemical aquatic processes have primarily focused on the development of onsite sensors or analyzers for nutrients, gases, and some metals (Johnson et al., 2007; Lourião-Cabana et al., 2010; Namour et al., 2010; Superville et al., 2011). These onsite instruments tend to be relatively expensive (15,000 to >50,000 USD) and most instruments only measure a single analyte (Johnson et al., 2007). Onsite analyzers/sensors are rarely able to provide the multi-element detection capability and low detection limits of laboratory-based methods so there will always be value in collecting a water sample and taking it back to the laboratory for analysis.

Advances in high-sensitivity analytical instruments such as inductively coupled plasma mass spectrometry (ICP-MS) now provide routine sub parts per billion detection of over 50 elements with only a few milliliters of sample (Lamothe et al., 2002). Our understanding of biogeochemical processes is greatly enhanced when analytes with differing reaction pathways are detected. For example, in acid mine drainage locations where pH may fluctuate between acidic and neutral conditions, the geochemical cycling and eco-toxicity of pH-sensitive metals (e.g. Al, Pb, Cu) may be completely different from less pH-sensitive metals (e.g. Zn, Cd) (Nordstrom, 2011).

Recent advances in water sampler design have primarily focused on development and application of passive diffusion samplers which collect a single time-integrated sample (Vrana et al., 2005; Kot-Wasik et al., 2007). In the simplest terms, passive water samplers rely on the diffusive transfer of analytes from the

medium (water) through a semi-permeable barrier to a sample collection chamber (Allan et al., 2006; Vrana et al., 2005). Passive samplers have many attractive features including: small size; low-cost (10–100 USD); simple to deploy; require no power or electronics; provide analyte pre-concentration; no water depth limitations; and can be deployed for days to a few months at a time. Membrane composition determines what compounds will diffuse into the sample collection chamber and many different classes of compounds (organics, pesticides, pharmaceuticals, metals, etc.) can be sampled with passive diffusion samplers (Vrana et al., 2005; Mills et al., 2007; Pesavento et al., 2009; Balistrieri et al., 2012). Analyte uptake depends on a number of environmental and physical factors that affect the diffusive transfer such as water temperature, turbulence, membrane/gel properties and bio-fouling and passive diffusion samplers require extensive laboratory and field calibration for proper use (Vrana et al., 2005). While diffusion-based samplers can provide information about time weighted average analyte concentrations, these water samplers are not well suited for examining the details of high-frequency aquatic processes (Shaw and Mueller, 2009) and passive diffusion samplers will not be examined further.

This review article will begin with an example of the challenges in remote water sample collection followed by a discussion of currently available high-frequency water sampling technology. Next, a brief look at recent USGS field applications of automated high-frequency water sampling will be presented followed by a discussion of potential future directions for water sampling. Selected USGS data from acid mine drainage studies in Colorado will be used to illustrate the advantages of high-frequency water sampling for different scientific objectives. The goal of this review article is to illustrate the utility of new automated water sampling technology. A detailed discussion of sampling sites, analytical methods and interpretation of geochemical results are beyond the scope of this article and can be found in the cited literature.

1.1. Limitations of traditional water sampling methods

Fig. 1 illustrates the basic problem of matching water sampling frequency with temporally changing water quality in a remote, difficult to access location. The Standard Mine is an abandoned precious metal mine site located at an elevation of 3350 m near the town of Crested Butte in central Colorado, USA. The Standard Mine was listed as a US Environmental Protection Agency Superfund site in 2006 due to high levels of Zn, Cd, Pb, and Mn issuing from the mine adit (Manning et al., 2011). Access to the mine site is by 4WD vehicle from mid-June to late October. Deep snow from November to June requires snow machines and long backcountry ski trips through avalanche prone areas to access the Standard Mine in winter. Hand-collected samples were analyzed for over 40 elements by ICP-MS and results for Pb and Mn

are presented here to demonstrate contrasting geochemical responses to temporally varying conditions (Manning et al., 2011).

Fig. 1 shows data from automated daily monitoring of flow and conductivity out of the Standard Mine adit and Pb and Mn data from hand-collected grab samples. Adit flow begins to increase in mid-April due to snowmelt runoff, peaks in early June, and decreases to low values during the summer. Conductivity tends to decrease with increasing flow but there is a lot of variability (Fig. 1).

During winter 2010, USGS personnel used 4WD vehicles, snow machines and skis to reach the mine site and collected four bi-monthly grab samples from late March to May (Manning et al., 2011). During the initial snowmelt runoff in mid-April, Pb concentrations spiked from <0.1 ppm to over 1.5 ppm (Fig. 1A), while Mn concentrations decreased from 11 ppm to 7 ppm (Fig. 1B). In early May, flow out of the adit decreased, Pb levels decreased toward low baseline values and Mn concentrations increased toward winter high values. Increasing flows from mid-May through June showed elevated Pb levels (Fig. 1A). Mn showed a minimum concentration during maximum flow from the adit (Fig. 1B). The intensive field efforts during the deep winter demonstrated that early snowmelt changes in flow have a dramatic effect on Pb and Mn concentrations at the Standard Mine Superfund site (Manning et al., 2011). Estimated field costs for salary (3 scientists), vehicles (snow machines), travel and sampling equipment were 2500 USD per sample for a total of 10,000 USD for four over-winter samples.

From June to September the Standard Mine is accessible by 4WD vehicle and four samples were collected (Fig. 1). Pb concentrations were elevated during the peak snowmelt runoff in June and lower during the low flow summer period (Fig. 1A). Mn had the opposite trend; lowest concentrations during maximum runoff in June and high concentrations during low flow periods (Fig. 1B). Estimated field costs for salary, vehicles travel and sampling equipment were 1000 USD per sample for a total of 4000 USD for four samples.

Access to remote sites typically limits water sample collection to a few samples collected during the more accessible summer period and this low-frequency sampling rarely captures the details of transient events. Higher frequency water sampling with hand-collected grab sampling is labor intensive and often cost prohibitive. The intense winter and summer water sampling at the Standard Mine provided 8 grab samples during a 7-month period with an overall estimated cost of 14,000 USD or 1750 USD per sample. The need for reliable, low-cost automated water sampling is clear.

2. Commercially available automated water samplers

The high expense of collecting water samples spurred the development of automated water samplers. Most commercially

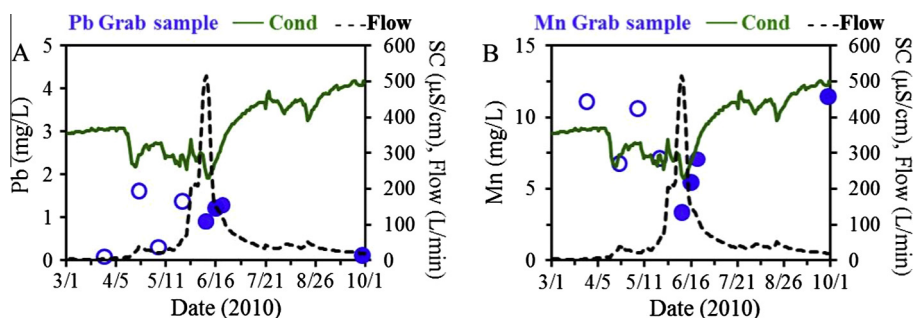


Fig. 1. Standard Mine March to September 2010 data for conductivity (—), flow (---), Pb (A) and Mn (B). Summer 4WD access provided 4 grab samples (●). Winter snowmobile and backcountry ski access provided 4 additional grab samples (○). Snowmelt runoff beginning in April lead to dramatic changes in Pb and Mn concentrations.

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