MiniSipper: A New, High-capacity, Long-duration, Automated In Situ Water Sampler for Acid Mine Drainage Monitoring

Thomas Chapin[1], Christina Progess[2], Andrew Todd[1]

[1]*USGS, Box 25046, MS 964D, Denver Federal Center, Denver, CO 80225, tchapin@usgs.gov, atodd@usgs.gov*
[2]*EPA, 1595 Wynkoop St, Denver, CO80202, Progess.Christina@epa.gov*

Abstract The US Geological Survey (USGS) has developed the MiniSipper, a low-cost, automated, *in situ* water sampler to provide high-resolution, year-round, sampling for acid mine drainage monitoring at remote sites. The MiniSipper typically collects 250 five mL acid preserved water samples and operates unattended for 8–12 months for over-winter and snowmelt runoff sampling. Year-round, high-resolution metal data from two different abandoned mines in CO, USA document opposite water quality responses to snowmelt runoff and demonstrate the advantages of MiniSipper technology in difficult sampling environments.

Keywords high-resolution sampling, acid mine drainage, seasonal variations, *in situ* water sampler

Introduction

Abandoned mines are often located in remote, high-elevation areas that are very challenging to sample, especially during the inaccessible 7–8 month winter period. Hand-collected ‘grab’ samples are the most common type of water sampling in remote areas and grab sampling typically collects a few samples per year at times when the site is easily accessible. Grab sampling can be very labor intensive and expensive, with significant costs for personnel salary, field vehicles and sampling equipment. Thus high-resolution grab sampling in remote as well as snowbound areas is usually not feasible nor affordable. Automated samplers could provide water sampling at these remote, difficult to access, or snowbound sites, but currently available automated samplers are typically large, heavy, collect 24 1 L samples, and are not well suited for operation in freezing conditions.

The US Environmental Protection Agency (EPA) is currently evaluating remediation options at the abandoned Pennsylvania Mine near Keystone, CO, USA and the abandoned Standard Mine near Crested Butte, CO, USA (Fig. 1). Both mines are situated in high alpine watersheds at ≈ 3300 m above sea level and are snowbound for 7–8 months/a. The Pennsylvania and Standard Mines have large metal sulfide ore deposits and are significant point sources of acid mine drainage and toxic metals to streams that have both water supply and recreational use classifications. Local, state

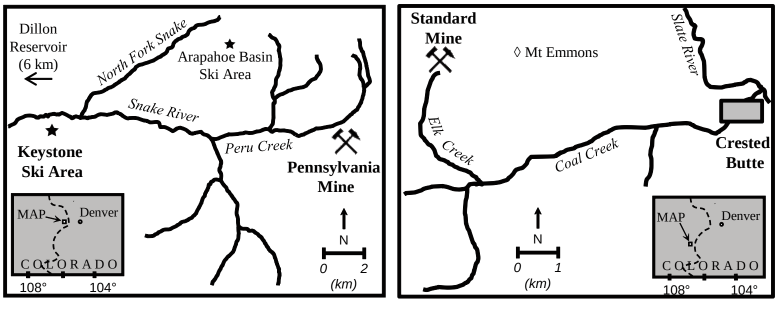

***Fig. 1** Location maps of the Pennsylvania and Standard Mines, CO, USA.*

and federal agencies are examining clean up options for the Pennsylvania and Standard Mines but their remediation designs are hampered by the limited amount of water quality data, especially metal data from major runoff events such as spring snowmelt runoff and large rainstorms. In order to better understand the effects of major runoff events, the EPA has contracted with the USGS to provide high-resolution water sampling at the Pennsylvania Mine and Standard Mine over the entire water year. The USGS has developed the MiniSipper; a small, lightweight, low-cost, high-capacity water sampler to address the limitations of current automated water samplers. This paper will discuss year-round high-resolution metal data collected by MiniSippers from the Pennsylvania and Standard Mines.

Methods

MiniSipper methods and analytical details can be found in Chapin and Todd (2012) and only a brief overview is presented here. The MiniSipper is a battery powered, automated, *in situ* water sampler that uses micro-pumps to inject filtered water samples, acid preservative, and a gas separation bubble into a long sample coil (Fig. 2). The MiniSipper typically collects 250 5 mL samples with <5 % carryover between samples. Sample volume, timing and number are adjustable and up to five hundred 2.5 mL samples can be collected. Sample filtration is provided by a 10 µm polyethylene filter which closely tracks 0.45 µm grab samples. After recovery, samples are analyzed by standard USGS ICP-MS methods for 44 elements (Lamothe *et al.* 2002). Total cost for MiniSipper parts is ≈\$3,000 USD. The small size, low power requirement, and *in situ* operation of the MiniSipper enable 8–12 month deployments and the MiniSipper operates in water under surface ice/snow for over-winter and snowmelt runoff sampling.

MiniSippers were deployed at the Pennsylvania and Standard Mine adits and sampled acid mine discharge every 3–7 days during winter and daily from spring to fall. Over-winter hand-collected grab sampling by USGS personnel required snow machine access and backcountry skiing to reach the Pennsylvania and Standard Mines from November through June. Comparison of MiniSipper results with hand-collected grab samples is an important validation check and MiniSipper results were typically within 10 % of grab sample results. Data gaps were caused by instrument failures or MiniSipper redeployments. Instrument reliability has improved and the MiniSipper now routinely operates for 8–12 months unattended.

Results and Discussion

The following discussion will focus on Cu, Mn, and Zn results as these toxic metals are representative of different geochemical responses to hydrologic events observed at both the Pennsylvania Mine and Standard Mine. We have high resolution annual data from 2009 through 2012 at both the Pennsylvania and Standard Mines and will examine subsets of this data.

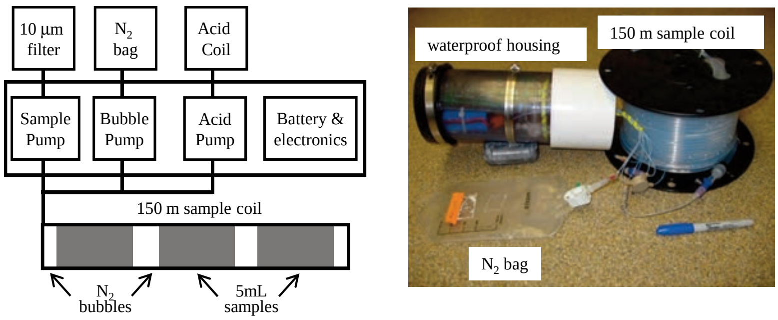

Fig. 2 *Schematic layout and photo of MiniSipper.*

Pennsylvania Mine

Metal concentrations at the Pennsylvania Mine site showed a consistent annual pattern with the lowest metal concentrations during the low-flow winter period and the highest metal concentrations during snowmelt runoff (Fig. 3). During snowmelt runoff, metal concentrations at the Pennsylvania Mine adit increased 2–15 times over late winter low-flow metal concentrations. After peak metal concentrations in mid-June, metal concentrations at the Pennsylvania Mine gradually declined over the next 6 months to low-flow winter (baseline) metal concentrations (Fig. 3). The gradual decrease in metal concentrations after snowmelt runoff can be interrupted if large summer thunderstorms lead to a second metal concentration and conductivity peak as observed in 2010 (Fig. 3). These secondary late-summer conductivity and metal peaks were not observed in 2009 (Fig. 3) or 2011–2012 (not shown).

Significant thunderstorms were observed in summer 2010 and led to dramatic changes in water quality flowing out of the Pennsylvania Mine. Fig. 4 shows the Zn concentration, flow and conductivity response to snowmelt runoff during June and large rainstorms at the end of July and beginning of summer of 2010 was similar to metal increases observed during the snowmelt runoff in June 2010 (Fig. 4). Metals concentrations declined slowly after the large late summer rain event, taking over a month to return to pre-rain metal concentrations (Fig. 4). Late summer increases in metal concentrations were not recorded in 2009, 2011, or 2012. High metal concentrations associated with high runoff at the Pennsylvania Mine likely indicate that a rising water table comes into contact with efflorescent salts or isolated mine pools which increases metal concentrations in the mine runoff (Butler *et al.* 2008, Nordstrom 2009, Chapin and Todd 2012).

Standard Mine

In contrast to the Pennsylvania Mine, most metals at the Standard Mine (*e.g.* Mn) showed a dilution signature with lowest metal concentrations during maximum snowmelt runoff and highest metal concentrations during the low-flow winter period (Fig. 5). Zinc concentrations were high during the winter low-flow period, increased during the initial snowmelt runoff in April and May, and were lowest during maximum snowmelt runoff (Fig. 5). The Zn

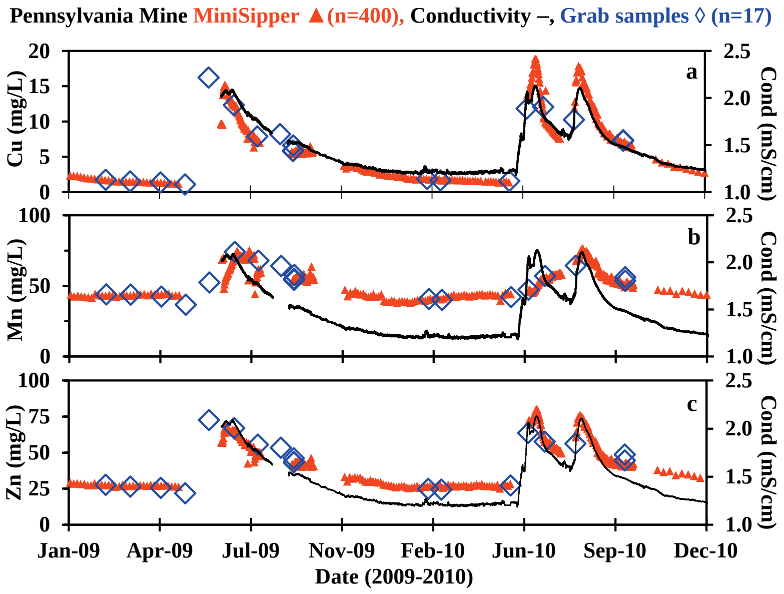

Fig. 3 *Two years of conductivity and Cu (a), Mn (b) and Zn (c) concentrations at the Pennsylvania Mine (n=400). Large blue symbols represent hand-collected grab samples (n=17)*

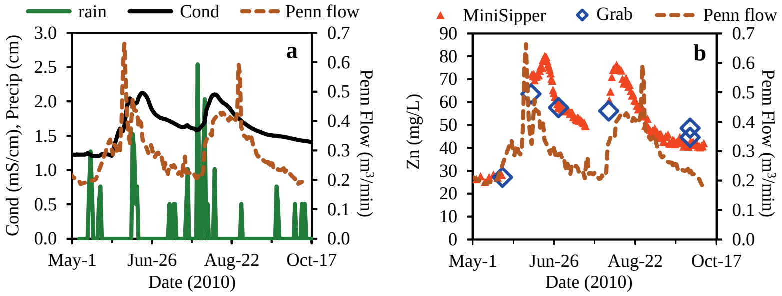

Fig. 4 Pennsylvania Mine conductivity and flow response to snowmelt runoff and large summer rainstorm event (a). Zinc response to snowmelt runoff and late summer rain event (b).

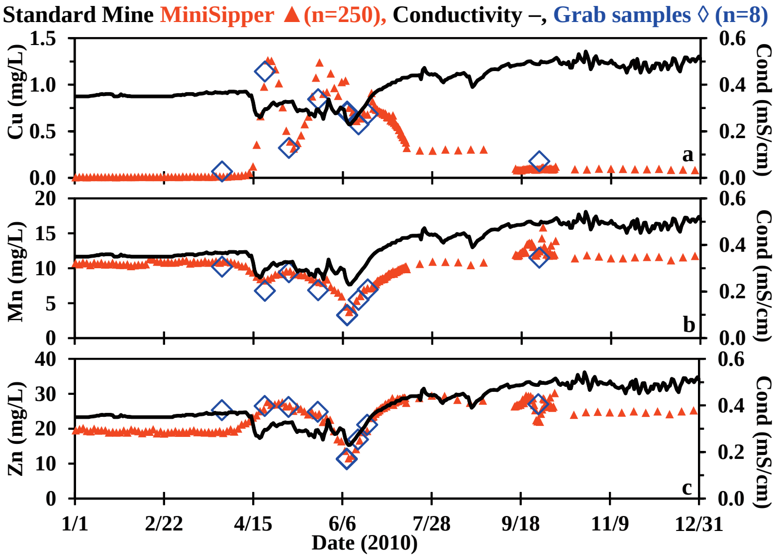

Fig. 5 Annual conductivity and Cu (a), Mn (b), and Zn (c) patterns at the Standard Mine (n=250). Hand-collected grab samples are in blue (n=8).

pattern suggest that initial snowmelt runoff pushed elevated Zn waters out of the mine workings and then Zn concentrations were diluted during maximum snowmelt runoff. Metals sensitive to pH changes (*e.g.* Cu) showed very different behavior at the Standard Mine, with lowest values during the winter low-flow period and transient high concentration spikes during initial snowmelt runoff (Fig. 5).

Fig. 6 shows the water quality details during snowmelt runoff in 2010 at the Standard Mine and we observed some interesting responses for pH sensitive metals. During the November-April low-flow winter period, Cu concentrations were low (<0.1 mg/L), pH was above pH 6, and conductivity was steady. In mid-April temperatures warmed and initial snowmelt led to an increase in flow from the Standard Mine and a decrease in conductivity (Fig. 6). The initial snowmelt pulse caused a drop in pH (pH >6 to pH 3) and a large spike in Cu concentrations (<0.1 to 1.25 mg/L, Fig. 6). Initial snowmelt runoff pH and metal spikes have been observed in other snowpack dominated acid mine drainage sites(Sondergaard *et al.* 2008). An early May snowstorm dropped temperatures and refroze the snowpack. This resulted in a decrease in flow, increase in pH (pH 3 to pH5), and decreased Cu concentrations to ≈ 0.3 mg/L for a few weeks (Fig. 6). In late May 2010, the area warmed again and snowmelt runoff resumed, resulting in an increase in flow, decrease in pH, and increase in Cu concentrations (Fig. 6). During maximum snowmelt runoff in mid-June, waters issuing from the Standard Mine had pH values between 3–4 and relatively high Cu concentrations (0.6–1.0 mg/L). After peak snowmelt runoff, Cu concentrations decreased during summer and remained low through the fall and winter. Other pH sensitive metals (Al and

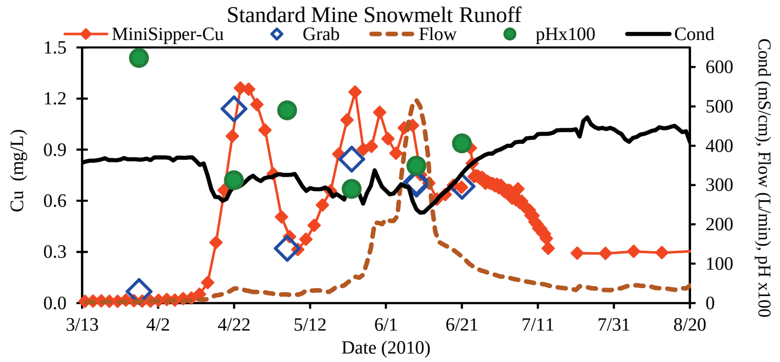

Fig. 6 *Details of early snowmelt effects on pH and MiniSipper Cu concentrations. Large blue symbols and pH data are hand-collected grab samples.*

Pb) displayed the same pattern as Cu (not shown). MiniSipper results were confirmed by fortuitously-timed USGS grab sampling which required snow mobile and backcountry ski access to the Standard Mine at two week intervals from late March through June 2010 (blue diamond symbols, Manning *et al.* 2011). This early snowmelt pattern was observed again in 2011 so the early pulses in pH and pH sensitive metals may be a common response at the Standard Mine (not shown).

Metal-Conductivity Correlations

Toxic metals such as Cu and Zn were highly correlated with conductivity at the Pennsylvania Mine (R^2> 0.9, Fig. 7), but were poorly correlated with conductivity at the Standard Mine (R^2< 0.4, Fig 7). High-resolution conductivity data is relatively easy and inexpensive to collect and conductivity could be used as a proxy for metal concentrations where metals are highly correlated to conductivity. This opens up the potential for low-cost, real-time metal flux estimates using real-time conductivity and flow data. Conductivity based metal estimates would be a valid approach at the Pennsylvania Mine but not at the Standard Mine. Robust conductivity-metal correlations require high-resolution metal and conductivity data throughout the entire water year. One of the greatest advantages of MiniSipper technology is the ability to inexpensively collect water samples during the entire year, especially during inaccessible periods.

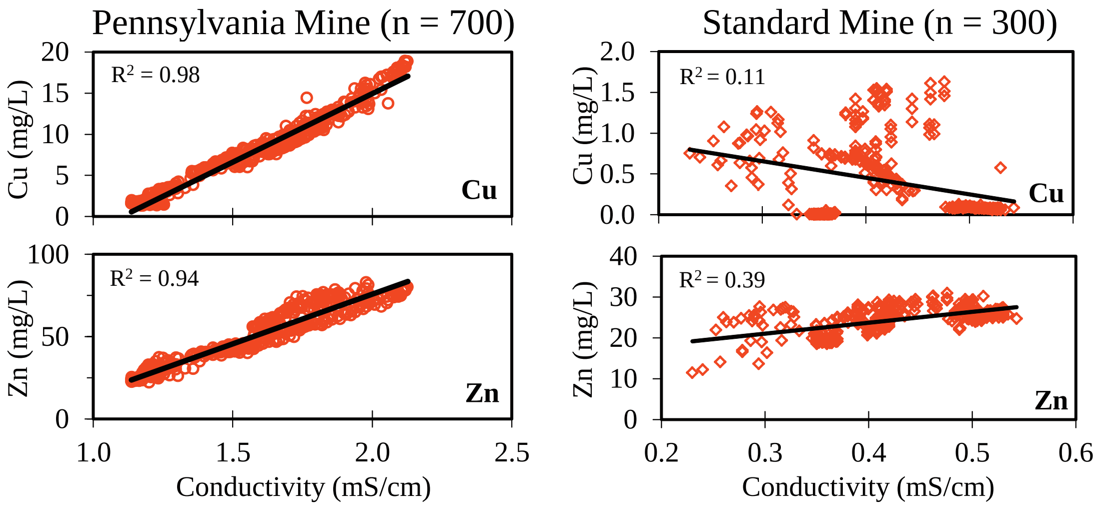

Fig. 7 *Conductivity-metal correlations for the Pennsylvania and Standard Mines.*

Conclusions

MiniSippers provide low-cost, high-resolution water sampling for year-round monitoring of acid mine drainage systems. We observed excellent agreement between hand-collected grab samples and MiniSipper results at both the Pennsylvania and Standard Mines. MiniSipper sampling provided a detailed look at metal responses to hydrologic events that had not been previously documented.

The MiniSipper is a very flexible platform and is easily adapted to other sampling challenges. MiniSippers have been used in tracer studies; in high-resolution monitoring of watersheds impacted by wildfires; and deployed underground for year-long, high-resolution monitoring of acid mine drainage sites. Other MiniSipper applications currently undergoing field-testing are the Borehole MiniSipper and the Event Response MiniSipper. The Borehole MiniSipper is a smaller instrument that fits down a 5 cm borehole and collects 52 water samples over an entire year. The Event Response MiniSipper has a depth-sensitive trigger that puts the MiniSipper into a faster sampling mode to capture the details of fast transient events such as flash flood events.

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