



Estimating instream constituent loads using replicate synoptic sampling, Peru Creek, Colorado

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SUMMARY

The synoptic mass balance approach is often used to evaluate constituent mass loading in streams affected by mine drainage. Spatial profiles of constituent mass load are used to identify sources of contamination and prioritize sites for remedial action. This paper presents a field scale study in which replicate synoptic sampling campaigns are used to quantify the aggregate uncertainty in constituent load that arises from (1) laboratory analyses of constituent and tracer concentrations, (2) field sampling error, and (3) temporal variation in concentration from diel constituent cycles and/or source variation. Consideration of these factors represents an advance in the application of the synoptic mass balance approach by placing error bars on estimates of constituent load and by allowing all sources of uncertainty to be quantified in aggregate; previous applications of the approach have provided only point estimates of constituent load and considered only a subset of the possible errors. Given estimates of aggregate uncertainty, site specific data and expert judgement may be used to qualitatively assess the contributions of individual factors to uncertainty. This assessment can be used to guide the collection of additional data to reduce uncertainty. Further, error bars provided by the replicate approach can aid the investigator in the interpretation of spatial loading profiles and the subsequent identification of constituent source areas within the watershed.

The replicate sampling approach is applied to Peru Creek, a stream receiving acidic, metal-rich effluent from the Pennsylvania Mine. Other sources of acidity and metals within the study reach include a wetland area adjacent to the mine and tributary inflow from Cinnamon Gulch. Analysis of data collected under low-flow conditions indicates that concentrations of Al, Cd, Cu, Fe, Mn, Pb, and Zn in Peru Creek exceed aquatic life standards. Constituent loading within the study reach is dominated by effluent from the Pennsylvania Mine, with over 50% of the Cd, Cu, Fe, Mn, and Zn loads attributable to a collapsed adit near the top of the study reach. These estimates of mass load may underestimate the effect of the Pennsylvania Mine as leakage from underground mine workings may contribute to metal loads that are currently attributed to the wetland area. This potential leakage confounds the evaluation of remedial options and additional research is needed to determine the magnitude and location of the leakage.

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1. Introduction

Effective remediation of streams affected by acid mine drainage requires detailed knowledge in regard to the location and magnitude of constituent sources that have a detrimental effect on instream water quality. Detailed methods for quantifying constituent sources have been developed as part of the US Geological Survey's Toxic Substance Hydrology Program (Bencala and McKnight, 1987; Kimball et al., 2002, 2007, 2010; Runkel and Kimball, 2002; Verplanck et al., 2004; Runkel et al., 2007; Borrok et al.,

2009; Walton-Day and Poeter, 2009). These methods include the synoptic mass balance approach in which a 'snapshot' of stream water quality is obtained (Grayson et al., 1997; Runkel et al., 2009). Under the synoptic mass balance approach, numerous stream and inflow sites are sampled for the constituents of interest and estimates of streamflow are obtained at each stream site. Estimates of constituent load at each stream site are then determined as the simple product of concentration and streamflow. The resultant spatial profiles of constituent load may be used to identify and prioritize sources of metal contamination (Kimball et al., 2002; Runkel et al., 2007). This quantitative approach to watershed characterization has been used extensively within the United States as part of the Abandoned Mine Lands Initiative (Kimball et al., 2007)

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and within the European Union, in compliance with the Water Framework Directive (Mayes et al., 2008; Mighanetara et al., 2009; Banks and Palumbo-Roe, 2010; Gozzard et al., 2011).

The synoptic mass balance approach is predicated on the assumption that the sampling campaign is conducted under steady-state conditions in which constituent concentrations and streamflow are temporally constant within the study reach. Although strict adherence to this assumption is nearly impossible to obtain, approximate steady-state conditions are often present at the end of the summer when snowmelt subsides and low-flow conditions predominate. Assessment of instream water quality under low-flow conditions is also advantageous in that the low-flow period is often a critical time in which constituent concentrations and aquatic toxicity are at their maximum levels (Grayson et al., 1997; Besser and Leib, 1999).

Although the synoptic mass balance approach is theoretically straightforward, practical application is often confounded by laboratory and field sampling errors. These errors affect constituent concentrations and streamflow estimates and thus lead to uncertainty in constituent load. Further, deviations from the steady-state assumption due to diel cycling (McKnight et al., 1988; Sullivan et al., 1998; Nimick et al., 2003) and temporal variation in source loading (Runkel et al., 2009) may lead to the mis-identification of constituent sources (Gammons et al., 2007; Runkel et al., 2009). In light of these issues, a replicate approach to synoptic sampling is presented herein. The goals of the paper are twofold: first, a general approach that provides replicate spatial profiles of concentration, streamflow, and constituent load is presented. The replicate approach allows for the development of error bars that represent the aggregate uncertainty associated with individual load estimates and the relative contributions of various source areas. The replicate approach is applied to Peru Creek, an acid mine drainage stream in Colorado (USA). Second, results from the replicate approach are used with additional site-specific data and analyses to identify and quantify the primary constituent sources in the Peru Creek watershed. This spatially detailed approach extends and supplements earlier research efforts within the watershed (e.g. McKnight and Bencala, 1990; Sullivan and Drever, 2001a) and provides a template for planning remedial actions.

2. Field setting

Peru Creek originates near the Continental Divide in Summit County, Colorado, and flows approximately 11 km to its confluence with the Snake River. Downstream of this confluence, the Snake River flows past the Keystone ski area and into Dillon Reservoir, a water supply for the City of Denver. Historical mining activities have degraded the water quality of Peru Creek and the Snake River, and both water bodies have been placed on the State of Colorado's 1998 303(d) list of impaired waters (Todd et al., 2003; Strong and Flores, 2008). Mining activities within the Peru Creek watershed began in the late 1800s with the establishment of numerous hard rock mines (Lovering, 1935), and continued until the mid-1940s. The subject of this paper is a 1.3-km study reach in the vicinity of the Pennsylvania Mine, an abandoned mine on the northern slope of Decatur Mountain, south of Peru Creek (Fig. 1). Ore-bearing veins of galena, pyrite, chalcocite, and quartz were mined for gold, silver, lead, copper, and zinc (Lovering, 1935).

The study reach begins upstream of the Pennsylvania Mine and ends downstream of Cinnamon Gulch, a tributary drainage with numerous abandoned mines (Wood et al., 2005). The study reach includes three potential source areas that contribute metals and acidity to Peru Creek. The first source area includes discharge from the Level F adit of the Pennsylvania Mine and leachate generated by infiltration of this discharge through nearby waste rock piles.

The Pennsylvania Mine consists of six levels of interconnected mine workings that are currently inaccessible due to the collapse of adits that access the lower (Level F) and upper (Level C) levels of the mine (see "Underground mine workings", Fig. 1). Acidic, metal-rich mine water from Level F seeps out of the collapsed adit and flows down the hillside, entering Peru Creek 218 m below the top of the study reach (known as the "Pennsylvania Mine inflow" in the sections that follow). This mine drainage causes an order-of-magnitude increase in dissolved metal concentrations in Peru Creek and a decrease in pH (Sullivan and Drever, 2001a). Immediately to the west of the F level adit lies a second source area, consisting of the Pennsylvania Mill and wetlands that lie between the mill and Peru Creek (known herein as the "wetland area"; Fig. 1). The wetland area is underlain by highly organic soils, with mill tailings covering the western third of the area (Emerick et al., 1988; Wood et al., 2005). Vegetation is dominated by water sedge (*Carex aquatilis*) and bog birch (*Betula glandulosa*), and waters within the wetland are acidic and metal-rich (Emerick et al., 1988). The third source area is a 250-m subreach where Cinnamon Gulch enters Peru Creek as three distinct inflows (Fig. 1). The western extent of this source area includes waste rock, tailings, and ruins associated with the Brittle Silver Mill, where ore was processed following its construction in 1882. Acidic, metal-rich waters discharge from the collapsed Phiupsilon Tunnel (Wood et al., 2005), located immediately upgradient from the mill site (see "Draining adit", Fig. 1).

Quantitative estimates of mass loading from the three source areas are needed to guide the formulation of remedial action plans for the Peru Creek watershed. Estimates of mass loading from the F level adit, for example, are needed to assess the potential benefits of eliminating or decreasing the adit flow by constructing a mine tunnel bulkhead. Although numerous investigators have sampled the Peru Creek watershed (Moran and Wentz, 1974; McKnight and Bencala, 1990; Fey et al., 2002; Wood et al., 2005), existing data sets do not provide the spatial resolution needed to separately quantify the three source areas. This task is confounded by two site-specific factors. First, loading from the Pennsylvania Mine may not be limited to the surface discharge emanating from the collapsed F level adit. Substantial quantities of water and constituent mass may be passing from the mine workings into the wetland area through the subsurface. As such, loading from source areas one and two may be intermingled and difficult to separate. Mixing analyses used to address this confounding factor are presented in Section 4.5. Second, successful application of the synoptic mass balance approach requires discrete sampling locations that capture all of the stream water that is moving downstream. The study reach includes numerous beaver ponds that distribute the waters of Peru Creek into multiple channels (Fig. 1); stream sampling locations are therefore limited to those areas where the distributed flow is merged into a single channel. As a result, several of the sampling locations consist of wide cross-sections that may exhibit considerable chemical variability with width. Collection of representative samples at these locations is therefore subject to uncertainty; this uncertainty is addressed by the replicate approach employed herein and the integrated sampling described in Section 3.1.

3. Methods

3.1. Overview

Identification of metal sources and quantification of constituent loads under the synoptic mass balance approach requires estimates of streamflow and constituent concentration. These quantities may be obtained using the tracer-dilution method and synoptic sampling (Bencala and McKnight, 1987; Kimball et al.,

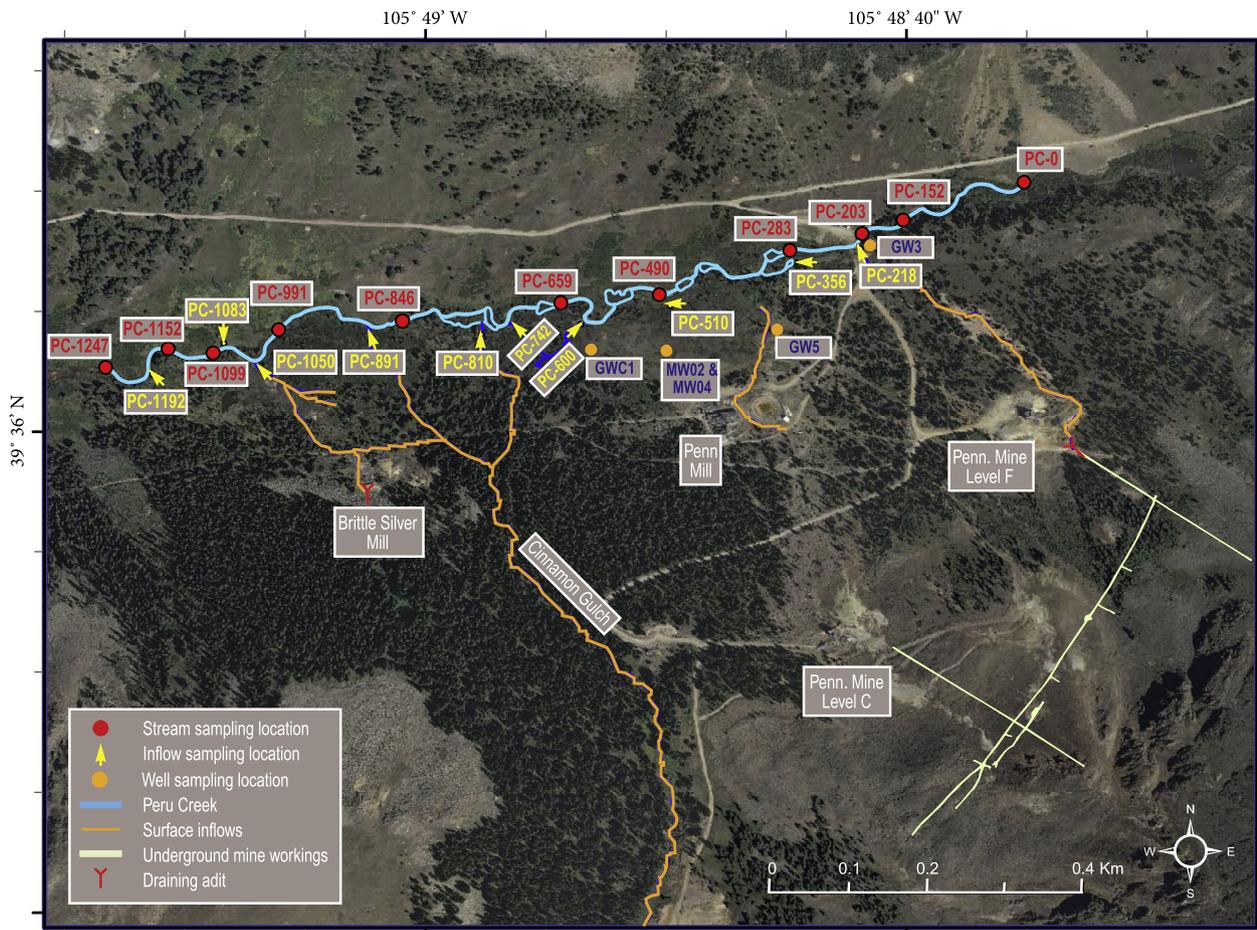


Fig. 1. Map of Peru Creek study reach including stream, inflow, and well sampling locations (base map from June 2009).

2002, 2007). The tracer-dilution method provides estimates of streamflow (Kilpatrick and Cobb, 1985), and synoptic sampling provides a description of instream and inflow chemistry (constituent concentration). Estimates of streamflow are multiplied by constituent concentrations at each stream location to obtain estimates of constituent load (mass/time), the primary quantity used to identify metal sources along the study reach.

Estimates of constituent load are subject to uncertainty due to errors associated with laboratory analysis and field sampling. Laboratory errors lead to uncertainty in constituent load as they affect both constituent concentration and tracer-dilution based estimates of streamflow. Sampling error is of particular concern for the Peru Creek study reach, due to hydrologic complexity that results from instream beaver dams and relatively wide stream cross sections. This complexity leads to variation in constituent concentration with respect to width as constituent sources (inflows) upstream of a given sampling location are not fully mixed with the stream. Similarly, tracer concentrations vary with width as inflow waters entering along the streambank will have background tracer concentrations and other parts of the cross section will have elevated tracer concentrations from the tracer injection. Estimates of average concentration may be obtained by performing width and depth integrated sampling within the cross section (US Geological Survey, 2006). Although this procedure reduces sampling error, the sampled water is unlikely to reflect the true, average concentration for the cross section. Uncertainty in estimating constituent concentration, streamflow (tracer concentration), and constituent load is therefore unavoidable.

Given the uncertainty discussed above, a replicate synoptic sampling approach was employed for the study described herein. Under this approach, all stream sites were sampled within a 4-h period. This initial synoptic sampling campaign was immediately followed by a second, replicate sampling effort in which identical techniques were used (Section 3.2). The resultant data set includes two spatial profiles of constituent concentration and two spatial profiles of streamflow that may be combined to create four profiles of constituent load. The four loading profiles are subsequently used to develop error bars that quantify the aggregate uncertainty associated with the loading analysis and the determination of metal sources (Section 3.5). Although the results that follow are specific to Peru Creek, the replicate approach is general in nature and may be applied to other watersheds affected by mine drainage.

A detailed description of the methods used to implement the replicate approach follows. Additional details and data are provided in the [Supplementary material \(Tables S1–S7, Figs. S1 and S2\)](#).

3.2. Tracer injection and synoptic sampling

A concentrated tracer solution was prepared by adding lithium bromide (LiBr) and lithium chloride (LiCl) to stream water collected at the injection site; the resultant injectate solution had Li and Br concentrations of 24.3 and 168.3 g/L, respectively. The continuous, constant-rate tracer injection was initiated at 9:47 h on September 10, 2009 at a rate of 98.9 mL/min. The injection was terminated at 17:55 h on September 11 following completion of synoptic sampling.

Synoptic samples were collected at 11 stream and 10 inflow sites (Fig. 1 and Table S1) on the morning of September 11, after instream concentrations of Li and Br had reached a steady-state plateau. Samples collected during this initial campaign comprise the PC1 data set described herein. All stream sites were resampled in the afternoon of September 11 to provide a replicate set of synoptic samples; samples collected during the replicate campaign comprise the PC2 data set. One field blank and one sequential replicate were collected during each sampling campaign (Tables S2–S6). Streamflow measurements were made at most stream sites to supplement the tracer-dilution estimates using a handheld Acoustic Doppler Velocimeter (ADV; SonTek/YSI, 2009). Collection of stream samples proceeded in the downstream-to-upstream direction, to avoid contaminating samples with resuspended streambed materials. Stream samples were collected as quickly as possible (Table S2; subject to safety, quality assurance, and logistical constraints) in an effort to minimize effects of diel metal fluctuations (Nimick et al., 2003) and variations in source loading (Runkel et al., 2009). Stream sampling locations were placed so as to bracket known surface inflows. Stream and inflow sampling sites are identified herein using a PC prefix followed by a numeric value indicating the distance (in m) from the top of the study reach to the sampling location, as measured along Peru Creek (Fig. 1). Inflow samples are further classified as being right- or left-bank inflows, where ‘right’ and ‘left’ are from the perspective of an observer who is walking downstream. Samples were collected from five wells on the south side of Peru Creek (Fig. 1) on September 13, 2009 using standard USGS techniques (USGS, 2006).

Sampled inflows ranged from small springs to well-defined tributaries such as Cinnamon Gulch (Fig. 1). Inflow samples were collected as close to Peru Creek as possible (generally <3 m away from the stream), such that the samples accurately represent additions to the study reach. Collection of stream samples was dependent on site specific factors. Samples from narrow cross sections (~1 m) were obtained by the grab technique; samples from wide cross sections (>1 m) were collected using a DH-81 sampler to provide a width and depth integrated sample (USGS, 2006). Water temperature was measured in situ using an alcohol thermometer. Samples were transported to a central processing area where 125-mL aliquots were prepared for cation and anion analyses. On-site processing included filtration, measurement of pH and specific conductance, and preservation of samples for iron speciation. The pH probe was periodically checked using standard solutions and recalibrated as needed over the course of the day. Filtration was completed using 0.45-micrometer capsule filters.

Aliquots for cation analysis were acidified to pH < 2.0 with ultra-pure HNO₃. Total recoverable and dissolved cation concentrations were determined from unfiltered and filtered samples, respectively, using inductively coupled argon plasma-mass spectrometry (“dissolved” is used herein as an operational definition that refers to the concentration of the filtered sample; some colloidal material may pass through the 0.45 micrometer filter). Cation concentrations are reported for silver (Ag), aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), silicon (Si), strontium (Sr), sulfur (converted to sulfate, SO₄), uranium (U), vanadium (V), and zinc (Zn) (Tables S3–S6).

Dissolved anion concentrations were determined from filtered, unacidified samples by ion chromatography using the quality-assurance procedures described by Kimball et al. (1999). Anion concentrations are reported for bromide (Br) and chloride (Cl) (Table S7). Aliquots for iron speciation were placed in amber bottles and preserved with concentrated HCl to fix the ratio of ferrous to ferric iron in filtered samples (To et al., 1999). Ferrous and total dissolved iron concentrations were determined by spectrophotom-

etry (Brown et al., 1970; Table S7). Alkalinity was determined from filtered, unacidified samples (Table S2).

3.3. Temporal sampling

Temporal sampling and water quality monitoring activities were conducted within the Peru Creek watershed September 7–12, 2009 to determine the extent of diel constituent cycling and variations in source loading. A water quality sonde was placed in the outflow from the collapsed Level F adit (see “Draining adit”, Fig. 1) to monitor specific conductance. Values of specific conductance were recorded at 1 min intervals from 21:00 h on September 7 to 14:00 h on September 9. Water quality samples were collected at PC-203, PC-659, and PC-1099 over a 24-h period (18:20 h, September 10 to 23:20 h, September 11; Tables S9–S12). Water quality sondes monitored dissolved oxygen, pH, specific conductance, and temperature at these locations (Table S8). Samples were collected every 1.5–2.0 h by the grab technique (for details on sample processing and laboratory analysis, see Section 3.2).

3.4. Estimating streamflow by tracer dilution

Under the tracer-dilution method, a conservative tracer is continuously injected at a constant rate and concentration. Given sufficient time, all portions of the stream become fully mixed with the tracer-laden water, and concentrations at a given instream site reach a steady-state plateau. Decreases in plateau concentration with stream length reflect dilution of the tracer by additional water entering the channel (surface and/or ground-water inflow). Consideration of this dilution allows for the calculation of streamflow at each site (Kilpatrick and Cobb, 1985; Kimball et al., 2007):

$$Q = \frac{Q_{INJ} C_{INJ}}{C_P - C_B} \quad (1)$$

where C_B is the background tracer concentration (samples PC1-0 and PC2-0, Table S7), C_P is the tracer concentration at plateau, C_{INJ} is the injectate concentration, Q_{INJ} is the injection rate, and Q is the streamflow estimate. Bromide concentrations from the PC1 and PC2 data sets were used with Eq. (1) to develop two spatial profiles of streamflow. The resultant tracer-dilution streamflow estimates were subject to the quality-control checks detailed in the [Supplementary material](#).

3.5. Loading analysis

Estimates of constituent load provide an objective means of determining the sources that have the greatest effect on instream water quality. To this end, the study reach was divided into 10 stream segments that are demarcated by the 11 stream sampling sites (Fig. 1). The change in mass load from one stream site to the next may be used to determine if a given segment is a source (increase in load with distance) or a sink (decrease in load) for a given constituent.

Constituent loads were calculated as the simple product of streamflow and constituent concentration. Most constituents were transported conservatively through the study reach as low pH conditions inhibited precipitation and sorption reactions. As a result, total recoverable and dissolved concentrations are often comparable and the dissolved concentrations were used in the loading analyses for most constituents. Use of dissolved concentrations for this analysis is advantageous as profiles of total recoverable concentration are affected by sampling artifacts (i.e. a portion of the total recoverable concentration is attributable to sediment transport and floating debris; this portion varies from sample to sample). Total recoverable concentrations were used in the loading analysis for Ag, As, Cr, Fe, Pb, and V, as these constituents were subject to

instream reactions and use of dissolved concentrations would underestimate constituent loading.

Four profiles of constituent load were developed by combining the two spatial profiles of constituent concentration with the two profiles of streamflow (PC1 concentrations multiplied by PC1 streamflow, PC1 concentrations multiplied by PC2 streamflow, PC2 concentrations multiplied by PC1 streamflow, and PC2 concentrations multiplied by PC2 streamflow). Median values of constituent load were determined at each stream location by taking the median value from the four profiles. Error bars representing the range in load at each stream location were set using minimum and maximum values from the four profiles.

Cumulative instream load is equal to the sum of all increases in constituent load (Kimball et al., 2002). For a given stream segment, the cumulative instream load is increased if the constituent load increased, and held constant if the constituent load decreased. The cumulative instream load thus represents the total amount of loading within the study reach (whereas the constituent load represents the net amount of loading after chemical reaction). Stream segments in which the cumulative instream load increased are considered sources of constituent mass. The percent contribution of each source is given by:

$$\text{percent contributions} = 100 \left(\frac{\Delta \text{load}}{L_{1247} - L_0} \right) \quad (2)$$

where Δload is the within-segment increase, and L_0 and L_{1247} are the cumulative instream loads at the upstream and downstream ends of the study reach, respectively.

Percent contributions from multiple segments were grouped to represent the total contribution from each of the three source areas (Pennsylvania Mine, Wetland Area, and Cinnamon Gulch; e.g., the total contribution from Cinnamon Gulch is the sum of the contributions to the three segments in which it enters). Percent contributions for each group were developed by taking the median contribution from the four loading profiles; error bars on the percent contributions were set using the minimum and maximum percentages from the four profiles.

Development of error bars on profiles of constituent load and percent contributions represents a straightforward, empirical means to quantify the aggregate amount of uncertainty that arises from multiple factors, including: (1) laboratory analyses of constituent and tracer concentrations, (2) field sampling error, and (3) temporal variation in concentration from diel constituent cycles and/or source variation. Given estimates of aggregate uncertainty, site specific data and expert judgement may be used to qualitatively assess the contributions of individual factors to uncertainty, as discussed in Section 5.3. Note the development of error bars is restricted to constituent load (rather than streamflow and/or concentration), as constituent load is the primary quantity used for source identification and targeting areas for remediation.

3.6. Inflow characterization

As noted in Section 2, water and constituent mass may be passing from the mine workings into the wetland area via the subsurface. Discharge from the wetland area may therefore be a mixture of water leaving the mine and subsurface waters at the base of the Cinnamon Gulch watershed. This possibility may be explored through a simple two-member mixing model in which the observed concentration of a given wetland inflow is expressed as a linear combination of water leaving the collapsed mine workings and water from lower Cinnamon Gulch:

$$C_{\text{inflow}} = \Gamma C_{\text{PMI}} + (1 - \Gamma) C_{\text{CG}} \quad (3)$$

where C_{inflow} is the concentration of an inflow draining the wetland area, C_{PMI} is the concentration of the Pennsylvania Mine inflow (PC-218), C_{CG} is the concentration of the most upstream Cinnamon Gulch inflow (PC-810), Γ is the fractional contribution of the mine workings to the inflow ($\Gamma < 1$), and all concentrations are in terms of the dissolved phase. This equation assumes that: (1) wetland inflow concentrations are the result of conservative mixing between the mine waters and Cinnamon Gulch; (2) constituent concentrations of the Pennsylvania Mine inflow (as observed September 11, 2009) are equal to the constituent concentrations of the water that left the mine workings at some unknown time (i.e. traveltime through the wetland is unknown). Eq. (3) was used to calculate Γ values for three inflows in the wetland area (PC-510, PC-600, or PC-742; Fig. 1) using a suite of constituents that are considered nominally conservative at low pH (Ca, Co, Li, Mg, Mn, Sr, SO_4 , Zn).

Further characterization of inflow waters was obtained using a form of cluster analysis known as partitioning around medoids (Kaufman and Rousseeuw, 1990). Concentrations, in millimoles/L, were log transformed and converted to standard normal variables for the analysis. Using Euclidian distance in multivariate chemical space as a measure of similarity, each sample was assigned to the cluster of the nearest medoid, providing an objective means of grouping samples in terms of the chemical distinctions. These groups were visualized using biplots of the first two principal components.

4. Results

The complete data set includes chemical analyses for 24 different cations (Section 3.2; Tables S3–S6). The sections that follow focus on pH and 9 constituents that are commonly associated with mine drainage (Al, As, Cd, Cu, Fe, Mn, Pb, SO_4 , Zn); these constituents are denoted as the “constituents of interest” in the text that follows.

4.1. Streamflow

Tracer-dilution streamflow estimates based on the PC1 and PC2 data sets increase linearly with distance from ~ 55 L/s near the Pennsylvania Mine inflow to nearly 100 L/s downstream of Cinnamon Gulch (Fig. 2A). Stream reconnaissance conducted prior to synoptic sampling indicates that surface inflow is dominated by inflow waters emanating from the left (south) bank of Peru Creek; nine of ten sampled inflows enter Peru Creek from the left bank (Fig. 1). This dominance of left bank inflow is consistent with local topography and aspect, with the south side of study reach draining the steep, north-facing slopes of the Continental Divide. Given this observation, increases in flow within the study reach can be attributed to the three source areas, with the Pennsylvania Mine, wetland area, and Cinnamon Gulch contributing 14%, 27%, and 46% of the flow, respectively (Fig. 2B).

4.2. Constituent concentration and pH

Spatial profiles of pH for sampled inflows and stream sites are depicted in Fig. 3A. Values of instream pH are greater than 6.0 at the top of the study reach, and exhibit a sharp decrease to ~ 4.6 immediately downstream from where the Pennsylvania Mine inflow (PC-218) enters Peru Creek. Inflow waters downstream of the Pennsylvania Mine have pH values that are comparable (PC-356, PC-1192, Cinnamon Gulch #2 and #3) or less than (PC-510, PC-600, PC-742, Cinnamon Gulch #1) instream pH; instream pH therefore remains at ~ 4.6 through the end of the study reach. The lone right-bank inflow, PC-1083, has a circumneutral pH, sug-

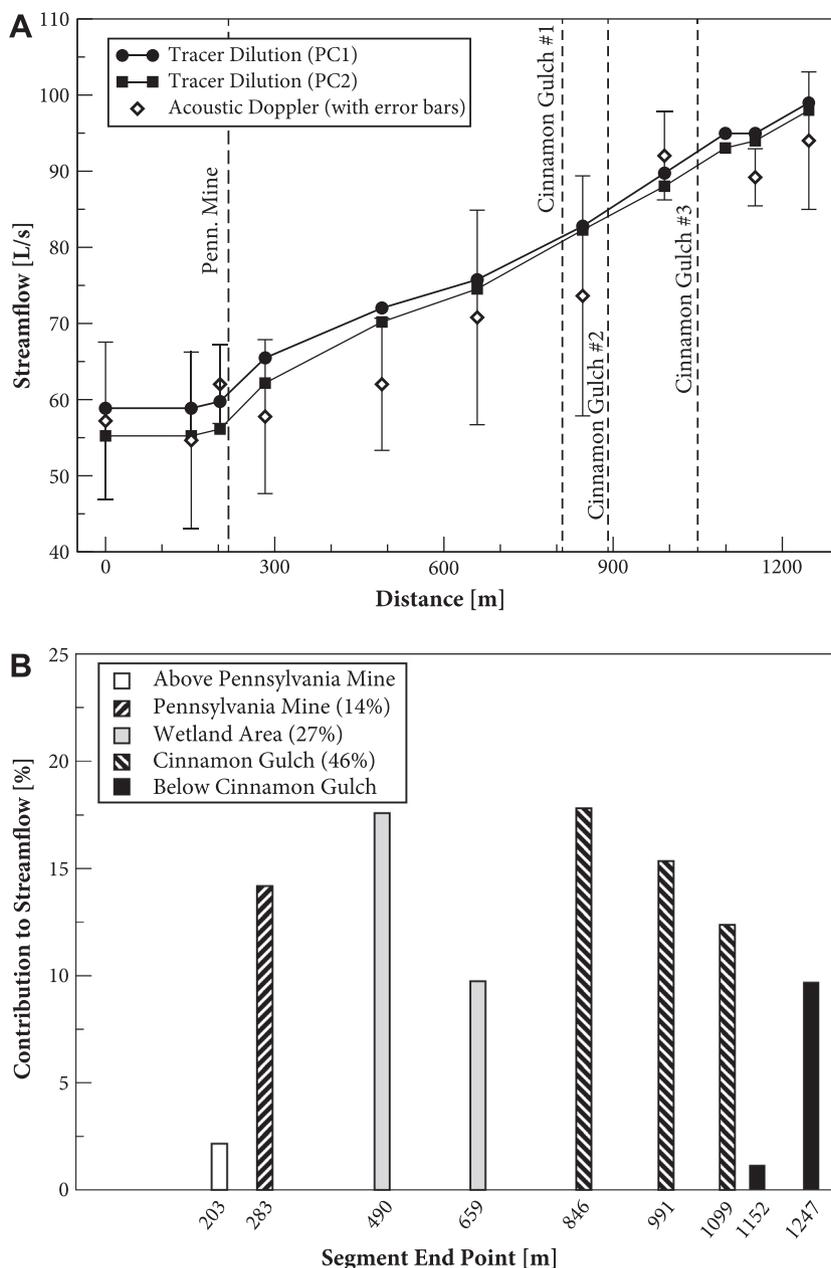


Fig. 2. (A) Replicate profiles of tracer-dilution streamflow estimates and streamflow measurements by Acoustic Doppler Velocimeter (ADV; error bars are described in the Supplementary material). (B) Percentage of streamflow increase attributable to specific stream segments and source areas.

gesting a source of clean water from the north side of the watershed (Fig. 3A).

Instream concentrations of the constituents of interest increase as water from the Pennsylvania Mine inflow (PC-218) enters Peru Creek (Fig. 4A–C, J–L, S–U). Al, Mn, and SO₄ stream concentrations gradually increase as Peru Creek flows past the wetland area and the distributed inflows from Cinnamon Gulch (Fig. 4A, L, T). Instream concentrations of Cd, Cu, and Zn also increase through the wetland area, exhibiting a slight decrease in the Cinnamon Gulch subreach (Fig. 4C, J, U). Concentration increases along the wetland area are consistent with the high concentrations of the inflows that drain the wetland (PC-356, PC-510, PC-600, PC-742; Fig. 4D, F, M, O, W, X). Total recoverable concentrations of instream Al, Cd, Cu, Mn, SO₄, and Zn (Tables S3–S4) are generally equal to dissolved concentrations, such that solid phases are not present in the water column. This lack of a solid-phase suggests that these

constituents are being transported conservatively through the study reach, consistent with depressed pH (Fig. 3A) that inhibits precipitation and sorption reactions. These results are consistent with Sullivan and Drever (2001b), where Cu, Mn, and Zn were found to be primarily in the dissolved phase.

In contrast to the other constituents of interest, As, Fe, and Pb have total recoverable stream concentrations that exceed the dissolved concentrations, indicating the presence of solid phases that are likely the result of precipitation (Fe) and/or sorption (As, Pb) reactions (Fig. 4B, K, S; dissolved As concentrations are below the detection limit and are not shown). Peak concentrations of As and Fe are observed immediately downstream of the Pennsylvania Mine inflow, and instream concentrations decrease through the end of the study reach, presumably due to the settling of the solid phase material (Fig. 4B and K). Instream concentrations of Pb remain relatively constant as Peru Creek flows past the wetland area,

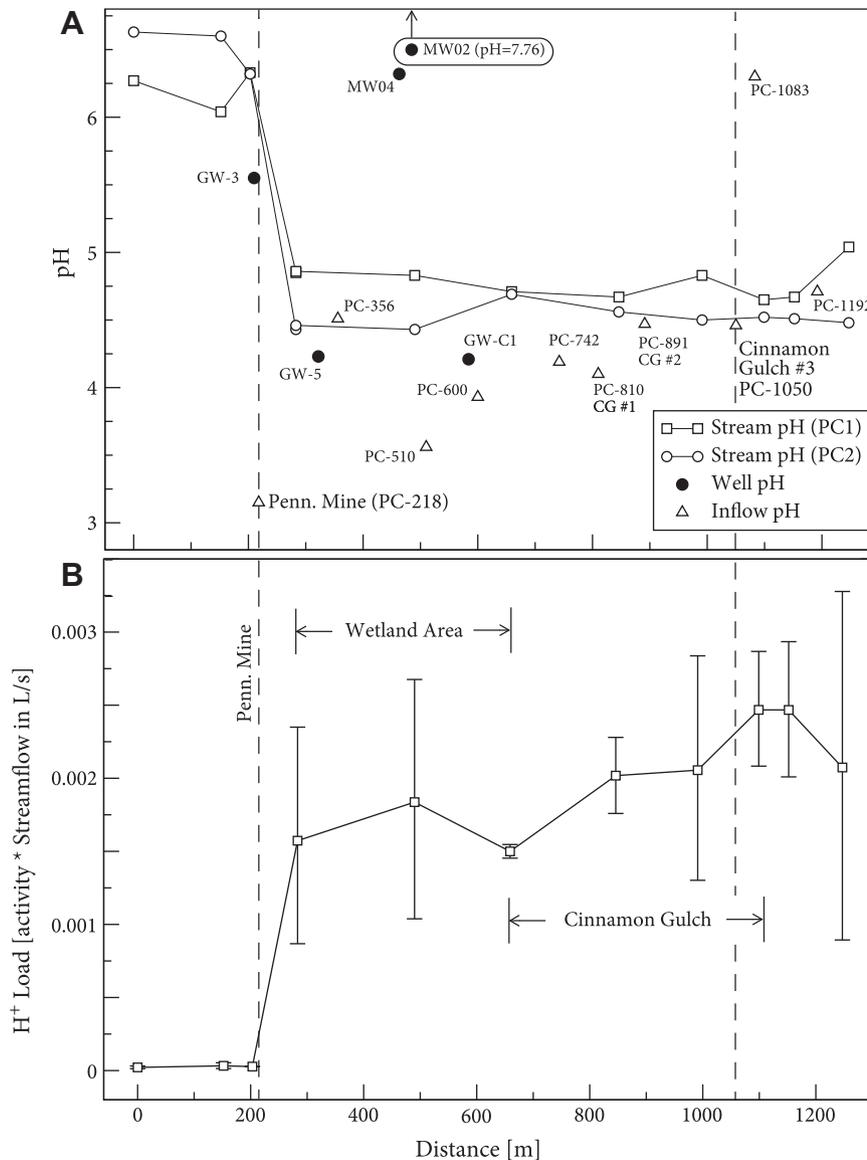


Fig. 3. (A) Spatial profile of pH at stream, inflow, and well sites. (B) Spatial profile of H⁺ load based on measurements of instream pH. Error bars denote minimum and maximum load estimates.

and increase sharply in response to the high concentration of the third Cinnamon Gulch inflow (Fig. 4S and V). Other constituents exhibiting reactive behavior (as indicated by total recoverable concentrations in excess of dissolved), include Ag, Cr, and V (Tables S3–S6).

Dissolved concentrations of Cd and Zn exceed chronic aquatic life standards (CDPHE, 2005) along the entire study reach (Fig. 4C and U), suggesting the presence of natural and/or mining affected sources for these constituents upstream of the Pennsylvania Mine. Concentrations of Al, Cu, Fe, Mn, and Pb exceed chronic aquatic life standards for portions of the study reach downstream of the Pennsylvania Mine (Fig. 4A, J–L, S; chronic standards for Al and Fe are in terms of total recoverable concentrations, CDPHE, 2005). Concentrations of Ag, As, Cr, Ni, and U are below the chronic standard for the entire study reach (Tables S5–S6).

4.3. Temporal sampling

Specific conductance values for the outflow from the Level F adit range from 1670 to 1700 $\mu\text{S}/\text{cm}$ over a 41-h period that

precedes synoptic sampling. The small range of the conductance values (30 $\mu\text{S}/\text{cm}$; <2%) suggests that the concentration of the Pennsylvania Mine inflow (PC-218) is not subject to substantial temporal variation during the time period of interest. Similarly, instream pH values during the day on September 11 are nominally constant, varying <0.1 pH units (6.76–6.82, 4.65–4.75, and 4.56–4.62 for PC-203, PC-659, and PC-1099, respectively). Temporal variation in the dissolved concentrations of Al, Cd, Cu, Mn, SO₄, and Zn at PC-203, PC-659, and PC-1099 is also minor (maximum coefficients of variation for these constituents at the three sites are 5%, 4%, 7%, 5%, 5%, and 5%, respectively). Total recoverable concentrations for the reactive constituents of interest are more variable (maximum coefficient of variation is 26%, 29%, and 14% for As, Fe, and Pb, respectively).

Despite the relatively small variations noted above, some of the constituents of interest exhibit systematic changes associated with diel metal cycling. Values of instream pH at PC-203, for example, are steady during nighttime hours and increase during the morning and early afternoon (Fig. S3A). These changes are consistent with the photosynthesis-induced pH cycles observed in other

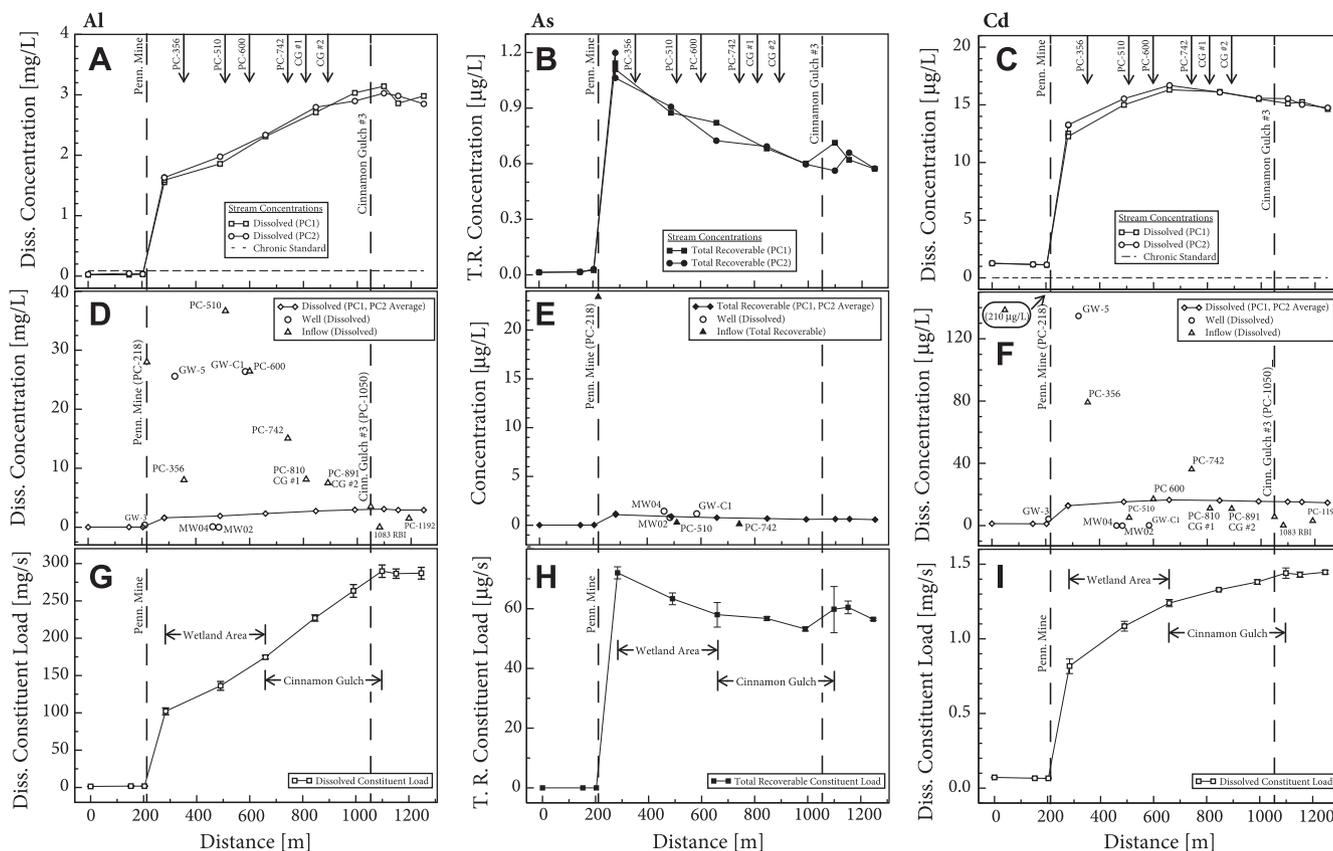


Fig. 4. (A–C, J–L, S–U) Spatial profiles of dissolved and/or total recoverable stream concentration from PC1 and PC2 sampling campaigns. (D–F, M–O, V–X) Spatial profiles of inflow, well, and average stream concentration. Dotted lines on Mn, SO₄, and Zn plots show inflows as a mixture of adit water and Cinnamon Gulch. (G–I, P–R, Y, Z, AA) Spatial profiles of constituent load. Error bars denote minimum and maximum load estimates.

circumneutral waters (Nimick et al., 2003). Values of pH below the Pennsylvania Mine Inflow (PC-659 and PC-1099), in contrast, increase during nighttime hours and decrease during the day (Fig. S3B). These changes may be attributable to small changes in streamflow which in turn affect the dilution of the Pennsylvania Mine Inflow (i.e. flow increases during nighttime hours as evapotranspiration decreases; increased flow results in higher pH as the Pennsylvania Mine Inflow makes up a smaller proportion of the total streamflow). Dissolved Fe concentrations at all three sites increase at night and decrease during the day (Fig. S3C–D), suggesting an inverse relationship between solubility and temperature (Table S8; Gammons et al., 2005). Observed changes in dissolved Pb concentrations at all three sites are consistent with pH-dependent sorption of Pb onto hydrous ferric oxides (Fig. S3E–F; Dzombak and Morel, 1990; Nimick et al., 2003). Similarly, dissolved Zn concentrations above the Pennsylvania Mine Inflow (PC-203, Fig. S3G) decrease during the day as pH increases, consistent with sorption.

4.4. Constituent loads

As discussed in Section 4.2, the Pennsylvania Mine inflow (PC-218) has a large effect on instream concentrations. This effect and the effects of other source waters are formally quantified using constituent loading profiles. Spatial loading profiles for pH (in terms of the hydrogen ion) and the constituents of interest are depicted in Figs. 3B and 4 (panels G–I, P–R, Y, Z, AA). The effect of the Pennsylvania Mine is clear, as loads for the hydrogen ion and the constituents of interest all increase from 203 to 283 m (stream sites PC-203 and PC-283 bracket the Pennsylvania Mine inflow).

Loading from the wetland area and Cinnamon Gulch is also evident, as the loading profiles for Al, Cd, Cu, Mn, SO₄, and Zn increase throughout these subreaches (Fig. 4G, I, P, R, Y, Z, AA). The loading profile for Pb indicates little or no loading from the wetland area (283–659 m), and substantial loading from Cinnamon Gulch (659–1099 m; Fig. 4Y). In contrast to the other constituents, Pb loading from Cinnamon Gulch is dominated by the third inflow (PC-1050).

Instream loads of Al, Cd, Cu, Mn, SO₄, and Zn exhibit a continuous increase in response to loading from the various source areas. These constituents do not form solid phases at low pH, such that they are transported conservatively and any loss of instream load is negligible. Instream loads for As and Fe, in contrast, exhibit a gradual decrease downstream from 283 m (Fig. 4H and Q). This decrease is indicative of a settling process that removes constituent mass following the formation of solid phase material by precipitation and/or sorption reactions (total recoverable concentrations of As and Fe exceed the dissolved concentrations, indicating the presence of a solid phase; Fig. 4B and K).

Loading from the three source areas is summarized in Fig. 5 where the percent contribution attributed to the Pennsylvania Mine, wetland area, and Cinnamon Gulch is presented for various constituents. The importance of a given source area is constituent specific (e.g. the Pennsylvania mine is the dominant source for As; Cinnamon Gulch is the dominant source for Pb).

4.5. Inflow characterization

Wetland inflow concentrations for a suite of nominally conservative constituents (Ca, Co, Li, Mg, Mn, Sr, SO₄, and Zn) support the

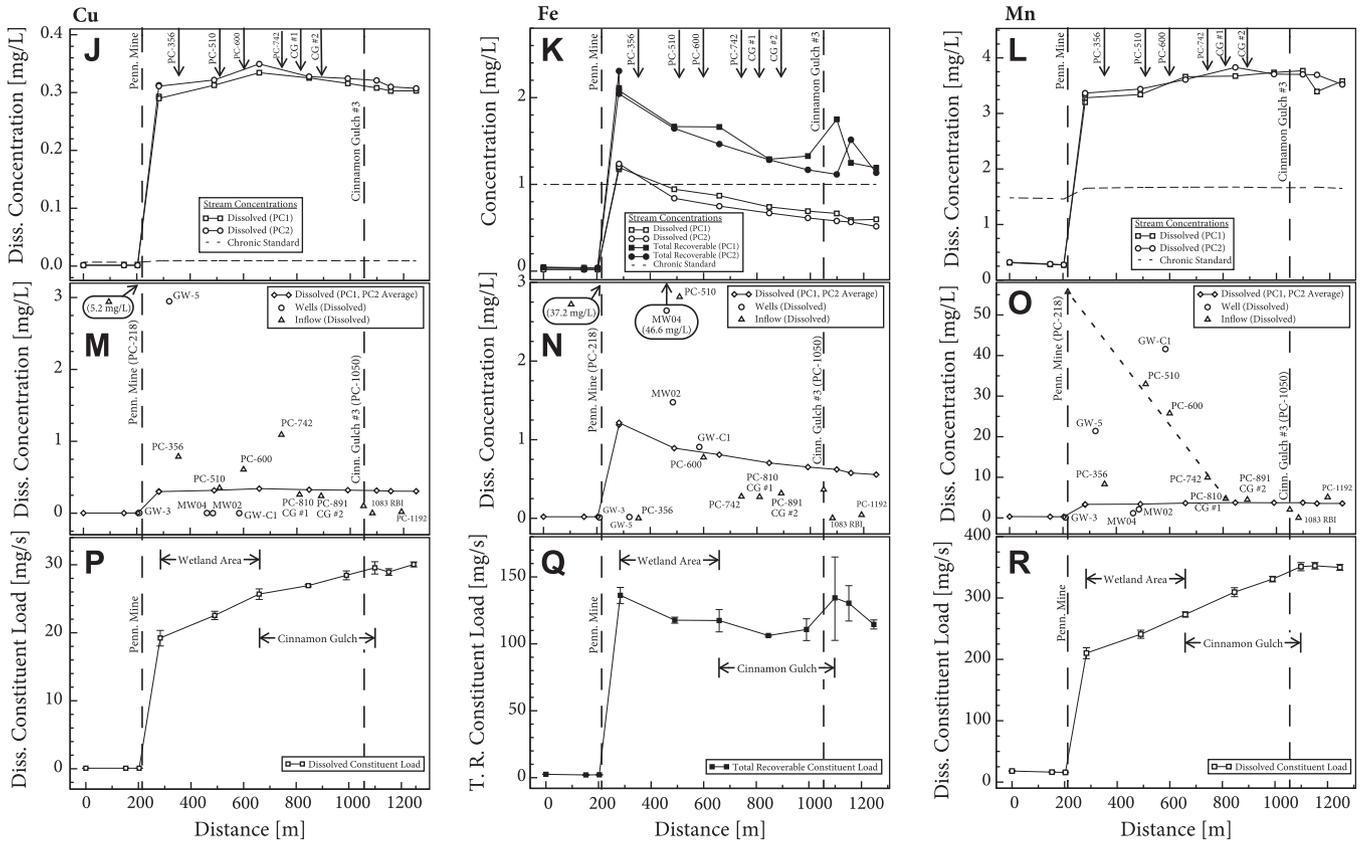


Fig. 4. (continued)

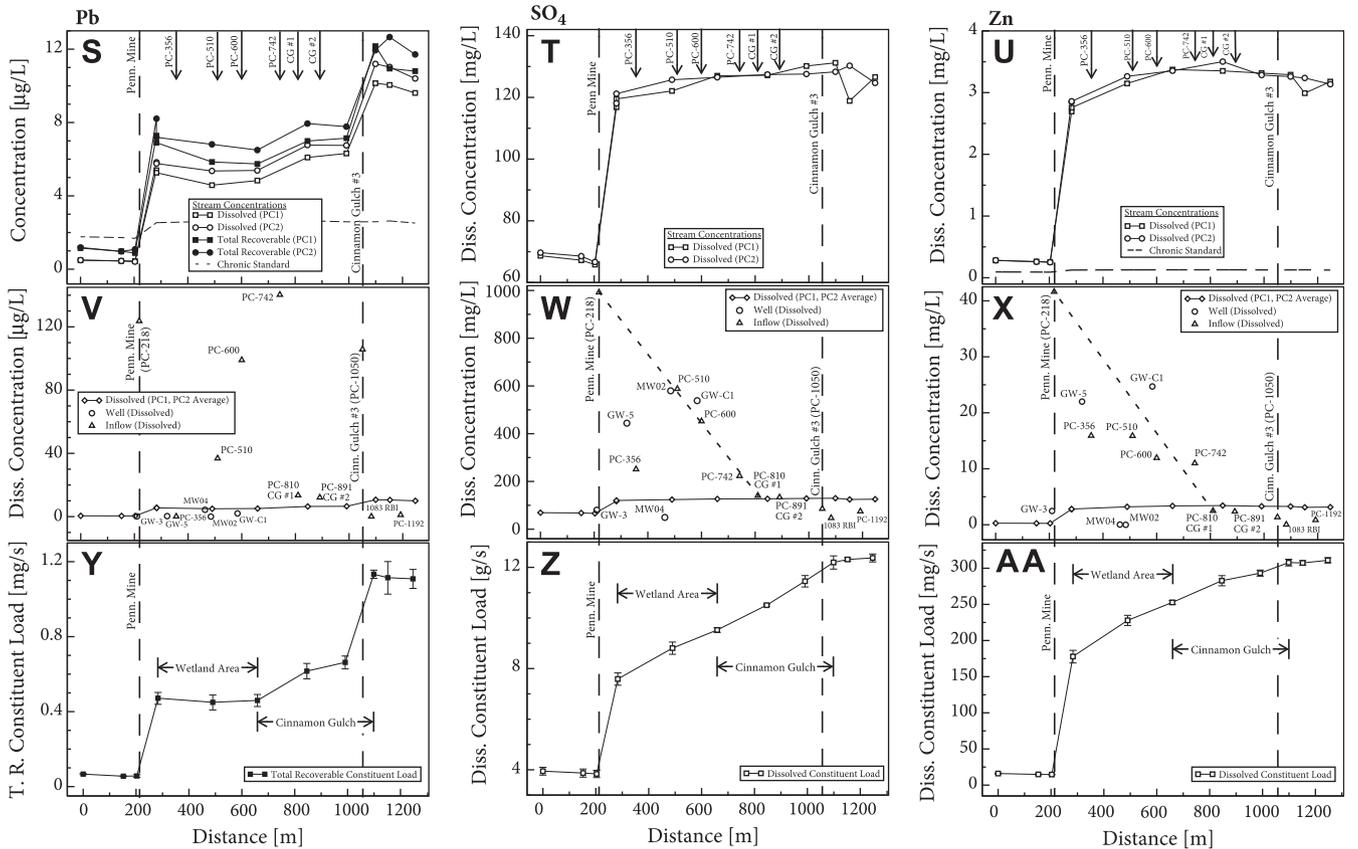


Fig. 4. (continued)

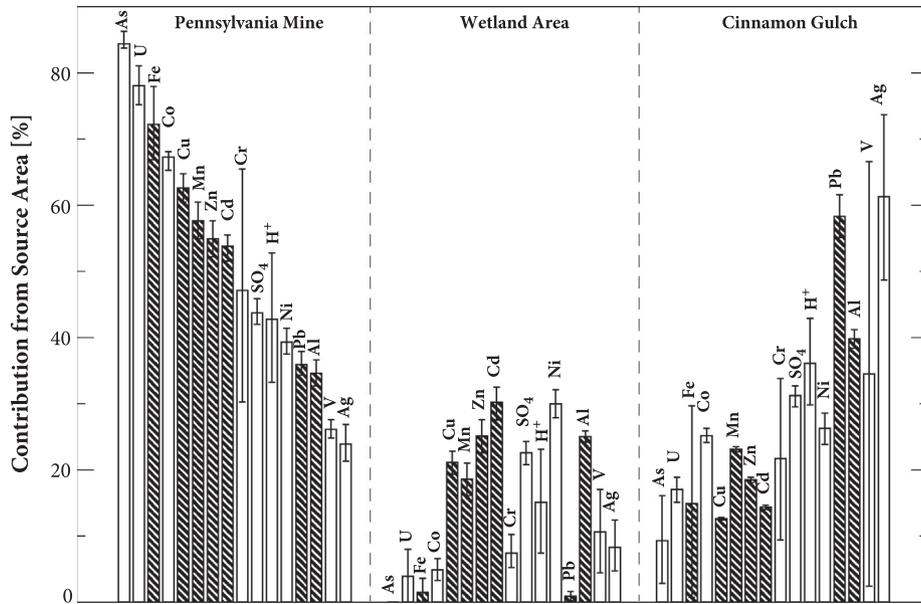


Fig. 5. Percent contribution of source areas to overall load within the Peru Creek study reach. Percent contributions are based on dissolved concentrations for most constituents; total recoverable concentrations are used for Ag, As, Cr, Fe, Pb, and V. Constituents with concentrations in excess of chronic aquatic life standards (Colorado Department of Public Health and Environment, 2005) are shown with cross-hatched bars.

hypothesis that the wetland contains a mixture of water from the Pennsylvania Mine workings and the Cinnamon Gulch watershed. Observed concentrations of inflows emanating from the wetland (PC-510, PC-600, or PC-742) can be expressed as a mixture of water from the Pennsylvania Mine inflow (PC-218) and Cinnamon Gulch (PC-810) (see dashed line in Fig. 40, W, X). These mixtures are formally quantified using the two-member mixing model (Section 3.6), as shown in Fig. 6. Median values suggest that water from the mine workings makes up 49%, 31%, and 10% of the water discharging at PC-510, PC-600, and PC-743, respectively.

This analysis supports, but does not confirm, movement of water from the mine workings to the wetland area. Other analysis methods provide conflicting results in regard to mixing. A biplot obtained from cluster analysis (Section 3.6), for example, places the three wetland inflows between the two end members (the

Pennsylvania Mine inflow and Cinnamon Gulch), supporting the simple mixing analysis. An analysis of Sr isotopic ratios, in contrast, only supports the mixing analysis for PC-510. Further, the apparent influence of the Pennsylvania Mine inflow on the wetland waters may be entirely coincidental; water in the wetland area may be in contact with mill tailings (Emerick et al., 1988; Wood et al., 2005) that impart a chemical signature that is similar to that of the Pennsylvania Mine inflow. In addition, the chemistry of the wetland soils and waters may resemble that of the Pennsylvania Mine inflow due to a previous attempt at remediation; as documented by Huskie (1987) and Emerick et al. (1988), a leachline system was used in the 1986 to divert water from the Pennsylvania Mine inflow to the wetland area. Given these complexities, additional research will be needed to determine the location and magnitude of leakage from the workings.

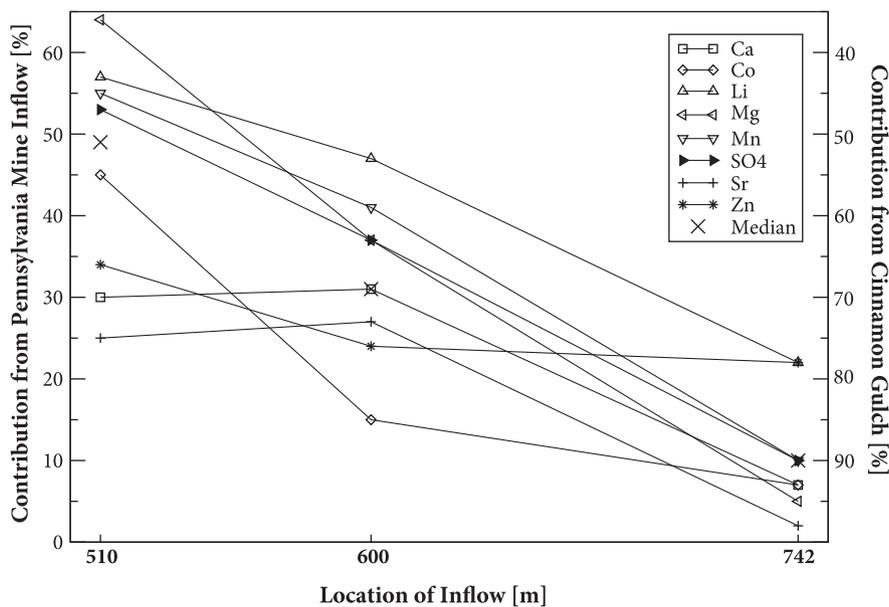


Fig. 6. Contribution of Pennsylvania Mine inflow and Cinnamon Gulch to three left-bank inflows based on two-member mixing analysis.

5. Discussion

5.1. Streamflow

5.1.1. Mass conservation

Recent publications highlight the importance of tracer mass recovery and the potential ramifications for constituent mass loading (e.g. [Bencala et al., 2011](#)). Of particular concern is the potential for mass loss through extended subsurface flow paths that do not re-enter the main stream channel over the time scale of interest ([Payn et al., 2009](#)). Tracer mass loss via these subsurface flow paths will result in overestimation of streamflow and a subsequent overestimation of constituent mass loads. Due to this possibility, tracer-based estimates of streamflow must be checked for mass conservation, an exercise that requires a secondary, independent estimate of streamflow. Possible techniques that provide this secondary estimate include traditional streamflow measurements (by current meters or ADV), slug tracer injections ([Covino et al., 2010](#); [Szeftel et al., 2011](#)), and/or flume measurements. Experimental results ([Schmadel et al., 2010](#)) indicate that incomplete lateral mixing leads to considerable uncertainty in slug-based estimates of streamflow, and this issue is pertinent to the present application due to wide cross-sections (Section 2). ADV streamflow measurements (Fig. 2A) are therefore used herein to check for mass conservation, as described below. Additional details on the use of slug injections and flumes are provided in the [Supplementary material](#).

Streamflow measurements by current meters or ADV are compromised in mountain streams due to non logarithmic velocity profiles ([Jarrett, 1984](#)), and the documented errors have given rise to the use of the tracer-dilution method in these environments (e.g. [McKnight et al., 1988](#)). ADV measurements in Peru Creek are highly uncertain (error bars, Fig. 2A), owing to irregular cross-sections at most stream sampling locations (see photographs, Fig. S1). The uncertainty indicated by the error bars in Fig. 2A is also evident upon inspection of the spatial streamflow profile provided by ADV; this profile, if strictly interpreted, indicates flow losses in two stream segments that were clearly gaining water (segments bracketing the Pennsylvania Mine inflow and the third Cinnamon Gulch inflow, Fig. 2A; photographs in Fig. S2A, H). As such, the check on tracer mass balance relies on a general comparison that uses all of the ADV data rather than single point comparisons. Three ADV measurements exceed the tracer-dilution estimates (0.3–7% exceedance based on the average of PC1 and PC2), and seven ADV measurements are lower (4–13%), with the majority of the tracer-dilution estimates falling within the ADV error bars (Fig. 2A). Single point comparisons of these estimates would indicate a gain of tracer mass for the three exceedances (a physical impossibility as there are no sources of bromide within the watershed), whereas the remaining seven comparisons would indicate a loss of tracer mass. The general comparison of ADV and tracer-dilution estimates, however, indicates that mass is conserved; loss of mass would cause the tracer-dilution profile to diverge from the ADV profile in the downstream direction, as in Fig. 5 of [Bencala et al. \(2011\)](#). The fact that the majority of ADV measurements are lower than the corresponding tracer-dilution estimates is indicative of flow through the hyporheic zone that is not captured by the ADV measurements ([Zellweger et al., 1989](#)).

5.1.2. Streamflow estimation techniques for synoptic sampling

Continuous, constant rate injections have long been the method of choice for quantifying streamflow when conducting synoptic studies in mountain streams ([Bencala and McKnight, 1987](#); [Zellweger et al., 1989](#)), due to several advantages. These advantages include: (1) the ability to quantify the total amount of streamflow

that transports constituent mass (current meter or ADV measurements do not account for hyporheic flow, and this results in an underestimate of constituent load), (2) the ability to reliably quantify the hydrologic parameters that govern constituent transport ([Wagner and Harvey, 1997](#)), and (3) the ability to quantify streamflow at numerous synoptic sampling locations over a short time period. This third advantage is of particular importance for the work described herein and synoptic studies in general. Given a continuous injection, streamflow estimates at synoptic sampling locations are based on tracer concentrations from the water quality samples collected by the field team. Sample collection (and hence estimation of streamflow) is therefore expedited and constituent load may be quantified at numerous stream sites using data that is collected over a relatively short time period. Further, the time associated with each streamflow estimate corresponds directly to the time associated with the constituent concentrations, as both quantities are based on the same water quality sample.

Alternate methods of estimating streamflow such as ADV or slug injections increase the time required at each sampling location. This increase in time has two ramifications that potentially increase the uncertainty of the estimated constituent loads. First, the increased time between collection of samples at adjacent stream sites increases the potential for temporal variation in water quality to adversely affect load estimates (Peru Creek samples were collected as quickly as possible, Section 3.2). Second, the number of sites sampled on a given day is reduced, thereby decreasing the spatial coverage of the study and/or eliminating the ability to conduct replicate synoptic sampling campaigns. The applicability of these alternate techniques is also limited due to accuracy concerns (Section 5.1.1 and [Supplementary material](#)). For the case considered here, construction of spatial loading profiles using ADV measurements is clearly inappropriate, given the erroneous flow losses suggested by the measurements. These flow losses occur in stream segments that bracket the Pennsylvania Mine inflow and the third inflow from Cinnamon Gulch (Fig. 2A), and flow loss in these segments is extremely unlikely given the observed changes in constituent concentrations and pH (Figs. 3 and 4, Section 4.2) and obvious visual identification of inflowing waters (see photographs, Fig. S2A and H).

5.1.3. Selection of conservative tracers

Implementation of the synoptic mass balance approach requires estimates of streamflow at all of the stream sampling locations within the study reach. For the case of Peru Creek, stream sampling locations have both circumneutral (upstream of the Pennsylvania Mine) and acidic (downstream of the Pennsylvania Mine) pH (Fig. 3A). A LiBr tracer was therefore selected based on theoretical considerations that suggest conservative transport of the anion (Br) at circumneutral pH, and conservative transport of the cation (Li) under acidic conditions (Figs. 8.1 and 8.2 in [Dzombak and Morel, 1990](#)). Despite these theoretical considerations, use of Li concentrations to estimate streamflow results in a spatial profile that is in excess of the Br-based profile and the ADV measurements (streamflow at the end of the study reach as estimated by ADV, Br dilution, and Li dilution is equal to 94.0, 98.5, and 110.6 L/s, respectively). The fact that Li-based streamflow profiles exceed the Br-based profiles suggests a loss of Li to streambed sediments ([Zellweger, 1994](#); loss of Li will result in a lower concentration, and higher flow estimate, Eq. (1)). Loss of Li appears to increase in the downstream direction, as the tracer dilution profile diverges from the ADV measurements (i.e. the maximum difference between the profiles is at the end of the study reach; as with a similar comparison presented in Section 5.1.1, this comparison is based on the ADV data taken as a whole). These results are in contrast to related research in the Cinnamon Gulch watershed, where Li and Br-based streamflow profiles are comparable (unpublished data,

September 2009). The primary difference between the two studies appears to be pH, with more acidic conditions being observed in the Cinnamon Gulch study reach (pH 3.4–3.8, versus 4.3–4.9 for Peru Creek). This observation suggests a pH cutoff of ~ 4.0 , above which Li should not be considered conservative. Further research should be conducted in a controlled laboratory setting to confirm and/or refine this estimate for acid mine drainage waters. The conservative behavior of Br at low pH is consistent with Zellweger (1994), where Br was conservative in a stream with a pH of 3.6. Tracer investigations of streams with acidic and circumneutral waters may therefore be able to utilize NaBr or KBr, rather than the more costly LiBr tracer used in Peru Creek.

5.2. Constituent loads and implications for remediation

The loading results presented herein are based on two synoptic sampling campaigns conducted September 11, 2009 under low-flow conditions. Evaluation of constituent loading under low-flow conditions has important implications for remediation as the identified sources contribute metals and acidity over the entire hydrologic year (e.g. discharging adits). In addition, previous investigations of the Peru Creek watershed have noted an increase in constituent concentrations with decreasing streamflow as the effects of snowmelt subsidence (Moran and Wentz, 1974; Sullivan and Drever, 2001a). Low-flow conditions therefore represent a critical time period in which constituent sources are relatively undiluted and instream concentrations are near their maximum levels. Note, however, that the results of synoptic sampling represent a snapshot in time that is not applicable to other critical time periods such as rainfall–runoff events that introduce additional sources of constituent loading (e.g. runoff from mine dumps and tailing piles). The effects of these additional sources and consideration of other flow regimes is beyond the scope of the discussion that follows.

5.2.1. Contributions of source areas and potential controls on the Pennsylvania Mine inflow

Constituent loading from the Pennsylvania Mine inflow, wetland area, and Cinnamon Gulch is summarized in Fig. 5. Constituents may be grouped based on the proportion of loading attributed to the Pennsylvania Mine inflow:

- *More than one half.* More than 50% of the As, U, Fe, Co, Cu, Mn, Zn, and Cd loading within the study reach is attributable to Pennsylvania Mine inflow (84%, 78%, 72%, 67%, 63%, 58%, 55%, and 54%, respectively). This group includes 5 of the 7 constituents that exceed the chronic aquatic life standards (Cd, Cu, Fe, Mn and Zn; Section 4.2, cross-hatched bars, Fig. 5).
- *More than one third (but less than one half).* Over 33% of the Cr, SO₄, H⁺, Ca, Mg, Ni, Pb, and Al loading within the study reach is attributable to the Pennsylvania Mine inflow (47%, 44%, 43%, 41%, 41%, 39%, 36%, and 35%, respectively). This group includes 2 of the constituents that exceed the chronic aquatic life standards (Al and Pb; Section 4.2, cross-hatched bars, Fig. 5)
- *Less than one third.* Less than 33% of the Sr, V, Ag, Na, Si, K, and Ba loading within the study reach is attributable to the Pennsylvania Mine inflow (33%, 26%, 24%, 22%, 16%, 14%, and 3%, respectively). The Pennsylvania Mine inflow has relatively little effect on the loading profiles for these constituents; this finding is consistent with the work of Sullivan and Drever (2001a), in which K, Na, and Si were found to be unaffected by the Pennsylvania Mine.

These results indicate that the Pennsylvania Mine inflow is an appropriate focus for remedial actions, for two reasons. First, although the Pennsylvania Mine inflow accounts for only 14% of

the streamflow (Fig. 2B), it accounts for more than half of the loading for several constituents (Fig. 5). More importantly, it accounts for more than half of the loading for 5 of the 7 constituents that exceed the aquatic life standards (Cd, Cu, Fe, Mn and Zn). In addition, it accounts for more than one third of the loading for the remaining two constituents that exceed the standards (Al and Pb), while none of the constituents in the final group (less than one third) are a water quality concern in Peru Creek. Second, the Pennsylvania Mine inflow represents a single, point source discharge that may be relatively straightforward to remediate. The wetland area, in contrast, consists of diffuse seeps, springs, and groundwater inflow that may be hard to isolate and treat. Further, remedial actions on Cinnamon Gulch would address a much smaller percentage of the loading for most constituents and involve a larger quantity of water (46% of the streamflow, Fig. 2B).

The loading analysis provides a means to make rough, rudimentary estimates of constituent concentrations that might result from remedial actions. The effects of a bulkhead that reduces discharge from the Pennsylvania Mine inflow, for example, can be determined from mass balance considerations, i.e. the post-remediation load is equal to the pre-remediation load minus the load attributed to the Pennsylvania Mine inflow. For the case of dissolved Zn, the post-remediation load at the end of the study reach is equal to 148 mg/s (311–163 mg/s, Fig. 4AA). This quantity can be divided by the post-remediation flow (98.5–5.9 L/s, Fig. 2A), yielding a post-remediation concentration of 1.6 mg/L. Results from simple mass balance calculations such as this should be used with caution, as a bulkhead is unlikely to completely eliminate flow from the Pennsylvania Mine (the bulkhead may leak, and water behind the bulkhead may seep out at other locations). In addition, the mass balance approach does not consider the pH-dependent geochemical reactions that affect dissolved metal concentrations (Walton-Day et al., 2012). For the case considered here, the calculations implicitly assume that (1) load at the end of the study reach is unaffected by geochemical reactions, and (2) the remedial action does not alter instream pH. In reality, the load at the end of the study reach is the net effect of loading from source areas and geochemical reactions (natural attenuation); assumption (1) therefore results in an overestimation of constituent removal (some of the constituent load from the Pennsylvania Mine inflow would be attenuated by geochemical reactions before reaching the end of the study reach; subtraction of the entire load therefore overestimates the effects of remediation). Further, the Pennsylvania Mine inflow is a substantial source of acidity (Fig. 3B) and the placement of a bulkhead would result in an increase in instream pH. This increase in pH could in turn lead to precipitation and sorption reactions that affect most of the constituents of interest. Failure to consider these reactions (assumption 2) therefore underestimates constituent removal. Rigorous consideration of remedial alternatives thus requires techniques that consider both changes in mass loading and instream geochemistry, such as reactive transport modeling (Runkel and Kimball, 2002; Runkel, 2010; Runkel et al., 2012).

Consideration of remedial options is also confounded by hydrologic complexity that is common at many abandoned mine sites. As noted in Section 2, the Pennsylvania Mine inflow drains the F level of the mine, and some water within the mine workings may be leaking into the wetland area (see Section 4.5). In the example presented in the previous paragraph, it is assumed that bulkhead placement would eliminate 100% of the loading from the Pennsylvania Mine inflow. The actual reduction may be more or less than 100%, depending on the location and magnitude of the leakage to the wetland. If the leakage is occurring along the southeast-to-northwest portion of Level F (Fig. 1), it may be possible to eliminate loading from the Pennsylvania Mine inflow and some portion of the wetland loading by placing the bulkhead upgradient from the

adit portal (thereby decreasing the amount of leakage, and increasing the overall load reduction). If the leakage occurs along the southeast-to-northwest crosscut (Level C, Fig. 1), bulkhead placement could result in an increase in wetland loading as water builds up behind the bulkhead and increases the hydraulic head that drives the leakage (effectively decreasing the overall load reduction). The complexity of the mine site hydrology therefore introduces considerable uncertainty that should be addressed through additional investigations that identify the location and magnitude of leakage from the mine workings. Potential investigations include direct physical examination of the underground mine workings, and indirect geophysical techniques (e.g. Minsley et al., 2010; McClymont et al., 2011).

5.2.2. Al and Pb loading and constituent sources in the vicinity of the Brittle Silver Mill

Although the Pennsylvania Mine inflow is the primary source area, considerable loading is also attributable to the wetland area and Cinnamon Gulch. Of particular concern is Al and Pb, two constituents with low-flow concentrations that exceed the chronic aquatic life standards. Sources within the wetland area and Cinnamon Gulch contribute 65% and 59% of the constituent load for Al and Pb (Fig. 5). The spatial loading profile for Al exhibits a linear increase throughout the wetland area and the three stream segments that comprise Cinnamon Gulch, indicating spatially uniform contributions from sources over an 800 m subreach (Fig. 4G). The Pb loading profile, in contrast, indicates negligible loading from the wetland area, and spatially variable loading within the Cinnamon Gulch subreach (Fig. 4Y). This spatial variability is dramatic, with the majority of the Pb loading associated with the third stream segment; the stream segment ending at 1099 m accounts for only 27% of the Cinnamon Gulch inflow (Fig. 2B), while accounting for 70% of the Pb load attributable to Cinnamon Gulch. The load increase associated with the third segment is consistent with the observed inflow concentration of the third Cinnamon Gulch inflow that is ~8 times larger than the concentrations of the first two inflows (Fig. 4V). Sampling by Wood et al. (2005) also indicates a higher concentration for the third inflow (49 µg/L for the third inflow, versus 10 µg/L for the second; July 2001).

Variability in the Pb loading profile and inflow concentrations suggests a source located downgradient from where Cinnamon Gulch separates to form the second and third inflows (PC-891, PC-1050, Fig. 1). A potential source emanating from the hillside immediately upgradient from the Brittle Silver Mill was identified during field reconnaissance on July 21, 2010 (see “Draining adit”, Fig. 1). Although a complete water quality sample was not obtained, field parameters (pH = 4.4; specific conductance = 126 µS/cm) are in good agreement with data from Wood et al. (2005), and the water is presumed to be flowing from the collapsed Phiupsilon Tunnel. Data reported by Wood et al. (2005) for the Phiupsilon Tunnel (Pb = 2–5 µg/L) cannot account for the high concentration of the third inflow, however, and drainage from the tunnel may not be the direct source of Pb. Waters from the tunnel may contribute indirectly, as they may acquire Pb as they flow over the tailings, mine dumps, and ruins in the vicinity of the Brittle Silver Mill before joining the third Cinnamon Gulch inflow. Another potential source is the tailing piles that are adjacent to the third Cinnamon Gulch inflow, downgradient of the Brittle Silver Mill (figures 30–32 in Wood et al. 2005). Further sampling efforts will be required to accurately identify the Pb source associated with the third Cinnamon Gulch inflow.

5.2.3. Arsenic (As) loading and potential remobilization following remediation

Dissolved concentrations of As at all stream sites are below the analytical detection limit (<0.12 µg/L) and the total recoverable

concentrations therefore reflect the total concentration of solid-phase As within the water column. Total recoverable concentrations of As and Fe both increase sharply at 283 m due to the Pennsylvania Mine inflow (Fig. 4B, E, K, N), and generally decrease through the end of the study reach. The presence of solid-phase As is indicative of arsenate (As(V)) sorption onto solid-phase Fe (difference between total recoverable and dissolved concentrations, Fig. 4K), a process that potentially eliminates dissolved phase As at pH < 5 (Dzombak and Morel, 1990). Total recoverable constituent loads for As and Fe (Fig. 4H and Q) decrease downstream of 283 m, indicating that the observed decreases in concentration are not due to simple dilution; decreases in total recoverable loads for As and Fe indicate solid-phase material is settling to the streambed. The observed settling is consistent with field observations (orange, Fe-coated streambed) and Fey et al. (2002) who found elevated As concentrations in the streambed immediately downstream from the Pennsylvania Mine inflow. Deposition of As-laden materials to the streambed has likely occurred over an extended time period and a considerable amount of As has probably accumulated in the sediments. This contamination of the streambed should be considered when designing a remediation plan as remedial activities that increase pH could potentially result in the desorption of As (in contrast to the other constituents of interest, sorption of As decreases with increasing pH; Dzombak and Morel, 1990). Dissolved As concentrations would therefore be expected to increase during the post-remediation period as As desorbs and bleeds out of the streambed.

5.3. Synoptic sampling with replication

As described in Section 3.5, the replicate approach to synoptic sampling allows for the development of error bars on individual load estimates (Figs. 3B and 4G–I, P–R, Y, Z, AA) and the relative contribution of source areas (Fig. 5). The error bars shown in the figures depict the range of estimates (minimum and maximum values), centered around median values. Minimum, maximum, and median values were used for this purpose due to the relatively small sample size (i.e. the four loading profiles provide four estimates). An alternative to this approach is to develop error bars based on the standard deviation of the four estimates. The standard deviation of the load estimates at each stream site was therefore calculated and compared to the range given by the minimum and maximum values. This analysis indicates that the minimum and maximum values are generally 0.9–1.3 standard deviations away from the median values. The error bars placed on the individual load estimates (Figs. 3B and 4G–I, P–R, Y, Z, AA) thus represent the approximate 73% confidence intervals (assuming a normal distribution and 1.1 standard deviations above and below the center).

The error bars reflect the aggregate uncertainty in load estimates that is associated with (1) laboratory analyses of constituent and tracer concentrations, (2) field sampling, and (3) temporal variations in concentration that arise from diel cycles and/or source variation. Consideration of these factors represents an advance in the application of the synoptic mass balance approach by placing error bars on estimates of constituent load and by allowing all sources of uncertainty to be quantified in aggregate; previous applications of the approach have provided only point estimates of constituent load and considered only a subset of the possible errors. Kimball et al. (2007), for example, presents an equation that quantifies the error in the load estimate as a function of errors in constituent concentration and streamflow. These errors are in turn based on estimates of the analytical uncertainty associated with laboratory-determined constituent and tracer concentrations. As such, the approach does not consider sampling error, a potentially large source of uncertainty in streams such as Peru Creek where wide cross-sections make collection of representative

samples a difficult task (see Section 3.1). Runkel et al. (2005) used the results from sequential replicate samples as a means to consider both laboratory and field sampling error. Replicate samples were collected for only a subset (<5%) of stream sites (Runkel et al., 2005), however, effectively ignoring the fact that field sampling errors are inherently site-specific. Further, the replicates were collected sequentially (<2 min. apart), such that the effects of temporal variation were not quantified.

Error bars developed using the replicate approach represent the aggregate effects of the various sources of uncertainty. Given estimates of aggregate uncertainty, site specific data and expert judgement may be used to qualitatively assess the contributions of individual factors to uncertainty. This assessment can be used to guide the collection of additional data to reduce uncertainty. For the case considered here, uncertainty in loading estimates attributable to temporal variation is minimal (Section 4.3), and error bars reflect the uncertainty associated with laboratory analyses and field sampling. These errors are constituent and location specific, and relatively wider error bars result for those constituents and locations with substantial differences in PC1 and PC2 concentrations. Large differences in PC1 and PC2 hydrogen ion activities (as represented by pH, Fig. 3A), for example, lead to wide error bars (Fig. 3B). The wide error bars thus reflect the difficulties in obtaining accurate pH measurements of acid mine drainage waters in a field setting. PC1 and PC2 concentrations of the conservative constituents of interest, in contrast, are in close agreement (Al, Cd, Cu, Mn, SO₄, and Zn, Fig. 4A, C, J, L, T, U), and narrow error bars (Fig. 4G, I, P, R, Z, AA) indicate relatively little uncertainty from laboratory analyses and field sampling (n.b. the anomalously low PC1 concentrations at 1152 m for Al, Mn, SO₄, and Zn were determined to be in error and were not used within the loading analysis; this difference in the PC1 and PC2 concentrations is not reflected in the error bars.).

Differences in the total recoverable Pb concentrations for PC1 and PC2 lead to error bars that are wider than those for the conservative constituents of interest at most locations along the study reach (Fig. 4S and Y). Given the negligible uncertainty of the laboratory analyses indicated by the error bars for the conservative constituents of interest, the wider error bars for Pb are likely due to the use of total recoverable concentrations within the loading analysis (see discussion of sampling artifacts, Section 3.5). Sampling artifacts may also be responsible for uncertainty in Ag, Cr, and V, constituents with loading analyses based on total recoverable concentrations (wide error bars, Fig. 5). Some uncertainty in the Ag and Cr loads may also be attributed to laboratory analyses, as concentrations of Ag are near the detection limit and Cr is elevated in one of the field blanks (Table S3). Despite the relatively wider error bars for Pb, the identification of source areas appears to be clear cut and uncompromised (narrow error bars, Fig. 5).

As with Ag, Cr, Pb, and V, error bars for As and Fe are generally wider than those for the conservative constituents of interest, and some of this uncertainty may be attributed to the use of total recoverable concentrations. Additional uncertainty in the As and Fe loads is apparent for the stream segment bracketing the third Cinnamon Gulch inflow, where the error bars at the segment end point (PC-1099, Fig. 4H, Q) overlap the load estimates at the neighboring stream sites. Contributions of As and Fe from the Cinnamon Gulch source area are therefore more uncertain than the corresponding contributions from the Pennsylvania Mine (Fig. 5). The source of this additional uncertainty appears to be sampling error, as total recoverable As and Fe concentrations from the PC1 data set increase immediately downstream of the third Cinnamon Gulch inflow (PC-1099), and a similar increase is observed farther downstream (PC-1152) in the PC2 data set (Fig. 4B and K). The increased concentrations observed in both data sets are likely the result of the third Cinnamon Gulch inflow, as the stream segment ending at PC-1152 does not contain any surface inflows and very

little water enters between 1099 and 1152 m (Fig. 2A). The PC2 data set therefore appears to be affected by sampling error, where the source entering upstream of PC-1099 is not detected until the following stream site, PC-1152. Sampling error at PC-1099 may be attributable to the use of grab sampling techniques rather than width and depth integrated sampling (Table S2). Despite this additional uncertainty, the overall conclusions regarding As and Fe are unchanged, as contributions from the dominant source area (Pennsylvania Mine) have relatively narrow error bars (Fig. 5).

In summary, the replicate approach to synoptic sampling allows for development of error bars that quantify aggregate uncertainty and provide a means to assess the accuracy of the source area contributions. The quantitative focus on aggregate uncertainty is appropriate as it provides a straightforward means to determine the degree to which individual load estimates and contributions of source areas are affected by uncertainty (i.e. load estimates and percent contributions are evaluated in light of their error bars, as discussed above). This quantitative focus is supplemented by a qualitative analysis of the individual factors comprising aggregate uncertainty. For the case of Peru Creek, the analysis provided by the replicate approach lends confidence to the loading analysis presented in Section 3.5. The success of this endeavor is attributable to the negligible effects of temporal variation (little diel cycling and/or source variation), selection of representative stream sites (minimal sampling error), and precise laboratory analyses. Other applications of the approach may not be so fortunate, and analyses from these applications may be used to guide the collection of additional data to more accurately define source contributions.

6. Conclusions

The foregoing analysis has direct implications for similar studies of contaminated streams and specific implications for Peru Creek. The primary conclusions are as follows:

- The replicate approach to synoptic sampling allows for the development of error bars that reflect the aggregate uncertainty in load estimates. Evaluation of error bars lends credence to the loading profiles and source contributions that are quantified herein. Other applications may be subject to a greater uncertainty, prompting the investigator to conduct additional data collection efforts to reduce uncertainty (Section 5.3).
- Loading analyses for nominally conservative constituents should be conducted using dissolved concentrations to avoid sampling artifacts associated with total recoverable concentrations, whereas analyses for reactive constituents should be conducted using total recoverable concentrations such that constituent loads are not underestimated. Use of total recoverable concentrations in the present application leads to more uncertainty in the load estimates and source contributions, indicating that loads for reactive constituents are more difficult to quantify (Sections 3.5 and 5.3).
- Contrary to theoretical considerations, Br acts as a conservative tracer at low pH (from 3.4 to 4.9), whereas Li is non-conservative at pH > 4.0. Additional research in a laboratory setting should be conducted to evaluate these tracers for acid mine drainage waters (Section 5.1).
- Application of the synoptic mass balance approach to the Peru Creek study reach indicates that (1) concentrations of Al, Cd, Cu, Fe, Mn, Pb, and Zn exceed aquatic life standards (Section 4.2), (2) loading within the study reach is dominated by effluent from the Pennsylvania Mine (Section 5.2.1); (3) a substantial source of Pb exists within lower Cinnamon Gulch in the vicinity of the Brittle Silver Mill (Section 5.2.2), and (4) substantial quantities of solid-phase As may exist on the streambed (Section 5.2.3).

- Interpretation of source area contributions and evaluation of remedial options is confounded by the potential leakage of the Pennsylvania Mine workings to the wetland area. Additional research to determine the magnitude and location of the leakage should be conducted prior to the implementation of remedial actions (Sections 2, 4.5 and 5.2.1).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2013.02.031>.

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