Multiple injected and natural conservative tracers quantify mixing in a stream confluence affected by acid mine drainage near Silverton, Colorado

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Abstract:

The acidic discharge from Cement Creek, containing elevated concentrations of dissolved metals and sulphate, mixed with the circumneutral-pH Animas River over a several hundred metre reach (mixing zone) near Silverton, CO, during this study. Differences in concentrations of Ca, Mg, Si, Sr, and SO_4^{2-} between the creek and the river were sufficiently large for these analytes to be used as natural tracers in the mixing zone. In addition, a sodium chloride (NaCl) tracer was injected into Cement Creek, which provided a Cl^- 'reference' tracer in the mixing zone. Conservative transport of the dissolved metals and sulphate through the mixing zone was verified by mass balances and by linear mixing plots relative to the injected reference tracer. At each of seven sites in the mixing zone, five samples were collected at evenly spaced increments of the observed across-channel gradients, as determined by specific conductance. This created sets of samples that adequately covered the ranges of mixtures (mixing ratios, in terms of the fraction of Animas River water, %AR). Concentrations measured in each mixing zone sample and in the upstream Animas River and Cement Creek were used to compute %AR for the reference and natural tracers. Values of %AR from natural tracers generally showed good agreement with values from the reference tracer, but variability in discharge and end-member concentrations and analytical errors contributed to unexpected outlier values for both injected and natural tracers. The median value (MV) %AR (calculated from all of the tracers) reduced scatter in the mixing plots for the dissolved metals, indicating that the MV estimate reduced the effects of various potential errors that could affect any tracer. Published in 2006 by John Wiley & Sons, Ltd.

KEY WORDS   surface-water mixing; natural tracers; tracer injection; acidic stream; mixing ratio; Animas River, CO

INTRODUCTION

Conservative tracers used in hydrologic studies include a variety of injected solutions, as well as natural cations, anions, and isotopes (Kendall and Caldwell, 1998; Herczeg and Edmunds, 2000). Conservative tracer injections are commonly used to estimate discharge, particularly in streams where conventional measurements are not possible or practical (Kilpatrick and Cobb, 1985; Zellweger, 1994; Kimball *et al.*, 2001). When tracer injection techniques are coupled with solute-transport calculations, reach- and basin-scale constituent loading and attenuation processes can be assessed, which have been particularly useful in studies of streams affected by acid mine drainage (Chapman, 1982; Harvey and Fuller, 1998; Kimball *et al.* 2002; Runkel and Kimball, 2002).

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Chemical reactions and mixing and transport processes in ground and surface waters can be identified and quantified by techniques utilizing naturally occurring solutes that can serve as conservative tracers (Chapman *et al*., 1983; Kennedy *et al*., 1986; Paulson, 1997). Several conservative tracers are often needed to resolve complex flow paths and hydrograph separations involving inputs from multiple sources (components; Hooper *et al*., 1990; Rice and Hornberger, 1998; Hoeg *et al*., 2000). In both simple and complex systems, concentrations of tracers in the mixing components (end-members) can be difficult to quantify because of temporal and spatial variability and other factors, all of which contribute to uncertainties in mixing calculations (Jenkins *et al*., 1994; Burns *et al*., 2001; Carrera *et al*., 2004). Although a single conservative tracer can estimate the (relative) inflows in a two-component system, such as a simple two-stream confluence, two or more tracers provide additional estimates that can be used to calculate a range or a mean or median value (MV) that is likely to be more accurate (McKnight *et al*., 1992; Sullivan and Drever, 2001; Schemel *et al*., 2004). In addition, unusual or unlikely results can be identified and assessed when several estimates from multiple tracers are available (Rice and Hornberger, 1998). Advantages of multiple conservative tracers can most easily be applied when many potential tracers are available naturally, an attribute that can vary widely among hydrologic systems.

Streams that drain mineralized areas or catchments impacted by mining activities typically carry substantial loads of dissolved metals and other products of mineral weathering primarily because oxidation of pyrite and other sulphides produces low-pH waters capable of dissolving a variety of minerals (Nordstrom and Alpers, 1999). As a result, these acidic tributaries can supply high concentrations of many natural conservative tracers to their confluences with circumneutral-pH streams, in which concentrations are often much lower (Bencala *et al*., 1987; Filipek *et al*., 1987). The mixing ratio (the volumetric fraction of one component in a mixture) provides fundamental information for samples collected in the downstream mixing zone. Although mixing ratios can be calculated directly from measured discharges to confluences when downstream reaches are well-mixed (e.g. Foos, 1997), conservative tracers are needed to estimate mixing ratios for field samples collected within mixing zones where chemical gradients indicate that mixing is incomplete. In concept, all conservative tracers in a sample should yield the same value for the mixing ratio, and in a simple two-component system the concentrations of one tracer should plot as a straight line with respect to the mixing ratio (Bencala *et al*., 1987; Paulson, 1997). When field samples or laboratory mixtures prepared from natural waters cover a wide range of the mixing ratio, chemical reactions that occur in mixing zones can be identified by non-linear mixing plots (e.g. Schemel *et al*., 2000; Tonkin *et al*., 2002; Balistrieri *et al*., 2003). Identification and quantification of reactions and non-conservative processes are critical to the evaluation and restoration of streams affected by acid mine drainage (e.g. Chapman *et al*., 1983; Kimball *et al*., 2001; Runkel and Kimball, 2002).

In this study, we explore the usefulness of (1) a method to obtain detailed samples over a wide range of the mixing ratio downstream from the confluence of an acidic creek with a circumneutral-pH stream and (2) a simple method to establish robust estimates of mixing ratios for these samples based on multiple tracers. The sampling method was based on across-channel gradients in specific conductance, a property that has been used for hydrograph separations and as a surrogate for dissolved tracers (e.g. Matsubayashi *et al*., 1993; Gooseff and McGlynn, 2005). The study occurred during low-flow in late summer 1997, when it was practical to inject a 'reference' tracer as well as utilize natural tracers. Conservative transport for each tracer was verified by mass balances and mixing plots. Results from natural tracers were compared with results from the injected tracer and effects of sample filtration and variability in end-member concentrations were assessed.

Study area

Cement Creek drains a highly mineralized catchment in the Silverton caldera of the San Juan Mountains in southwest Colorado (Figure 1; Yager and Bove, 2002). Where Cement Creek joins the Animas River near the town of Silverton, its discharge is acidic (pH < 4), which is about 4 pH units less than that in the Animas River upstream of the confluence (upper Animas River; Church *et al*., 1997; Schemel *et al*., 2000). Many discrete and diffuse sources contribute to high concentrations and loads of dissolved metals and sulphate and low pH
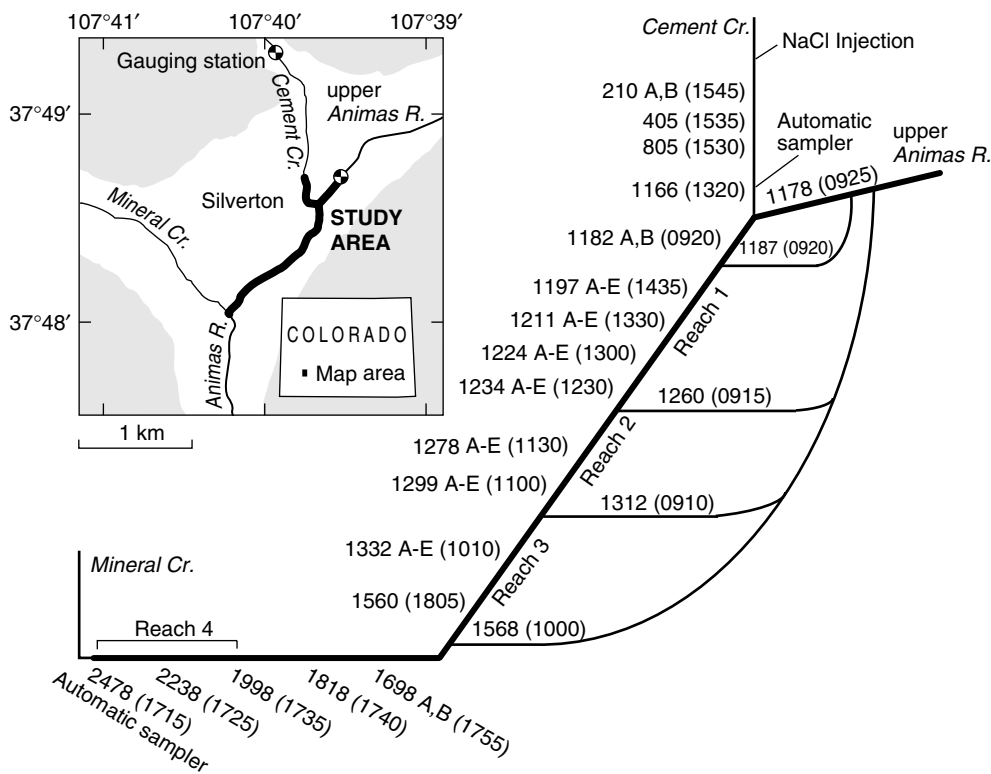
Figure 1. Map showing Cement Creek and Mineral Creek confluences with the Animas River near Silverton, Colorado, and diagram showing details of the study area, including sampling sites, sampling times (in parentheses), and locations of automatic samplers. Sites where multiple stations were sampled across the channel are shown by A, B (two stations) and A–E (five stations). Shaded areas on the map represent surrounding high-elevation mountains

in Cement Creek (Kimball *et al*., 2002). Although sources of acidity and metals also exist upstream in the Animas River, concentrations are greatly attenuated by particle formation and deposition, neutralization, and dilution before discharge reaches Silverton (Paschke *et al*., 2005). Neutralization of Cement Creek discharge in the downstream mixing zone of the Animas River forms Fe- and Al-rich colloidal precipitates, which sorb some trace metals (e.g. Cu, Pb, and Zn). In spite of large chemical gradients and multiple reactions, our previous study in 1996 (Schemel *et al*., 2000) showed that some dissolved substances are transported conservatively through this mixing zone, and suggested that these and other solutes might be suitable tracers if natural differences in end-member concentrations are sufficiently large.

Animas River discharge is low from late fall to early spring because of freezing temperatures at the high elevation (2800 m at Silverton). Discharges in the study area are highest (30–40 m^3 s^{-1}) during the late-spring snow melt, and they decline to lowest values (2 m^3 s^{-1}) by late summer (discharge data are from US Geological Survey (USGS) gauges on Cement Creek, #09358550, and the Animas River at Silverton, #09358000, shown on Figure 1; USGS, 1992–1997). About 75% of the total discharge to the study area is supplied by the upper Animas River during late summer. Although the Animas River inundates a broad floodplain during high discharge, flow through the study area during late summer 1996 and 1997 was restricted primarily to a few braids and a main river channel (Schemel and Cox, 2005). The first 150 m below the Animas River–Cement Creek confluence was a well-defined channel averaging about 0·4 m in maximum depth and 9 m in width. Over the next 200 m, channel width was generally greater and more variable, water depths were reduced, and a few side channels and pools affected circulation. After joining with the last braid from

the upper Animas River, flow was confined to a well-defined channel for 1 km before the confluence with Mineral Creek (Figure 1). The decrease in elevation between the Animas River gauge and Mineral Creek was about 10 m. More details of the Animas River–Cement Creek mixing zone during late summer 1996 and 1997 are given by Schemel and Cox (2005).

Year-to-year differences in weather, discharge levels, and streambed and bank movements can substantially affect the way Cement Creek and the Animas River mix during late summer. Although discharge levels were similar, mixing occurred more gradually in 1997 compared with 1996 because the Animas River discharge in 1997 was divided into more braids, which distributed inflow progressively over the first 400 m (Schemel and Cox, 2005). Agreement among gauged discharges indicated negligible groundwater inflow in late summer 1996 (Schemel *et al.*, 2000). In addition, the gravel substrate downstream from the Animas River–Cement Creek confluence was coated and clogged with Fe- and Al-rich precipitates during late summer, which inhibited flow through the streambed. These precipitates and other particles are suspended during periods of high flow, producing concentrations of particulate substances that are higher than during late summer (Church *et al.*, 1997). Concentrations of most dissolved substances are typically highest during periods of low flow.

METHODS

The 1997 study area included reaches of the upper Animas River and Cement Creek downstream from their respective USGS gauges, the main channel where discharges from the two streams progressively mixed, and a (downstream) well-mixed reach extending to the confluence with Mineral Creek (Figure 1). Discharge values at 15 min intervals were obtained from the gauges on Cement Creek and the upper Animas River. During the late summer 1997 period of low flow, discharge from the upper Animas River was split into five braids below the gauge (see diagram in Figure 1). The first four braids supplied about half of the total Animas River inflow, and the remainder was supplied by a much larger braid that discharged farther downstream at site 1568 (Schemel and Cox, 2005). Site numbers used here refer to the distance (metres) downstream from the tracer injection point, which was 145 m downstream from the Cement Creek gauge. For simplicity, we use the term 'mixing zone' to refer to all main-channel sites downstream from the confluence of Cement Creek with the first braid (site 1178) from the upper Animas River.

Tracer injection

A sodium chloride (NaCl) solution was injected into Cement Creek using computer-controlled metering pumps that assured a constant injection rate of about 3 g s^{-1} NaCl (Kimball *et al.*, 2002). The injection began on 10 September 1997, 22 h before samples were collected at the sites, and continued through the sampling period. Samples for anion analysis (Cl$^-$ and SO$_4^{2-}$) were collected at hourly intervals with automatic samplers located on Cement Creek just upstream of the mixing zone (Figure 1; site 1166) and at the downstream end of the study area (site 2478). Time-series samples were not collected in the upper Animas River, where concentrations were much lower than in Cement Creek and expected variations would have very small effects on mixing and mass-flow calculations.

Sample collection and processing

The sampling strategy varied among the sites shown in Figure 1. One sample was collected midstream in each of the five braids of the upper Animas River (sites 1178, 1187, 1260, 1312, and 1568). One or two (A, B; Figure 1) samples were collected in Cement Creek upstream of the mixing zone (sites 210 to 1166) and in the mixing zone (site 1182 and sites 1560 to 2478).

At each of seven sites in the mixing zone (1197 to 1332; transect sites), five stations (A–E; Figure 1) were sampled across the stream because of large, across-channel chemical gradients. Station locations were established in the following manner at each site. Near-surface measurements of specific conductance (SC)

were made with a portable meter at increments of 0·3–0·6 m across the stream transect. The range of SC values was used to establish five 'target values' at equal SC increments (ESCIs), and then the SC distribution measured across the transect was used to locate each sampling station (ESCI sampling strategy). The rationale for this approach was that a wider range and more equally spaced measurements of the chemical gradients might be obtained compared to sampling with equal-width increment (EWI) or equal-discharge increment (EDI) strategies.

As part of the station location procedure, discharges were estimated (from measurements of total water depth z and velocity at $0·6z$) at increments of 0·3–0·6 m across the transects, primarily so that mass flows could be calculated from the chemical data. Several teams were needed to conduct the site surveys and locate the stations before the samples were collected. This might have contributed to some additional uncertainty in the discharge estimates. For example, four (site) discharge values were estimated in the reach between sites 1197 and 1234, where there were no additional inflows. The range of values was equivalent to 13% of the mean value, and the coefficient of variation (CV, standard deviation divided by the mean) was 0·056, which was greater than the uncertainty in the chemical analyses described below.

All samples were collected over a 9 h period and processed on the same day. Water samples were collected using a vertically integrating sampler with a Teflon nozzle and polyethylene bottle. Even though stations were located by near-surface SC, vertically integrated samples were required for mass-flow calculations. All bottles and sampling nozzles were precleaned with dilute nitric acid and then rinsed with sample water at each station. Samples were kept cool and in the dark, and most samples were processed within 2 h after collection. After a sample was shaken for a few seconds, whole (W) samples were decanted for metal analyses and for SC, which was measured with a temperature-compensating (25 °C) meter at the sample processing site. A tangential flow filtration technique was used to prepare samples for dissolved metal (F and U) and anion (F) analyses. The F filtrates used 0·45 μm polycarbonate membranes and U filtrates used 10 kDa (approximately 0·001 μm pore size) regenerated cellulose membranes. All samples for metal analysis (125 ml) were acidified with 1 ml ultrapure nitric acid, whereas anion samples were not acidified. The filtration apparatus was cleaned with dilute nitric acid and rinsed with 18·2 MΩ deionized water between samples.

Analytical methods

Water samples were analysed for six metals (Ca, Mg, Mn, Na, Si, and Sr) with a Thermo Jarrel Ash inductively coupled plasma optical emission spectrometer (ICP-OES; any use of trade, product, or firm names is for descriptive purposes only and does not constitute endorsement by the US Government). Samples were diluted based on SC, so that most analytical values ranged between 0·5 and 3 mg l^{-1}, with the exception of Ca (30–50 mg l^{-1}). CVs for reference samples analysed twice during each analytical run ($n = 20$) were less than 0·015 for all metals except Na (0·044). Mean values for a standard reference material (AMW-3; Long and Farrar, 1994) agreed with the most probable values within 3% for Mg, Mn, and Na, and within 5% for Ca, Si, and Sr. Repeat analyses of field samples typically agreed within 4%.

Anion samples were analysed for Cl$^-$ and SO$_4^{2-}$ with a Dionex ion chromatograph. Previous analyses of reference materials by this method (Kimball *et al*., 1999) showed that mean values agreed with the most probable values within 3% for Cl$^-$ (CV $= 0·03$) and 5% for SO$_4^{2-}$ (CV $= 0·08$).

Calculations

Mixing ratios were calculated for all samples collected in the mixing zone ($n = 44$ for most analytes). Concentrations of metals and anions from each sample were used to calculate mixing ratios in terms of the percentage of upper Animas River water in each sample (%AR $= (V_{AR}/(V_{CC+AR}) \times 100$, where V_{AR} is the volume from the upper Animas River and V_{CC+AR} is the total volume of the mixture from both tributaries). By rearranging the mass balance equation for a two end-member (component) system,

$$[CC]V_{CC} + [AR]V_{AR} = [MZ]V_{CC+AR} \tag{1}$$

where [CC], [AR], and [MZ] are the concentrations in Cement Creek, the upper Animas River, and the sample from the mixing zone respectively, the following expression is formed:

$$\%\text{AR} = \frac{[\text{CC}] - [\text{MZ}]}{[\text{CC}] - [\text{AR}]} \times 100 \tag{2}$$

For these calculations, end-member concentrations for Cement Creek, [CC], were from the sample collected at site 1166. Results from the automatic sampler in Cement Creek were not used to adjust values for Cl^- or SO_4^{2-} end-members. End-member concentrations for the Animas River, [AR], were mean values from samples collected in all five braids.

Mass flows were calculated from the chemical data and measured or estimated discharges for selected sites. End-member concentrations (defined above) were used to calculate mass flows for Cement Creek and the upper Animas River. The USGS gauged discharge was used for Cement Creek, but discharges for the five Animas River braids were measured directly or calculated from measurements made at sites in the mixing zone. At the seven transect sites, discharge estimates were assigned to each station using the near-surface SC distribution across the site. Boundaries for calculation of station discharges were located at SC values that were halfway between adjacent target values. Mass flows for these sites were the totals of their five station values.

RESULTS

The hydrology of the mixing zone is described relative to three reaches between Animas River braids (Reach 1: sites 1187–1260; Reach 2: sites 1260–1312; Reach 3: sites 1312–1568) and a reach near the end of the study area (Reach 4: sites 1998–2478; Figures 1 and 2a). The upper Animas River contributed 40%, 47%, 55%, and 78% of the total flow in these four reaches respectively.

Differences in SC across the seven transect sites resulted from the progressive mixing of inflow from Cement Creek (SC = 846 μS cm^{-1}) with braids from the upper Animas River (mean SC = 260 μS cm^{-1}). All five braids discharged to the same side of the mixing-zone channel, resulting in mostly similar and consistent SC distributions among the seven transect sites in Reaches 1–3 (Figures 1 and 2a). The collection of five vertically integrated samples at each of the sites was guided by the (near-surface) location of equal-increment target values for SC. In most cases the SC values of the vertically integrated samples were greater than the near-surface target values, although these differences were typically small for samples collected on the low-SC side of the channel (Figure 2a). The differences were often greatest at stations near the high-SC side of the channel, but this varied among the sites. Overall, SC values for only four samples (of 35) exceeded the target values by more than 10%, and the greatest difference was only 14%. Because the samples usually encompassed a wider range than the target values, the sampling strategy was effective in producing samples with wide ranges of SC at increments that were representative of the across-channel gradients, satisfying an important objective. The widest ranges were observed at the four sites in Reach 1 and the single site in Reach 3 (1332), where flow was greater than in Reach 1 and (mean) SC was lower. Two samples collected where flow was greatest downstream from the fifth Animas River inflow (site 1698) showed similar values and lower SC (Figure 2a). The river was well mixed farther downstream in Reach 4, where only midstream samples were collected.

Among the seven transect sites, site 1332 had the greatest mean depth (0·36 m) and total flow (1·1 m³ s^{-1}; Figure 2b). Even though the median depth varied from 0·2 to 0·4 m among the sites, the shape of the channel and the distribution of flow (velocity) at site 1332 were similar to the other sites. The distribution of SC across the channel was also similar among most sites, although the ranges varied. The only site with a substantial difference in the distribution of SC was the first site immediately downstream from the confluence of Cement Creek with the first two braids from the upper Animas River (site 1197). At this site, there was a steep gradient in SC near the middle of the channel, rather than the more gradual change in SC across the channel
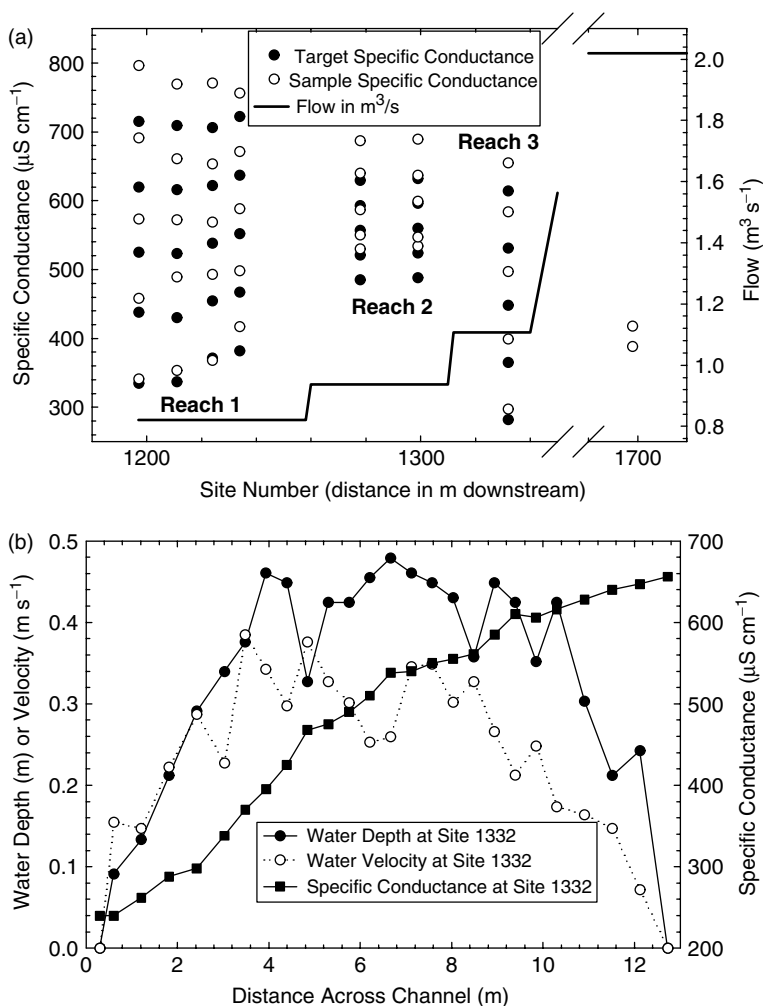
Figure 2. (a) Sample (measured) SC and target values used to locate sampling stations and total flow at the seven transect sites (1197, 1211, 1224, 1234, 1278, 1299, and 1332) and a downstream site (1698). Reach labels refer to diagram in Figure 1. (b) Across-channel water depth, velocity, and near-surface SC at site 1332

seen at site 1332 (Figure 2b) and the other sites. In general, across-channel mixing increased with distance downstream from an inflow. This was clearly a factor affecting the range and distribution of SC at the transect sites in Reach 1 (Figure 2a).

The median estimated (incremental) discharge for the 35 stations was 18% of the total flow at its respective transect site. This was close to 20%, the value for each station if an EDI sampling strategy had been used. One-half of the station discharges for the ESCI sampling strategy were within 6% of 20%, and discharges from only six stations were outside the 10–30% range. All but one of these six outliers were in Reaches 2 and 3.

Concentrations of metals, Cl⁻, and SO₄²⁻

Concentrations of metals, Cl^-, and SO_4^{2-} were highly correlated with SC in all of the samples ($r > 0.994$, except for Mn, $r = 0.977$). Metals, Cl^-, and SO_4^{2-} were more concentrated in Cement Creek than in the upper Animas River (Table I). Ca, Mg, Na, Si, and Sr were more concentrated by factors ranging from 2·8 to

Table I. Measured (end-member) concentrations in the Animas River braids (AR) and Cement Creek (CC), end-member concentrations predicted by linear regressions of measurements in the mixing zone against Cl^--based and MVs of the mixing ratio (%AR), and r^2 for regressions against Cl^--based and MVs of %AR[a]

Analyte	[AR] (mg l^{-1})			[CC] (mg l^{-1})			r^2	
	Measured	Predicted Cl^-	Predicted median	Measured	Predicted Cl^-	Predicted median	Chloride	Median
Calcium	44	46	44	154	150	151	0·986	0·998
Magnesium	2·6	2·7	2·6	7·6	7·6	7·7	0·983	0·997
Manganese	1·1	1·0	1·1	1·57	1·62	1·63	0·932	0·955
Sodium	2·0	2·1	2·0	6·2	6·5	6·5	0·984	0·994
Silicon	3·4	3·3	3·2	12·4	12·2	12·3	0·989	0·998
Strontium	0·42	0·44	0·44	1·66	1·62	1·65	0·986	0·998
Sulfate	90	94	92	470	472	477	0·994	0·991
Chloride	0·49	—	0·46	4·35	—	4·39	—	0·992

[a] Measured (end-member) concentrations were mean values of the five Animas River braids and values from site 1166 for Cement Creek. MVs of the mixing ratio were calculated from all of the analytes except Mn.

4·0 and SO_4^{2-} by a factor of 5·2. Before the injection of NaCl into Cement Creek, Na was more concentrated in Cement Creek by only a factor of 1·8, and the difference in concentration between the two streams was too small to estimate mixing ratios within a few per cent. In addition, Cl^- concentrations were nearly identical in the two streams. Therefore, neither Na nor Cl^- had sufficient (naturally occurring) differences in concentration that would make them good choices for tracers in this study. During the injection, however, Na was more concentrated by a factor of 3·1 and Cl^- by a factor of 8·9.

Samples collected in the mixing zone showed that Ca, Mg, Mn, Na, Si, and Sr remained primarily dissolved, rather than forming or sorbing to precipitates. Box plots comparing relative differences between whole and 0·45 μm filtered samples $((W - F)/W)$ and the two filtrates $((F - U)/F)$ generally showed small differences (Figure 3). Overall, 88% of the values were within 5% of zero, which was close to the expected analytical uncertainty. In most cases, values were evenly distributed and ranges of the mid-50 percentiles were similar in the $W-F$ and $F-U$ comparisons for each metal. MVs were close to zero for the $F-U$ comparisons. Slightly higher MVs in the $W-F$ comparison indicated generally small contributions from particles in the whole samples. Only Si showed a significant positive bias in the $W-F$ comparison, indicating a MV of about 3% particulate Si.

Calculation of mixing ratios

Values of the mixing ratio %AR were calculated based on concentrations of seven tracers, i.e. Ca, Cl^-, Mg, Na, Si, Sr, and SO_4^{2-}, in each sample from the mixing zone. Mn, which could serve as a conservative tracer for some applications (see below), was not used in the mixing ratio calculations because the concentration difference between the two streams was very small (0·47 mg l^{-1}; Table I) and the range in concentration among the Animas River braids was unexpectedly large (16% of the mean value). Comparisons of %AR values based on W and F samples showed mean differences of less than 2%AR for Ca, Mg, Na, and Sr; however, differences were much greater for Si because of particles present in the W samples. Values of %AR presented below were based on F-sample concentrations, because additional uncertainty might be introduced by particles in the W samples.

Among all of the analytes, Cl^-, the injected 'reference' tracer, had the greatest concentration factor, which suggested that this tracer might provide the most accurate estimates of the mixing ratio (Genereaux, 1998; Uhlenbrook and Hoeg, 2003). Therefore, %AR values based on the 'Cl^- reference' were used to evaluate %AR values based on each metal and SO_4^{2-} for each sample. Figure 4 shows differences between the sample
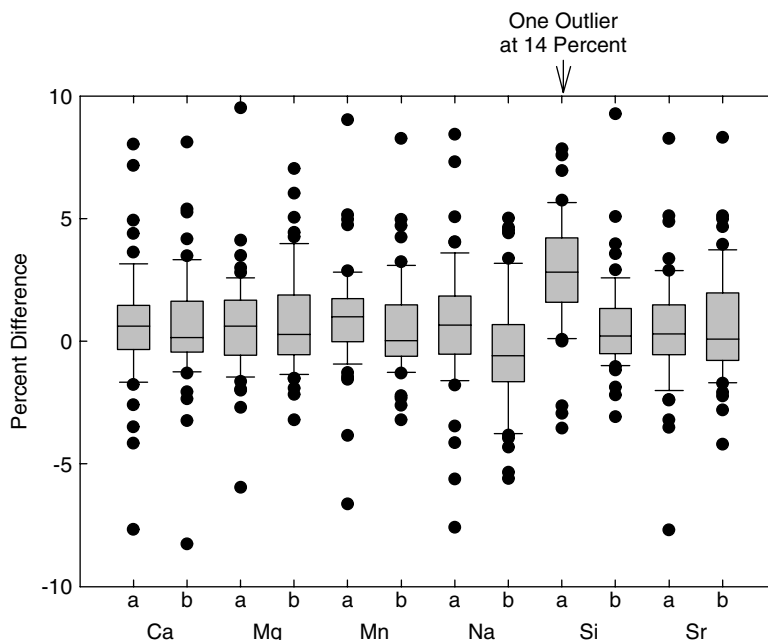
Figure 3. Box plots showing differences between whole samples (W), 0·45 μm filtrates (F), and 10 kDa filtrates (U). a: $[(W - F)/W] \times 100$; b: $[(F - U)/F] \times 100$
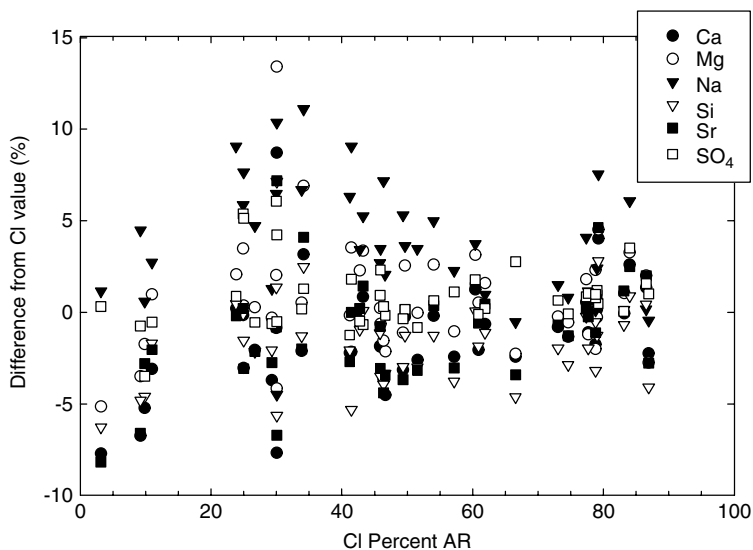

Figure 4. Differences between mixing ratio (%AR) values computed from Ca, Mg, Na, Si, Sr, and SO_4^{2-} and values based on the reference tracer, Cl^-, for samples collected in the mixing zone plotted against Cl^--based %AR

and Cl^--based %AR values plotted against the Cl^--based %AR value for all of the samples (44 for most analytes). With the exception of Na, most %AR values fell within 5% of the value based on the reference tracer. Na in Cement Creek was a mixture, with about 58% from natural sources and the remainder from the injectate. Values of %AR based on Na were typically in the high range (highest value for 34 samples). On
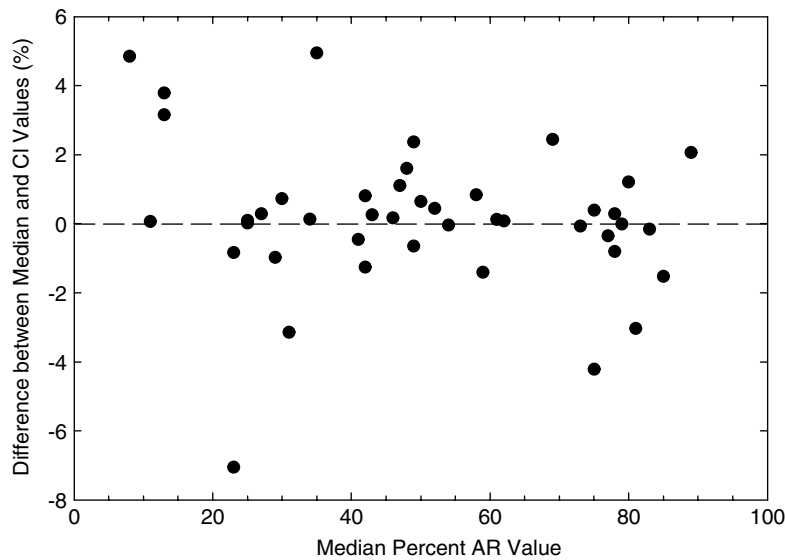
Figure 5. Differences between MV estimates of the mixing ratio (%AR) and values based on the reference tracer, Cl^-, for samples collected in the mixing zone plotted against the median %AR value

the low side, Si yielded the lowest values for 20 samples. Analytical and procedural errors potentially could influence any of the values, including those for Cl^-. Consequently, an MV was computed based on all seven tracers as a potentially more robust estimate of %AR for each sample.

Differences between the MV and Cl^--based %AR values were relatively small and within the levels of analytical uncertainty in most cases (Figure 5). Only eight of the differences equalled or exceeded 3%AR and only one was greater than 5%AR. Linear regressions of each analyte against the MV and Cl^--based values showed that slightly higher coefficients of determination r^2 were produced using the MV with all 6 metals (Table I). Even though differences in the r^2 statistic for regressions using the two %AR values were small, plots for the metals clearly showed less scatter in the data when the MVs were used. The example using Ca was representative of plots for the other metals (Figure 6). Only the plot for SO_4^{2-} using the Cl^--based value showed less scatter than its MV-based plot (not shown). Both Cl^- (injected) and SO_4^{2-} (natural) had concentration ratios that were higher than all six metals. End-member concentrations predicted by both the MV- and Cl^--based linear regressions were close to values measured in the field in most cases (Table I). One notable exception was for Na, where the measured concentration in Cement Creek was 5% lower than the predicted values.

Variability in discharges and concentrations

Over the sampling period, there was a small decrease in discharge, about 7% of the final total value based on data from the Cement Creek and upper Animas River gauges. There was likely some variability in concentrations as well, which was indicated by measurements of Cl^- and SO_4^{2-} (from the automatic sampler) in Cement Creek (Figure 7). Ranges in concentrations of Cl^- and SO_4^{2-} in Cement Creek over the sampling period were equivalent to about 6% of their mean values. In both cases, however, the end-member concentrations used in the %AR calculations (from site 1166) were slightly lower than concentrations indicated by the automatic-sampler data. Overall, the end-member concentration for SO_4^{2-} in Cement Creek was only 1·5% lower than the mean value (477 mg l^{-1}) for the sampling period, and the end-member concentration for Cl^- was 2·7% lower than the mean value (4·47 mg l^{-1}). The lowest concentrations of both Cl^- and SO_4^{2-} occurred in late afternoon, and there was an apparent trend of decreasing concentrations over the sampling
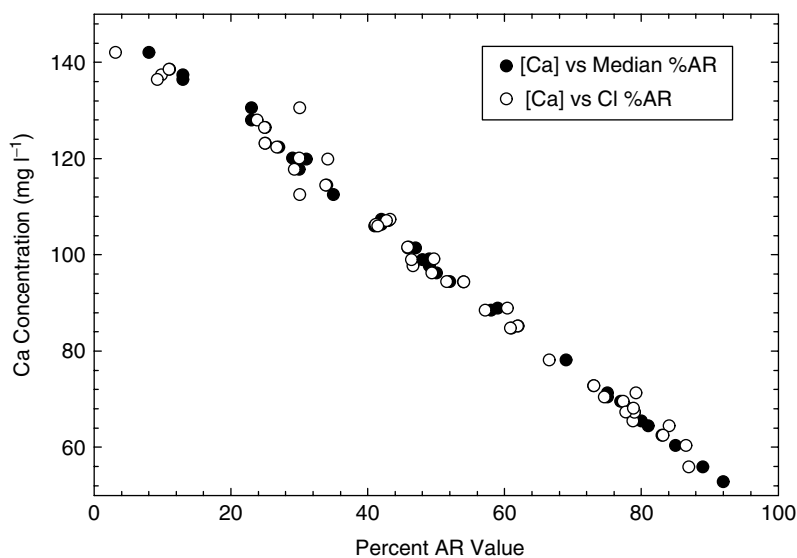
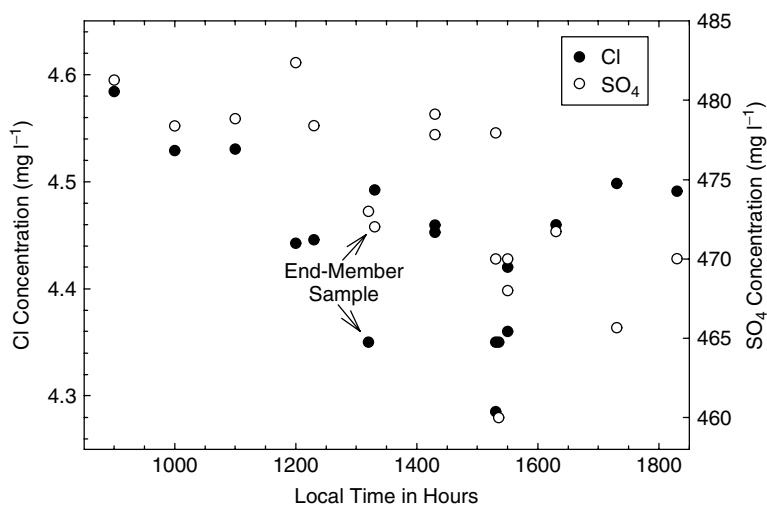Figure 6. Concentrations of Ca plotted against Cl^--based and MV estimates of the mixing ratio (%AR)

Figure 7. Concentrations of Cl^- and SO_4^{2-} from automatic sampler over the sampling period and the end-member sample values from site 1166 in Cement Creek

period, particularly for SO_4^{2-}. Possible effects of end-member concentration and discharge variability were evaluated by calculating %AR based on the Cement Creek and upper Animas River (gauge) discharges and the concentrations of Cl^- and SO_4^{2-} from the automatic sampler at the end of the study reach (Figure 8). The %AR values based on Cl^- and SO_4^{2-} were within 2%AR of the values estimated by the discharges. The total range of values for all three estimators was less than 3%AR over the sampling period.

The four sites in Cement Creek and the five braids of the Animas River were sampled over a period of time shorter than the entire sampling period (2·4 h, 0·7 h, and 9 h respectively; Figure 1). Measured values agreed within expected analytical uncertainty for all of the analytes except Na in Cement Creek and Mn in the Animas River, which had larger than expected ranges (6% and 16% of their mean values respectively).
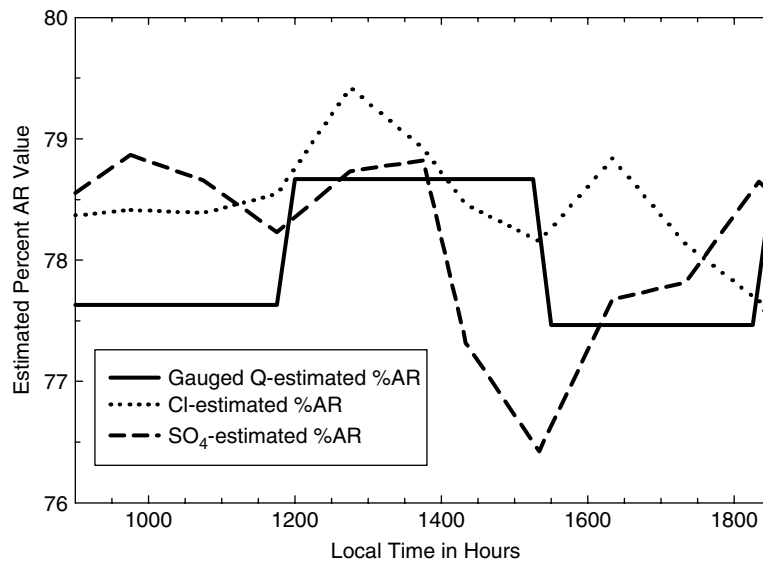
Figure 8. Percentage of total flow supplied by the upper Animas River over the sampling period based on (gauged) discharges Q (Cement Creek and the upper Animas River) and measurements of Cl^- and SO_4^{2-} from the automatic sampler at the end of the study area

Mass-flow calculations

In the region where large across-channel gradients were present, mass-flow calculations were based on five samples and incremental discharge measurements at each of the seven transect sites. For each analyte, the range of mass-flow values among the four sites in Reach 1 (1197–1234) was only a few per cent of the mean value for the reach. Mean values for all eight analytes were within 3% of the estimated inputs based on end-member concentrations and discharges. Mass-flow values for the two sites in Reach 2 (1278, 1299) agreed closely, and the mean value for each analyte was higher than the estimated input by 4–10%. This was similar to the results for the single site in Reach 3 (1332; not shown in Table II). Among the analytes, Na showed the greatest difference between the estimated input and mean mass-flow values (highest %TRANS; Table II) in all three reaches. Mean mass-flow values for the other metals were within 5% of the estimated inputs in all three reaches, but values for Cl^- and SO_4^{2-} were higher than estimated inputs by 8–11% in Reach 2 and Reach 3.

The river was relatively well mixed at the three sites in Reach 4 (1998–2478; Figure 1, Table II), where MV and Cl^--based %AR values from the samples, 78–79%, were in the range of the estimates shown in Figure 8. Mass-flow calculations were based on a single sample at each site and gauge values for the Cement Creek and upper Animas River discharges (total of $2.0 \text{ m}^3 \text{ s}^{-1}$ when the samples were collected). For each analyte, mass-flow values ranged only a few per cent among the sites and mean values for all eight analytes were within 4% of the estimated inputs (Table II).

DISCUSSION

Samples collected with the ESCI sampling strategy showed some unexpected results. Even though the median water depths were shallow at the seven transect sites, the consistent differences between (measured) sample and target SC values indicated substantial vertical gradients (increasing values with depth) within the mixing zone where strong across-channel gradients also existed. Consequently, results closer to the target values might have been obtained if the stations had been located by vertically integrated SC values. However, variability in discharges between the times when the near-surface SC distributions were measured and the samples were

Table II. Mass flows of metals, chloride, and sulphate at stream sites and mean values (MEAN) for mixing-zone reaches between Animas River inflows (braids). TOTAL IN is the total input from Cement Creek and upper Animas River inflows based on end-member concentrations and discharges from the gauges or field measurements. %TRANS is the percentage of the total input that was transported through the stream reach based on the MEAN and TOTAL IN values

	Ca (10³ kg day⁻¹)	Mg (kg day⁻¹)	Mn (kg day⁻¹)	Na (kg day⁻¹)	Si (kg day⁻¹)	Sr (kg day⁻¹)	Cl⁻ (kg day⁻¹)	SO₄²⁻ (10³ kg day⁻¹)
Reach 1								
1197	7·89	409	100	337	626	83	205	23·7
1211	7·55	395	97	322	607	81	198	22·3
1224	7·70	402	97	335	625	82	210	23·5
1234	7·86	408	100	337	628	84	205	23·1
MEAN	7·75	404	98	333	621	82	205	23·1
TOTAL IN	7·86	403	97	322	624	83	199	22·7
%TRANS.	98·7	100·0	101·2	103·3	99·6	99·3	102·8	102·0
Reach 2								
1278	8·80	460	111	378	698	94	223	25·7
1299	8·46	442	109	378	679	89	221	25·2
MEAN	8·63	451	110	378	689	91	222	25·5
TOTAL IN.	8·30	430	108	342	659	87	204	23·6
%TRANS.	103·9	104·9	101·9	110·4	104·6	104·4	108·8	107·9
Reach 4								
1998	11·7	631	193	518	898	120	226	30·3
2238	11·7	634	192	518	908	120	234	31·0
2478	11·8	655	187	502	913	121	227	30·3
MEAN	11·7	640	191	513	907	120	229	30·5
TOTAL IN.	11·5	649	197	509	941	121	232	30·2
%TRANS.	101·8	98·7	96·8	100·7	96·3	99·7	98·7	101·1

collected, and perhaps other factors related to the sampling procedure, might also have influenced the results. Even though the ESCI strategy used in this study could use some further development, the samples evenly covered the wide ranges in SC observed at the sites. In addition, mass-flow values estimated from these samples were consistent among sites within a reach and in most cases agreed with input values within the expected margins of error.

Agreement among mass-flow calculations and the linearity of concentrations plotted against values of the mixing ratio showed that dissolved Ca, Mg, Mn, Na, Si, Sr, Cl⁻, and SO₄²⁻ were transported conservatively through this mixing zone. Beyond issues of reactivity, formation of particles, and sedimentation, the data also indicated that there were no large additional sources in the study area. These results were consistent with our previous study (Schemel *et al*., 2000), when Mn, Mg, and Ca were found to be useful natural tracers. During that study, only one site in Reaches 1–3 was sampled using five stations across the channel, and an EDI sampling strategy was used. The samples yielded a narrow range of mixing ratios, 58–97%AR, which prompted the use of an alternative sampling strategy based on across-channel chemical gradients in the present study.

We did not collect samples based on EDI or EWI sampling strategies at the transect sites in the present study, but sample (SC) values based on these strategies could be estimated from the observed SC and discharge measurements. The observed near-surface SC distribution was used to assign a value for each station using both strategies, and these values were multiplied by the ratio of the ESCI value to the target value in order to compensate for the observed vertical gradients. These estimated sample-SC values were compared with the ESCI target values, because the target values were equally spaced across the observed SC ranges at each site, a sampling objective of our study. For the EDI strategy, the estimates for 26 samples (of 35) were within 10% of the ESCI target values, but only 13 estimates were within 10% for the EWI strategy. The highest

outliers were 40% and 63% for the EDI strategy and 27% and 33% for the EWI strategy. In comparison with our field results, either an EDI or EWI strategy might have produced samples at the transect sites that missed the target values to a greater degree than the ESCI strategy (31 samples were within 10% of the target value, and the highest outlier was 14%).

Because of sufficiently large (natural) concentration differences between the two streams, Ca, Mg, Si, Sr, and SO_4^{2-} were suitable natural tracers for estimation of mixing-ratio values. Mn, Na, and Cl^- could not be used as natural tracers because the differences between end-member concentrations were too small. Similarly, in an evaluation of natural tracers in the Snake River–Deer Creek confluence, Bencala *et al.* (1987) showed that, out of seven potential tracers, Ca, Cl^-, and Si were not suitable because of small concentration differences. Ca and Si were useful natural tracers in our study, showing that each potential tracer needs to be evaluated within the system that is being studied.

As a whole, consistent values of %AR among all of the tracers increased the level of confidence in estimating the mixing ratio beyond what might have been achieved with the injected Cl^- tracer alone. Potential errors in field sampling, sample processing, and analytical procedures could affect both natural and injected tracers. In addition, estimates of mixing ratios for an analyte could be biased if end-member concentrations are not accurately known, as appeared to be the case for Na (and perhaps to a lesser degree Cl^- and SO_4^{2-}) in this study. Low flows allowed the use of an injected tracer in this study, but identification of natural conservative tracers would be more important during higher discharges, which would make tracer injections impractical, costly, or technically challenging.

Although the concept of using multiple natural tracers is not new, the technique probably should be routinely applied to confluence studies involving acid mine discharges when results indicate unexpected levels of dilution, transformation, or loss by precipitation. For example, in their study of an upstream confluence of a circumneutral stream (pH 7·6; Illinois Gulch) with Cement Creek, Kimball *et al.* (2002) calculated discharges from the dilution of an injected tracer. Mass flows (loads) of total Al, Fe, and Zn indicated losses (13–20%) to the streambed in the mixing zone even though pH values remained less than pH 4 downstream from the confluence. In order to evaluate this result, we used their chemical data to calculate mixing ratios, and estimate from them the downstream loads of Ca, Mg, Sr, and SO_4^{2-}. All of these natural tracers were transported conservatively (within 4%) through this confluence, which supported the interpretation that reduced loads of reactive elements indicated losses in the mixing zone.

Sample filtration reduced the possibility that mineral particles, which could settle in the mixing zone, would affect the %AR and mass-flow calculations. Although a small contribution from particles was apparent in most cases, large particles (>0·45 μm) were significant only for Si, and differences between whole sample and filtrates for the other analytes were mostly within the range of analytical uncertainty. Furthermore, there were no significant differences between %AR calculations using *F*-sample and *U*-sample values for any of the analytes, indicating that concentrations of very fine colloids were insignificant and that ultra-filtration was not necessary for tracer applications using these conservative solutes in this mixing zone.

MVs for the mixing ratio, MV %AR, based on the *F* samples for all seven tracers agreed well with most estimates based on the Cl^- reference tracer. Although coefficients of determination, r^2, for regressions of the metals were higher when MV %AR was used, improvements over using Cl^--based values were very small. It was perhaps more important that scatter caused by a few samples was reduced in mixing plots using MV %AR from multiple tracers, which indicated possible errors in some Cl^--based values.

Collecting samples over a period of several hours does not produce truly synoptic results, and some variability in discharges and chemical concentrations must be expected. In this study, during the lowest flows of the summer, variability was minimal but still apparent. The automatic sampler data showed that the values used for end-member concentrations of Cl^- and SO_4^{2-} were lower than mean concentrations over the entire sampling period. Although the trends toward lower concentrations with decreasing flow and low concentrations in late afternoon remain unexplained, most of these variations were not much larger than the overall uncertainty in the measurements. Short-term variability in end-member concentrations might have contributed to high (measured) mass-flow values for Cl^- and SO_4^{2-} in Reaches 2 and 3, because concentrations

from the automatic sampler in Cement Creek were greater than the end-member concentrations when samples were collected in the mixing zone. Although we could not see a consistent pattern between station discharges and concentrations that would increase mass-flow estimates in Reaches 2 and 3, substantial differences among the estimated incremental discharges assigned to the stations still might have been an additional factor. In the case of Na, however, the measured end-member concentration for Cement Creek was lower than values predicted by linear regressions with both MV- and Cl^--based %AR values. This was consistent with Na-based %AR values which were higher than those for other analytes. Selecting a MV for the mixing ratio based on multiple tracers would likely compensate for different levels of variability among analytes and uncertainties in end-member concentrations.

CONCLUSIONS

In general, the strategy of using distributions of SC to locate sampling stations was successful at the sites where large across-channel gradients existed. The method might be improved by using vertically integrated SC values to locate the stations, but the objective of a wide range of evenly spaced values was achieved.

A stream rich in acid-mine or mineral-deposit drainage is a potential source of many natural tracers to confluences with circumneutral-pH streams. Utilizing multiple natural tracers can improve estimates of mixing ratios, as well as verify unusual or unexpected results in studies of stream confluences even when an injected tracer is used. Concentrations of potential tracers are often readily available, because most studies employ methods, such as ICP-OES, that are capable of measuring simultaneously both trace metals of interest and many major elements.

Although methods have been developed for reducing the effects of variable end-member concentrations on mixing ratios (Hooper, 2003; Carrera *et al.*, 2004), our calculations depended on relatively stable and representative end-member concentrations. At least some variability in %AR values among the analytes was attributable to temporal variations in end-member concentrations. The use of multiple tracers helped identify outlier values, and MVs reduced their effects.

Conservative transport of each natural tracer must be verified in the confluence being studied. This can be accomplished by comparisons of mass flows and by examinations of mixing plots involving an injected tracer or a robust estimate of the mixing ratio, such as the MV from multiple natural tracers.

Dissolved concentrations from filtered samples might provide more accurate estimates of the mixing ratio in confluences with abundant particles. For the major metals studied here, only Si showed significant particles in the whole samples, but filtration at 0·45 µm reduced the potential for errors in all of the tracers.

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