

Spatially Detailed Quantification of Metal Loading for Decision Making: Metal Mass Loading to American Fork and Mary Ellen Gulch, Utah

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Abstract Effective remediation requires an understanding of the relative contributions of metals from all sources in a catchment, and that understanding must be based on a spatially detailed quantification of metal loading. A traditional approach to quantifying metal loading has been to measure discharge and chemistry at a catchment outlet. This approach can quantify annual loading and the temporal changes in load, but does not provide the needed spatial detail to evaluate specific sources, which is needed to support remediation decisions. A catchment or mass-loading approach provides spatial detail by combining tracer-injection and synoptic-sampling methods to quantify loading. Examples of studies in American Fork, Utah, and its tributary Mary Ellen Gulch illustrate this different approach. The mass-loading study in American Fork treated Mary Ellen Gulch as a single inflow. From that point of view, Mary Ellen Gulch was one of the greatest sources of Fe, Mn, Zn, and colloidal Pb loads to American Fork. But when Mary Ellen Gulch was evaluated in a separate catchment study, the detailed locations of metal loading were identified, and the extent of metal attenuation upstream from the mouth of Mary Ellen Gulch was quantified. The net, instantaneous load measured at the mouth of Mary Ellen Gulch for remediation planning would greatly underestimate the contributions of principal sources within the catchment. Extending the detailed sampling downstream from Mary Ellen Gulch indicated the possibility of diffuse groundwater inflow from Mary Ellen Gulch to

American Fork. Comparing loads for Mary Ellen Gulch in the two studies indicates that metal loads could be substantially underestimated for planning purposes without the detailed catchment approach for the low-flow conditions in these studies. A mass-loading approach provides both the needed quantification of metal loading and the spatial detail to guide remediation decisions that would be the most effective in the catchments.

Keywords Metal loading · Mine drainage · Multivariate analysis · Remediation · Synoptic sampling · Tracer dilution · Utah

Introduction

Traditionally, quantifying the loads of solutes on a global, continental, or catchment scale has been accomplished by measuring discharge and concentration at fixed sites over time. This *outlet approach* has been successful for many applications. Determining the budget for carbon from continents to the oceans is an integral part of determining global cycles (Sarmiento and Sundquist 1992). Annual stream-water loads for nutrients (Aulenbach 2006) and suspended-sediment associated trace elements (Horowitz et al. 2001) have been calculated near the outlet of several of the largest river basins in the United States to evaluate temporal trends. On a smaller catchment scale, the approach can lead to understanding weathering and stream-flow processes (Aulenbach and Hooper 2006). However, when many possible sources of loading occur in a catchment, a spatially detailed approach that extends upstream from the outlet is needed to allow comparison among the various sources. This is the case for thousands of historic mining sites that occur on government-managed

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lands in the western United States, and throughout the world.

Land-management and regulatory agencies are often faced with the challenge of choosing which sites to remediate to reduce the impacts of metal contaminants and acidity on streams in mountainous catchments. Contributions of drainage from mines or altered rock are most appropriately compared in terms of the load they contribute to the stream and not in terms of their metal concentrations; the highest concentrations do not always have the greatest impact on a stream. The process of choosing sites for remediation requires a means to quantify the total metal load affecting a catchment and also the ability to compare the contributions from individual sources within the catchment.

To meet the need for quantifying load, we present a *catchment approach* that relies on detailed spatial sampling of stream and inflow sites (synoptic sampling) as well as tracer injection to estimate stream discharge along a study reach (Kimball et al. 2002; Miller and Miller 2007). Metal-loading studies from the North Fork of American Fork Canyon, Utah, provide an opportunity to compare metal loads calculated at two levels of spatial detail. Thus, the primary objective here is to compare the different degrees of sampling detail and to indicate the adequate spatial detail needed to make remediation decisions.

Methods

Mass-loading studies have been used to provide a catchment-scale context for the quantification of metal loads from abandoned and inactive mines. Together with geologic and biologic studies, mass-loading analysis provides much of the information that is needed to make science-based decisions for a catchment (Buxton et al. 1997). The mass-loading approach used here addresses the problem of solute-source determination (Kimball et al. 2002; Runkel et al. 2007). The approach is based on two well-established techniques: the tracer-dilution method (Kilpatrick and Cobb 1985) and synoptic sampling (Bencala and McKnight 1987). The tracer-dilution method provides estimates of stream discharge that are in turn used to quantify the amount of water entering the stream through tributary and groundwater inflow in a given stream segment. Synoptic sampling of stream and inflow chemistry provides a spatially detailed profile of water chemistry in the stream and for the inflows that influence the stream. When used together, these techniques provide an understanding of a catchment that includes both discharge and concentration, which then may be used to determine mass loading of chemical constituents associated with various sources of surface water and groundwater.

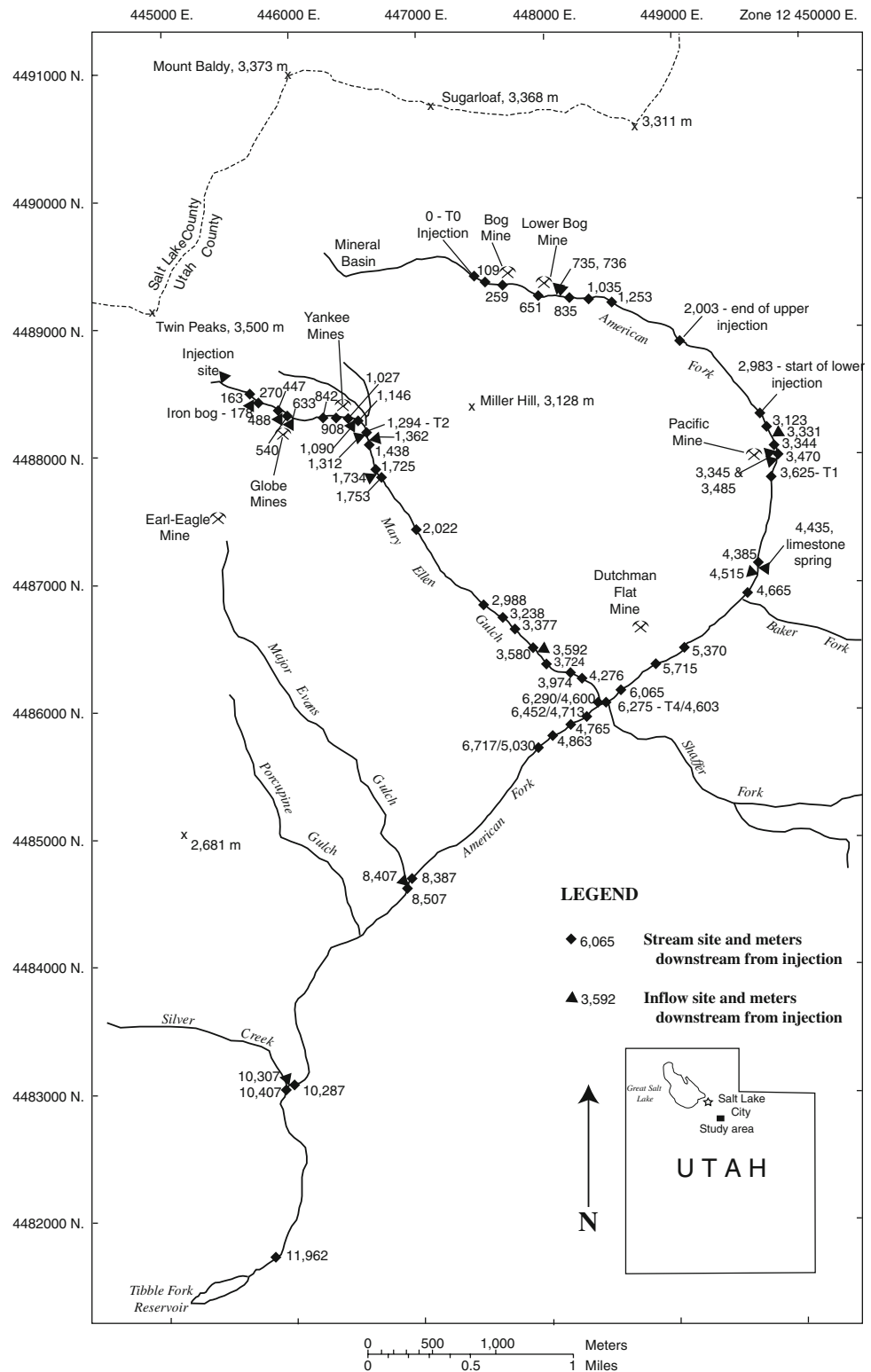
The tracer-injection and synoptic sampling approach were developed in a series of studies in St. Kevin Gulch, Colorado (starting with Broshears et al. 1993; Kimball et al. 1994) for determining mass-loading in mine-drainage streams. The approach has since been applied to meet various objectives. Examples of applications include a study of a heavily mined, hydrothermally altered catchment in Cement Creek, Colorado (Kimball et al. 2002), studies to contrast mined and unmined areas along the Red River, New Mexico (Kimball et al. 2006a) and Red Mountain Creek, Colorado (Runkel et al. 2007), and on a much smaller scale, a study to identify particular hydrogeologic connections through shear zones between a stream and mine pit lakes near Strawberry Creek, South Dakota (Kimball et al. 2006b). Detailed discussions of the equations used to calculate discharge and load are provided in a companion data report for American Fork and Mary Ellen Gulch (Kimball et al. 2009; available at URL: <http://pubs.usgs.gov/ds/443/>).

With the mass-loading approach, the in-stream load at any point along the study reach is calculated as the product of discharge and concentration (Kimball et al. 2009; Equation 1). The net change in load from one stream sampling site to the next, a stream segment, is calculated by subtracting the upstream value from the downstream value (Kimball et al. 2009; Equation 2). One can sum the net load for every stream segment that is positive to calculate a cumulative in-stream load, which can be compared to the sampled in-stream load at the mouth of the stream. If a solute is conservative, then the cumulative and sampled in-stream loads should be the same. However, if a given constituent is attenuated through physical, biological, or chemical processes, then the sampled in-stream load will be less than the cumulative in-stream load, and the difference between these two load estimates can be used to calculate the mass of solute attenuated within the stream course.

Study Area

The two mass-loading studies were carried out by the U. S. Geological Survey in cooperation with the U.S. Forest Service to support their efforts toward remediation (Fig. 1). The first study was in American Fork, which originates in Mineral Basin at an elevation over 3,000 m, and eventually drains to Utah Lake and through the Jordan River to Great Salt Lake at 1,280 m. The study reach for American Fork started upstream from the Bog Mine and continued to a point in the canyon downstream from the confluence with Mary Ellen Gulch, a distance of 6,717 m (Fig. 1). Additional samples were collected to evaluate loading from Major Evans Gulch, Silver Creek, and American Fork before it entered Tibble Reservoir (Fig. 1). Previous

Fig. 1 Location of study reaches, mines, and selected sampling sites, American Fork and Mary Ellen Gulch, Utah. Stream sites are indicated by diamond symbols and inflows by triangles. Four stream sites near the mouth of Mary Ellen Gulch show the downstream distance for both studies; the higher number is for the American Fork study



sampling identified high concentrations of metals in American Fork Canyon (Lidstone and Associates Inc., personal communication 1993). Also, samples of stream water and bed sediments have been collected by the U.S. Forest Service to help identify metal contamination in the

stream (Geszy, R., U.S. Forest Service, personal communication 1999). Over most of the study area, the stream has a steep gradient with cobble and boulder bed material. Numerous beaver dams affected the travel time through the study reach, and possibly affected the transport of metals.

The second study was in Mary Ellen Gulch, which also originates at an elevation over 3,000 m and drains to American Fork. The study reach within Mary Ellen Gulch started at a point upstream from historical mining activities, and continued downstream from the confluence with American Fork (Fig. 1); the total distance was 5,030 m. Both streams drain highly fractured and mineralized carbonate rocks of Paleozoic age as well as metasedimentary quartz and shale of the Late Precambrian Big Cottonwood Formation (Baker et al. 1966). The majority of mining in American Fork occurred at the Pacific, Dutchman, Bog, and Lower Bog mines. Mining in Mary Ellen Gulch occurred at the Globe and Yankee mines. The ores are associated with mineralization along fractures formed in the host rock during Miocene emplacement of the Alta Stock.

Tracer Injection and Sampling

Three different tracer salts were used in the field experiments (Table 1). The study reach in American Fork was divided into two injection reaches, with Cl (from NaCl) used as the tracer in the upper injection reach and Br (from LiBr) used as the tracer in the lower injection reach (Fig. 1). The tracer in Mary Ellen Gulch was also Br (from NaBr). Injection solutions were mixed in a garbage can using a consistent weight of salt for a given volume of stream water. Each mixture was pumped into an agricultural tank to get the total volume needed. The solution was pumped from the tank using a positive displacement piston pump (Fluid Metering, model QB), fitted with a rotational sensor to allow the control of revolutions by a Campbell CR10 data logger. The control by the data logger provides a means to set and maintain the pump rate for long periods, even as battery voltage decreases. Only with this pump control can downstream variations in tracer concentration be attributed to hydrologic changes and not to equipment deviations.

The mass-loading study in American Fork was conducted Oct 2–5, 1999 and the study in Mary Ellen Gulch was conducted Sept 10–15, 2000, both during low-flow conditions. Application of the method to low-flow conditions provides a focus on metal sources that enter the stream on a continuous basis, but does not address

transient, short-term loading that can result from storm or snowmelt runoff (Kimball et al. 2007). A critical step in our mass-loading approach was to walk the entire study reach and identify visible inflows and areas of likely groundwater inflow. Stream sampling sites were located upstream and downstream from these inflows and additional stream sampling sites were chosen in locations that appeared to bracket areas of potential groundwater inflow. These areas were identified during the stream reconnaissance by considering changes in vegetation, geomorphologic controls, and geologic structure. The intent of placing stream-sampling sites downstream from visible inflows was to capture both visible tributary inflow and additional subsurface inflow. Stream and inflow sites are referenced by the downstream distance (Fig. 1). Stream sampling sites upstream and downstream from the confluence of American Fork and Mary Ellen Gulch were sampled in both years to facilitate combining the studies, and the sites that were sampled in both studies show two distances in Fig. 1. Details of all the sampling locations are listed in Kimball et al. (2009). At this level of spatial detail in a catchment, changes in stream chemistry and discharge between stream sampling sites reflect a net metal load for specific segments, but the loads cannot always be attributed to specific sources. Impacts of sources on the stream, however, may be characterized by synoptic sampling.

Synoptic sampling began at the downstream end of each study reach and ended upstream from the tracer-injection sites. This downstream-to-upstream sampling order was followed in order to avoid disturbing the streambed prior to sampling. Inflow and stream sites that were considered well mixed were sampled by collecting from the main portion of flow. Sites that were not well-mixed, particularly downstream from tributaries, were sampled by equal width integration when the streams were sufficiently large (Ward and Harr 1990). Synoptic sampling gives a spatially intensive “snapshot” of chemistry and discharge so that in-stream loads can be quantified. Ideally, samples at all the sampling locations would be collected simultaneously, providing an instantaneous, truly synoptic description of stream water quality along the study reach. Personnel limitations generally preclude this, but samples were collected over a relatively short time period (less than 8 h) to minimize the effect of transient conditions, such as diel

Table 1 Details of tracer injections for the upper (U) and lower (L) American Fork and Mary Ellen Gulch

Injection	Tracer	Start	End	Injection rate (mL/min)	Injectate concentration (mg/L)	Volume injected (L)	Background concentration (mg/L)
U. American Fork	NaCl	10/5/1999 9:52	10/5/1999 16:15	207	194,810	79.3	0.83
L. American Fork	LiBr	10/2/1999 16:20	10/4/1999 17:30	297	112,570	611	<.2
Mary Ellen Gulch	NaBr	9/13/2000 10:40	9/14/2000 17:00	165	187,900	377	<.2

flow variations. Even this time period can be long enough to allow diel variations in some metal concentrations (Gammons et al. 2007; Nimick et al. 2003). As shown by Nimick et al. (2003), the concentrations of divalent metals such as Cd^{2+} , Mn^{2+} , and Zn^{2+} at any one location in a stream generally decrease from morning to afternoon. If a similar diel decrease occurred in the streams of the present study, it would mean that upstream concentrations in the afternoon would be lower than they had been in the morning. Thus, it is possible that the logistic constraints of synoptic sampling could have caused loads for some metals in the upstream portion of the study reach to be underestimated.

Water temperature was measured on site, and water samples were transported to a central field location for further processing. Samples were divided into several 125 mL bottles with different treatments at the central processing location: a raw (unfiltered) unacidified sample (RU), a raw acidified sample (RA), a 0.45- μm filtered unacidified sample (FU), and a 0.45- μm filtered acidified sample (FA). In addition, an ultra-filtered, acidified (UFA) sample was obtained using a 10,000 Dalton tangential flow filtration device. The UFA sample was to measure a more truly dissolved concentration than the FA sample because Al and Fe colloids, and other metals associated with such colloids, can pass through a 0.45- μm filter (Kimball et al. 1995). Use of ultra-filtered and unfiltered treatments provides two operationally-defined concentrations for each metal. In terms of the Al and Fe colloids and metals that may be associated with the colloids, the unfiltered, acidified sample (RA) is a measure of the total-recoverable concentration (dissolved + colloidal). This RA treatment does not digest aluminosilicate phases, but does digest the Al and Fe colloids in streams affected by mine drainage after acidification. Generally, at low flow, aluminosilicate particles were not observed in these samples. The UFA concentration represents the most truly dissolved metal concentration, but is still an operational definition. Colloidal metal concentrations are defined here as the difference between the total-recoverable (RA) and the ultra-filtered metal concentrations (UFA) for stream samples (Kimball et al. 1995). The filtered concentration (FA) is an operational measure of the dissolved metal concentration and provides the legal definition of dissolved concentrations. Aquatic standards for toxicity for Utah are based on 0.45- μm filtration (FA).

Anomalously high concentrations of Cu and Zn were noted in a few UFA samples, which was likely a result of contamination from brass fittings on the tangential-flow filtration apparatus. High values of Cu and Zn were replaced by the corresponding FA concentrations, but if both UFA and FA concentrations were affected, the RA concentration was used for filtered and total concentrations. For those samples affected by contamination (noted in

Table 3 of Kimball et al. 2009), the colloidal concentrations for Cu and Zn were calculated as the difference between RA and FA concentrations.

Specific conductance and pH were determined from the RU sample within hours of sample collection. Metal concentrations for the RA, FA, and UFA treatments were determined by inductively coupled plasma-atomic emission spectrometry-mass spectrometry (Lichte et al. 1987). Anion concentrations were determined from FU samples using ion chromatography (Brinton et al. 1996; Kimball et al. 1999). Total alkalinity was determined by titration from the FU sample (Barringer and Johnsson 1989).

Principal Components and Cluster Analysis

An important objective of synoptic sampling is to recognize patterns or chemical characteristics that can indicate the various sources of metals in the catchment. As water weathers different mineral assemblages, it obtains a distinct chemical signature, and that signature may lead to understanding various sources of solutes. *Principal components analysis* (PCA) is an analysis technique that can help identify distinctions among samples (Davis 2002). PCA involves the identification of a new set of axes (principal components) to account for variance and covariance and gives a better ‘view’ of the original data in multidimensional space. This view, using the PCA scores, helps identify distinctions among samples. Concentrations in millimoles per liter were log-transformed for the analysis to emphasize mass-balance and log-linear relations among variables. Combining PCA with a method of cluster analysis called *partitioning around medoids* further distinguishes groups of samples (Kaufman and Rousseeuw 1990). Using Euclidian distance in multivariate chemical space as a measure of similarity, each sample is then assigned to the cluster of the nearest medoid—a kind of multivariate median. Choosing the number of groups, or medoids, for inflows or stream sites was guided by the ability to explain a grouping in terms of geologic, hydrologic, or geochemical information. The same transformation of data was used for the cluster analysis, and the values were converted to standard normal variables before analysis. Filtered concentrations were used for inflow samples. Both filtered and colloidal concentrations of Al, Fe, Mn, and Zn were used for stream samples because changes in colloidal concentrations of stream samples often indicate important distinctions along the study reach (Kimball et al. 1995, 2003).

Characterization of Mine Drainage

Synoptic sampling provided detailed spatial information about the sources of mine drainage in the catchment and

changes that occurred in each stream segment along American Fork and Mary Ellen Gulch. Results of chemical analyses for all of the synoptic samples are published in an accompanying data report and can be viewed online (Kimball et al. 2009).

Inflow Chemistry

The chemical composition of water from inflows to both streams provides the background for understanding the character of mine drainage, the sources of metals in the catchment, and the causes of in-stream changes in water quality. Inflow samples were obtained from 37 locations in American Fork and Mary Ellen Gulch and were classified into four groups by cluster analysis. Results of PCA are indicated by the scores and loadings illustrated in Fig. 2. PCA scores (Fig. 2a) help to distinguish groups of inflows in a multivariate view. The meaning of ‘directions’ in the score plot is indicated by the direction of loading vectors (Fig. 2b). These vectors signify the direction in which a particular constituent concentration increases. Thus, samples from inflow group 1 occur in the direction of increased Ca, Mg, and alkalinity. This means that those samples have higher concentrations of Ca, Mg, and alkalinity than samples from inflow group 2.

With the ‘directions’ defined, three general groups of samples were distinguished. The majority of samples (inflow group 1) represent water that was unaffected by weathering of altered bedrock. Within inflow group 1, two samples are representative of small differences between samples from American Fork and Mary Ellen Gulch (Table 2). Most notably, the samples from American Fork had higher Ca, Mg, and alkalinity. Samples from Mary Ellen Gulch had slightly higher SO_4 and some higher metal concentrations. This likely represents the effect of weathering carbonate rocks in the American Fork catchment, particularly for inflows like the limestone spring (4,435 m). Samples from this group had relatively low metal concentrations (Table 2; Fig. 2).

Inflows that did not fall into the first inflow group were either affected by natural Fe bogs or fens (inflow group 2), or by mining (inflow groups 3 and 4). Four inflows (group 2, Table 2) drained water from the Bog Mine and the lower Bog Mine in American Fork (Fig. 1). Another sample drained a fen-like area at the head of Mary Ellen Gulch. All these samples had relatively high concentrations of Fe, Al, and SiO_2 , along with low pH (note the vectors to the lower right in Fig. 2b, including the higher H^+ , indicating lower pH).

Inflows affected by mining were classified into two groups (groups 3 and 4, Table 2; Fig. 2). The two groups drained several mine-affected areas including the Pacific Mine area in American Fork and mine wastes near the

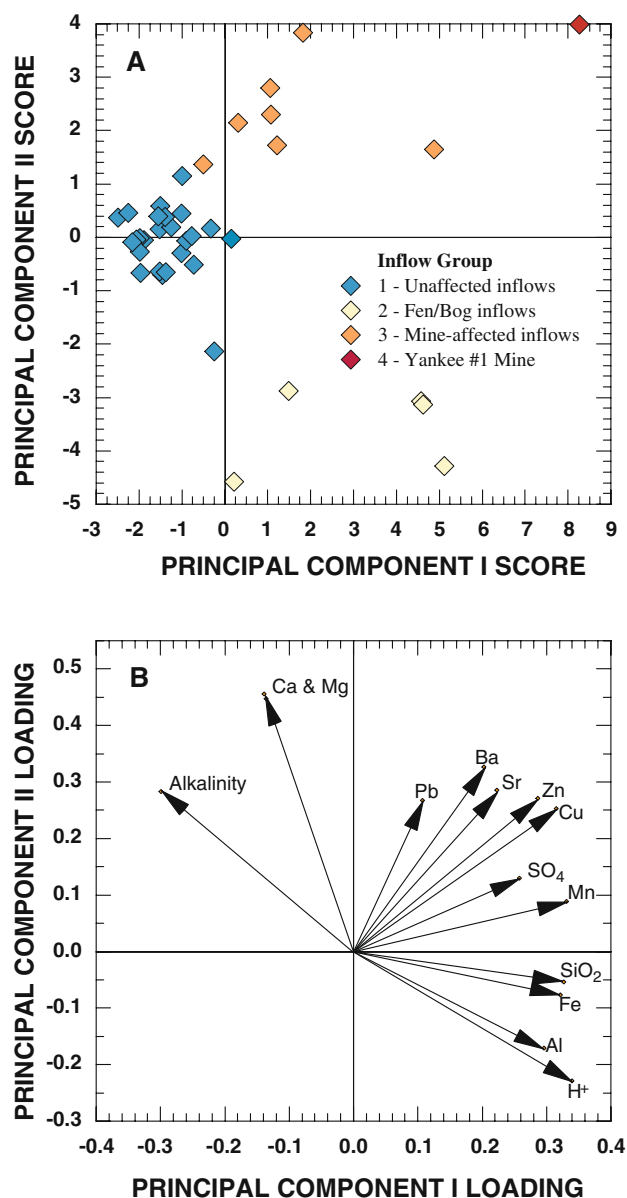


Fig. 2 Variation of **a** principal component scores showing cluster analysis groups and **b** principal component loadings for variables for inflow samples from American Fork, Oct 1999, and Mary Ellen Gulch, Sept 2000

Globe and Yankee mines in Mary Ellen Gulch. Even though these were generally high pH samples, they had higher base-metal concentrations than other inflow samples. For example, samples from American Fork, like the one from 3,475 m, which drained the Pacific Mine area, had notably higher Pb concentrations (Table 2). Finally, the inflow at 1,090 m in Mary Ellen Gulch drained the Yankee #1 Mine and was distinguished by high sulfate and metal concentrations (group 4; Fig. 2). This synoptic catchment sampling of inflows provides the means to distinguish the inflows affected by mining from those that are

Table 2 Representative samples for groups of inflow samples defined by cluster analysis, American Fork and Mary Ellen Gulch; ND, not determined; concentrations in mg/L

Group	Unaffected inflows		Bog or Fen inflows		Mine-affected inflows	Yankee #1 inflow
	American Fork	Mary Ellen	Bog Mine	Lower bog mine and Fe bog inflows		
No. of samples	12	13	2	3	6	1
Sample ID	AF-4435	ME-760	AF-59	AF-736	AF-3475	ME-1090
pH	7.92	8.08	6.52	5.42	8.1	5.95
Ca	43.4	34	11.6	10	44.6	30
Mg	20.1	14.3	4.5	3.3	23	12
Alkalinity as CaCO ₃	152	96.1	19	<1	172	24.6
SO ₄	21.1	26.6	41.8	54.4	36.3	100
Si	6.8	4	11.2	11.1	6.4	8.7
Al	<.021	.28	.026	.537	.047	.15
Ba	.052	.028	.041	.031	.126	.036
Cd	<.002	<.001	<.002	.013	.006	<.001
Cu	<.001	.017	<.001	.014	.037	.01
Fe, dissolved	.015	.026	.173	4.4	.051	.255
Fe, colloidal	.017	<.008	12.5	.401	1.6	7.5
Pb, total	<.015	<.006	<.015	<.015	.738	.015
Mn, dissolved	<.001	.007	.384	.281	.124	.017
Mn, colloidal	<.001	<.001	.069	.007	<.001	.193
Ni, dissolved	<.004	<.002	<.004	.011	<.004	<.002
Sr, dissolved	.047	.034	.034	.042	.063	ND
Zn, dissolved	.036	.054	<.001	.457	.64	.15
Zn, colloidal	.03	<.001	.138	.163	.384	.65

unaffected, and also provides distinctions among the mine-affected sites.

Stream Chemistry

Distinctions among groups of stream samples generally reflect sequential changes along the stream in response to contributions of sampled or unsampled inflows along the study reach. These changes in the chemical character of stream water help indicate which of the inflows have the most significant influence on in-stream water quality. Cluster analyses for samples from American Fork and Mary Ellen Gulch were done separately to point out the sequential changes along each stream.

For American Fork, cluster analysis was only used for samples through 6,717 m. The chemistry of samples downstream from 6,717 m is listed in Kimball et al. (2009), but is not discussed here. Cluster analysis distinguished five sequential sub-reaches of American Fork based on changes in water quality; the groups are represented by the chemical composition of samples in Table 3. A principal distinction was between the upper (groups 1 and 2) and lower (groups 3, 4, and 5) injection reaches. Overall, in the upper injection reach, samples had lower pH and alkalinity,

but higher SO₄ (Fig. 3a; Table 3). The increased alkalinity was accompanied by increases in Ca and Mg (Table 3), which suggests a source of water draining carbonate rocks that are abundant in that part of the American Fork Canyon (Baker et al. 1966). Additional carbonate was added by the limestone spring (4,435 m; Fig. 3a; Table 2).

Samples from the upper injection reach were divided into two groups (Fig. 3a; Table 3). The first group included samples that occurred upstream from the Lower Bog Mine that were less affected by mining. These samples had higher Ca, Mg, Sr, and alkalinity than the stream samples downstream from the lower bog mine (Table 3). The downstream samples of group 2 had higher concentrations of Al, SiO₂, Fe, Mn, and Zn, which all are likely products of a natural Fe bog and mine drainage.

In the lower injection reach, samples clustered into three groups. Samples between 2,983 and 3,470 m had the lowest metal concentrations of all the samples along the study reach (stream group 3). The upstream metals may have been removed during transit through the beaver ponds in the area between the injections. Downstream from the Pacific Mine, starting at 3,470 m, substantial increases in Zn and colloidal Pb occurred (Fig. 3b). Samples from 3,470 to 6,452 m were all grouped together (stream group

Table 3 Representative samples from groups of stream samples defined by cluster analysis, American Fork, Utah, Oct 1999; all concentrations are in mg/L; all values for dissolved and colloidal cadmium and dissolved lead were less than the detection limits

	1 Upper injection reach, less affected	2 Upper injection reach, more affected	3 Lower injection reach, near Pacific Mine	4 Lower injection reach, downstream from limestone spring	5 Downstream from Mary Ellen Gulch
No. of samples	7	4	9	7	1
Sample ID	AF-109	AF-1253	AF-3625	AF-5370	AF-6716
pH	7.80	8.13	8.42	8.43	7.97
Ca	31.0	25.0	33.3	36.0	36.2
Mg	11.2	9.11	15.6	17.0	16.6
K	.95	.98	.6	.59	.85
Alkalinity as CaCO ₃	84.3	58.5	128	144	141
SO ₄	39.7	39.9	15.0	13.8	16.4
Si	5.36	6.80	5.70	4.91	5.07
Al, dissolved	.042	.084	.041	<.021	<.021
Al, colloidal	<.021	.099	<.021	.038	.185
As, dissolved	.019	.003	.014	<.001	<.001
As, colloidal	<.002	.002	<.001	.010	.010
Ba, dissolved	.042	.044	.046	.491	.501
Cu, dissolved	<.001	<.001	.003	<.001	<.001
Fe, dissolved	.025	.026	.028	.027	.250
Fe, colloidal	.378	.750	.148	.077	.109
Pb, colloidal	<.011	<.011	.030	.014	.070
Mn, dissolved	.045	.072	.015	.007	.007
Sr, dissolved	.062	.054	.040	.042	.044
Zn, dissolved	<.001	<.011	.076	.065	.073
Zn, colloidal	.071	.130	<.001	.084	.064

4), but alkalinity, Ca, and Mg substantially increased downstream from the limestone spring at 4,665 m. Within this stream group, samples upstream from the limestone spring had higher metal concentrations than downstream samples (Fig. 3a). Downstream from the inflows draining the Pacific Mine, the occurrence of colloidal Pb is significant because it indicates possible groundwater drainage from the Pacific Mine similar to the sampled inflows, four of which had measurable Pb (Fig. 3b). This Pb is transported by Fe-rich colloids and could become available to the fish food web (Besser et al. 2001). Although diluted by the limestone spring, the colloidal Pb persisted downstream and then increased in the single sample of stream group 5, which was affected by the inflow of Mary Ellen Gulch. Downstream from Mary Ellen Gulch, the sample at 6,717 m had the highest metal concentrations, distinguishing it from all the other stream samples (stream group 5, Table 3). This sample was the second site downstream from Mary Ellen Gulch and had higher concentrations than the first sample downstream from Mary Ellen Gulch. The higher concentrations could be a result of diffuse groundwater inflow to American Fork from Mary Ellen Gulch, downstream from the confluence.

Along the study reach of Mary Ellen Gulch, distinct changes resulted in the classification of five stream groups by cluster analysis. These changes in chemical character also indicated the importance of particular inflows to the stream. The initial chemical character was set by drainage from a fen that discharged acidic, metal-rich water (163–447 m, group 1, Table 4). These samples had the lowest pH and the highest concentrations of dissolved Al, Cu, Fe, SiO₂, and Zn among the different stream groups in Mary Ellen Gulch (Fig. 4; Table 4), but the higher concentrations were a result of naturally acidic water, not mining. The small discharge from the fen was diluted downstream; at 540 m, pH had increased substantially and the metal concentrations were much lower (stream group 2). The inflows that caused the increase in pH also added alkalinity and diluted the SO₄ concentrations (Fig. 4a). Furthermore, the change in pH led to an increase in the percentage of colloidal Al. Downstream from this pH change, the stream encountered inflow from mine-waste piles near the Globe Mine and the adit discharge from the Yankee Mine, increasing the concentrations of some metals (stream groups 3 and 4, Table 4). Although acidic inflows at 932 m and 1,090 m caused in-stream pH and alkalinity to

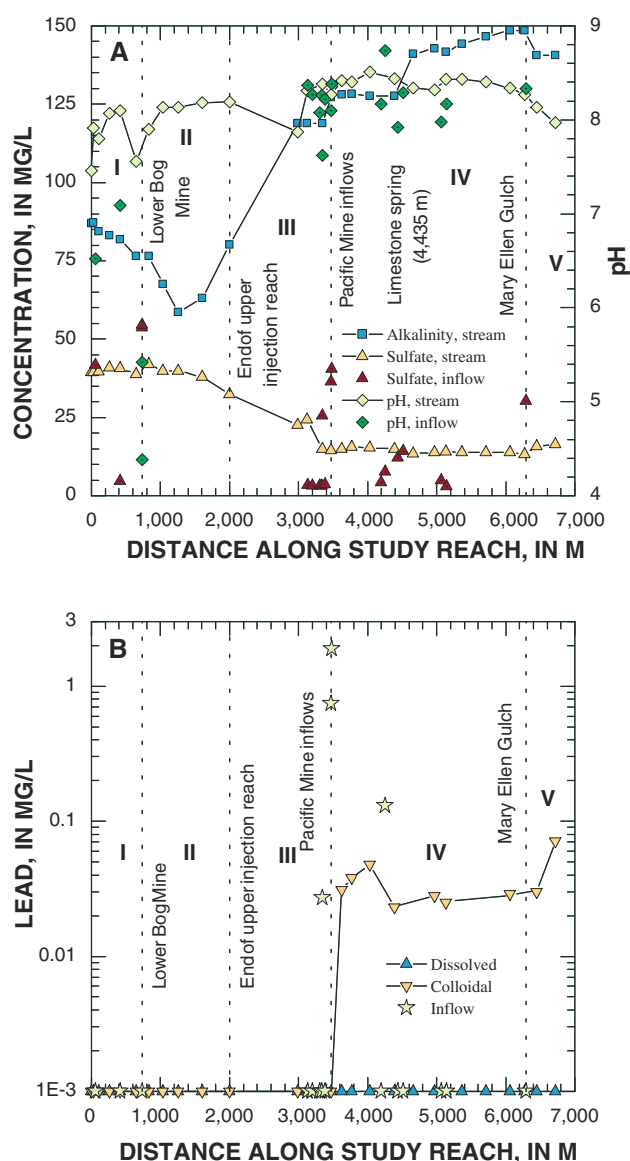


Fig. 3 Variation of **a** pH and concentrations of alkalinity and sulfate and **b** dissolved and colloidal lead with distance along the study reach, American Fork, Utah, Oct 1999

decrease (Fig. 4a), pH was still high enough that increases in metal concentrations principally occurred as increases in colloidal concentrations (figs. 4b, c, and d). The pattern of Fe colloids indicates the increase and the subsequent decrease downstream after these acidic, metal-rich inflows occurred (Fig. 4b). In samples of stream groups 3 and 4 (Figs. 4c and d), both Mn and Zn concentrations increased with the mine drainage inflows. Both metals were partially transformed to the colloidal phase, but only Mn concentrations substantially decreased as a result.

Downstream from the acidic, metal-rich inflows from the Globe and Yankee mine drainage, several inflows with pH greater than 7 were sampled. These inflows contributed

alkalinity to the stream, diluted the SO_4 concentration (Fig. 4a), and contributed to the decrease in Mn and Fe concentrations already noted. These changes resulted in a chemical character distinguished as a different stream group (Fig. 4; stream group 3, Table 4). The general chemical character of this group continued in samples of stream water down to, and including, the sample at the mouth of Mary Ellen Gulch.

At the confluence with upper American Fork, substantial changes in stream chemistry occurred and the samples downstream were distinguished as a separate stream group by the cluster-analysis technique (group 5, Table 4; Fig. 4). Some of these changes occurred in the short distance to the first sampling site downstream from the confluence (4,713 m), but other substantial changes occurred downstream from there in the three subsequent stream samples. These samples were obtained to investigate the possibility of groundwater inflow, which had been suggested by the American Fork synoptic sampling of October 1999 at 6,717 m (the same site as 5,030 m for the Mary Ellen Gulch synoptic study). A slight decrease in pH occurred between 4,713 and 4,765 m, suggesting that acidic water had entered the stream. Concurrent changes in metal concentrations of American Fork with the sample at 4,765 m are consistent with acidic, metal-rich inflow. Concentrations of Fe and Mn increased (Figs. 4b, c), and the increases were mostly colloidal. Similar increases were observed in 1999.

Ultra-filtrate stream samples from both American Fork and Mary Ellen Gulch indicated the presence of Fe colloids. Colloid occurrence was pH dependent and related to sources of acidic drainage from the fens and mines. In the upper acidic reach of Mary Ellen Gulch, colloidal Fe concentrations were lower than downstream concentrations where pH was >7.0 . At the higher pH, essentially all the Fe in the stream was colloidal. Cu and Zn were also present in the colloidal sample fraction because both Cu and Zn tend to sorb to the Fe colloids in mixing zones (Schemel et al. 2000; Smith 1999). Because of filter contamination, the trends of colloidal Cu and Zn were not clear. In Mary Ellen Gulch, however, the colloidal concentrations of Zn (Fig. 4d) and Cu were evident downstream from the Yankee #1 Mine inflow (Kimball et al. 2009). This corresponded to the abundant colloidal Fe that was available for sorption at the relatively high pH (Runkel et al. 1999). Also, colloidal Pb concentrations were evident in both American Fork and Mary Ellen Gulch; dissolved Pb concentrations were consistently less than the method detection limit of $0.01 \mu\text{g/L}$ (Kimball et al. 2009). In American Fork, the colloidal Pb was particularly important downstream from the Pacific Mine (Fig. 3b).

Table 4 Representative samples from groups of stream samples defined by cluster analysis, Mary Ellen Gulch, Utah, Sept 2000; all concentrations in mg/L

Constituent	1 Affected by fen upstream from mining	2 Downstream from neutral pH inflows	3 Mostly downstream from Globe and Yankee mines	4 Affected by Globe and Yankee mine drainage	5 Downstream from Upper American Fork
No. of samples	5	7	17	8	4
Sample ID	ME-270	ME-842	ME-2022	ME-1438	ME-5030
pH	3.96	8.33	8.36	8.29	8.47
Ca	6.70	22.0	33.5	27.0	34.0
Mg	1.95	9.08	13.8	12.1	16.6
K	.69	.56	.5	.54	.53
Alkalinity as CaCO ₃	<1	65.9	95.0	72.6	140
SO ₄	43.7	27.8	39.4	49.7	17.7
Si	8.90	4.70	4.80	5.30	4.50
Al, dissolved	1.70	.120	<.001	.091	<.001
Al, colloidal	.100	.060	<.001	.059	<.001
Ba, dissolved	.002	<.001	<.001	<.001	<.001
Cu, dissolved	.150	.011	.003	.009	.003
Fe, dissolved	.470	.014	.005	<.001	.008
Fe, colloidal	.020	.011	.198	.684	.117
Pb, colloidal	<.001	<.001	.004	<.001	.013
Mn, dissolved	.047	.005	.016	.04	.011
Sr, dissolved	.019	.036	.048	.046	.042
Zn, dissolved	.180	.047	.083	.091	.028
Zn, colloidal	<.001	<.001	.027	.069	.017

Quantification of Mass Loading

A catchment or mass-loading approach combines discharge and concentration to quantify mass loading and allow a complete comparison among metal sources. Changes in loading are also the basis for understanding the extent of the various processes affecting metal transport in the catchment. Furthermore, mass loading provides a means for comparison of the two approaches for calculating contributions from Mary Ellen Gulch. A brief description of discharge from the tracer-injection will set the hydrologic context in order to evaluate the principal sources of loading in American Fork and Mary Ellen Gulch.

Discharge

Results of Cl and Br determinations for synoptic samples from each injection reach are illustrated in Fig. 5. Sampled inflows from the upper injection in American Fork had measurable Cl concentrations that were much lower than the concentrations downstream from the injection. For the other reaches where Br was the tracer, injected tracer concentrations also were substantially higher than ambient background concentrations (Fig. 5). Each tracer profile indicates the increase in concentration downstream from

the injections and then the systematic decrease in concentration due to dilution by water entering the stream.

The calculated discharge for the upper injection reach in American Fork (0–2003 m) increased from 25 to 62 L/s (Fig. 5a). Slightly over half of this 37 L/s increase came from stream segments that had no visible inflows, and are thus associated with groundwater or dispersed subsurface inflow. Discharge for the lower injection reach, ending in the canyon downstream from Mary Ellen Gulch (6,717 m), increased from 62 to 155 L/s (Fig. 5b). Of the total 93 L/s increase, 8.6 L/s was contributed from segments that had no sampled inflow, and 30 L/s was from the limestone spring in the segment between 4,385 and 4,665 m. Including this spring, about 42% of the inflow in the lower injection reach can be deemed groundwater.

Discharge in Mary Ellen Gulch increased from about 2 L/s to about 45 L/s. Approximately 46% of this increase came from stream segments with no visible inflow, and consequently had groundwater input.

Principal Locations of Loading in American Fork

Major element and trace-element loading within American Fork occurred primarily at 9 locations (Fig. 6). Figures 6 and 7 are similar to those used by Walton-Day et al. (2005),

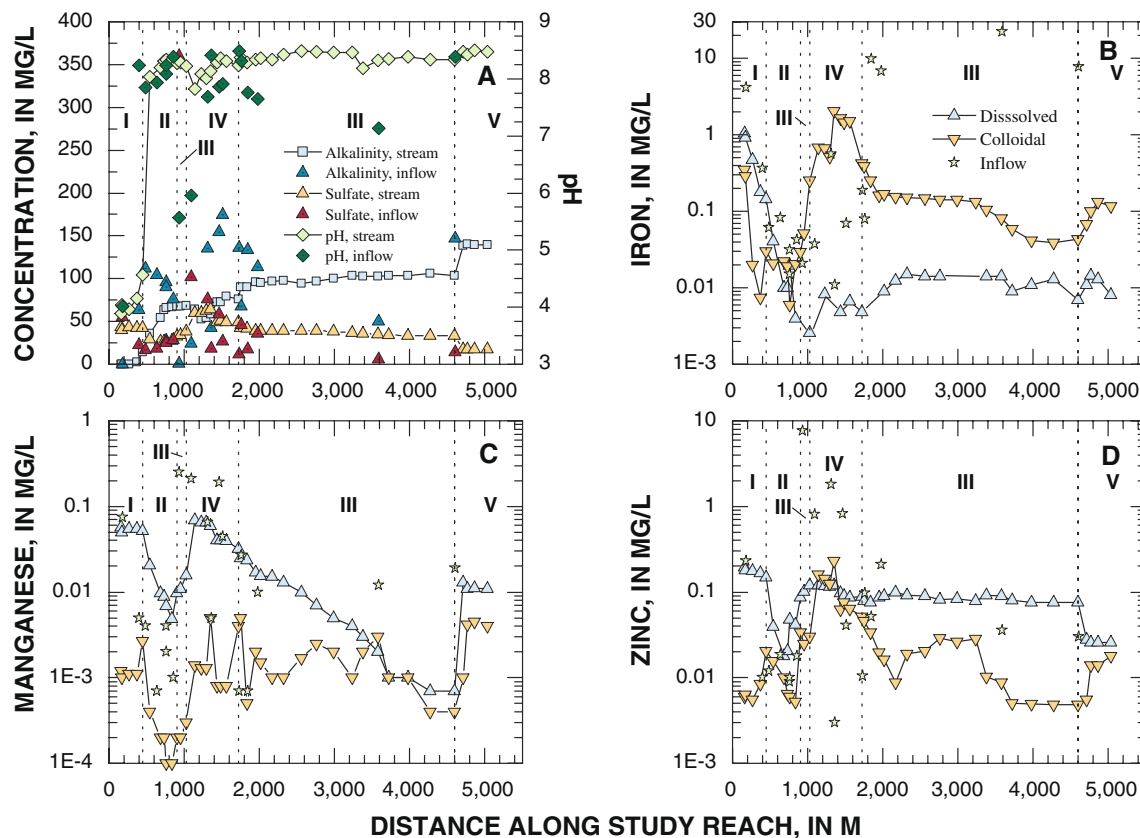


Fig. 4 Variation of **a** pH and concentrations of alkalinity and sulfate, **b** dissolved and colloidal iron, **c** dissolved and colloidal manganese, and **d** dissolved and colloidal zinc along the study reach, Mary Ellen Gulch, Utah, Sept 2000

and were calculated by first determining the change in load for each stream segment. The positive values of change were then summed to calculate the cumulative in-stream load. Finally, for each of the selected locations, the loading is expressed as a portion of the cumulative in-stream load along the entire study reach. Loading that did not occur in one of the 9 locations is shown as “other” loading. The absolute value of cumulative in-stream load is indicated for each constituent above the bar for the element. Loads are compared to portions of streamflow from the same selected locations. Any change in discharge from 6,452 to 6,717 m was not detectable by tracer dilution. Concentrations of several metals did increase in that stream segment, however, so for calculations of loading, 1 L/s of groundwater inflow was assumed. That quantity of inflow would have been undetectable by the tracer at the downstream point, but the calculated loads for that stream segment are only estimates.

Cumulative in-stream loading of major elements was greater than the trace element loading, reflecting the substantial weathering of carbonate rocks. Among the major elements (Fig. 6a), only the pattern of SO_4 substantially differed from the pattern of streamflow. Patterns similar to

streamflow for Ca, Mg, alkalinity, and SiO_2 indicate that the portions of these major elements are mostly the same for each of the locations along the study reach contributing solutes from bedrock weathering. The SO_4 pattern differs because its portion in the various inflows differs, suggesting the localized weathering of sulfide minerals. This major-ion weathering was substantial from upstream in Mineral Basin, labeled “upstream” in Fig. 6. Substantial contributions of SO_4 loading also came from the segment between 651 and 1,035 m that included the lower Bog Mine and also the segment between 6,275 and 6,452 m, which included Mary Ellen Gulch. The SiO_2 component indicated a substantial portion possibly coming from groundwater inflow downstream from Mary Ellen Gulch, based on the assumption of 1 L/s inflow (6,452 to 6,717 m). Loading of SiO_2 can indicate contribution from aluminosilicate weathering, which also would account for some of the loading of Ca and alkalinity. Graphs of loading profiles for selected metals in American Fork are given in Kimball et al. (2009).

Contributions of trace-element loading differed substantially from contributions of streamflow (Fig. 6b). This result indicates that the sources of metals were not always

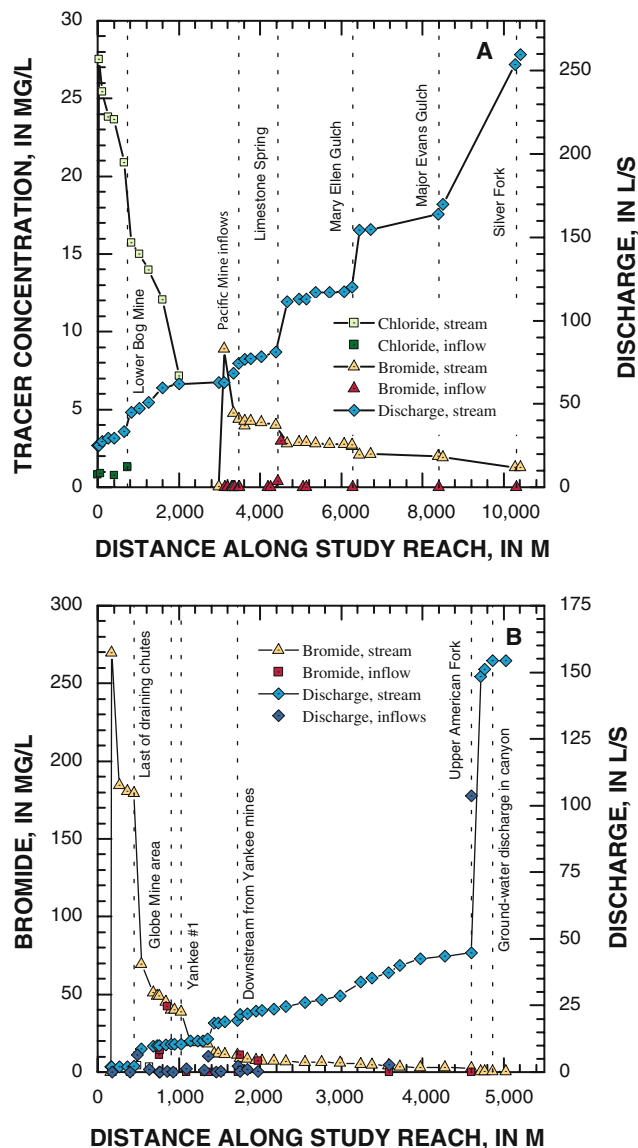


Fig. 5 Variation of tracer concentration and calculated discharge with distance along study reaches in American Fork and Mary Ellen Gulch, Utah

the locations of greatest streamflow generation. Instead, the greatest portions of trace-element loading corresponded to the locations influenced by mining. Most specifically, these areas included the Lower Bog Mine (651 to 1,035 m) for Fe, Mn, and Zn, the segment including the mouth of Mary Ellen Gulch (6,275 to 6,452 m) for Zn, and the segment downstream from the mouth of Mary Ellen Gulch (6,452 to 6,717 m) for Al, Cu, Fe, and Mn, although this last segment is based on the assumed inflow of 1 L/s. The Lower Bog Mine segment (651 to 1,035 m) and the Pacific Mine (3,344–3,625 m) also contributed substantial loading of Al, Fe, Mn, Pb (not shown), and Zn, but the overall metal loading was not as great in that segment as it was in other mine-related segments.

Principal Locations of Loading in Mary Ellen Gulch

Quantities of cumulative in-stream load from Mary Ellen Gulch (Fig. 7a) were smaller than those from American Fork. The calculation of portions in Fig. 7 includes the contribution from upper American Fork between 4,600 and 4,713 m but that loading was detailed by the American Fork study. However, that load contribution was larger than the cumulative in-stream load for several elements. The contribution of major ions was greatest in that stream segment, but this was not the case for any of the trace metals except Mn. The portions of Ca, Mg, alkalinity, and SO_4 loading were similar to the portions of increasing streamflow, with some small variations (Fig. 7a). The loading of SO_4 was greatest from the Yankee #1 mine (1,027–1,146 m), but a substantial load of SO_4 came from the mine-waste piles (1,294–1,354 m and 1,725–1,947 m). Graphs of loading profiles for selected metals in Mary Ellen Gulch are illustrated in Kimball et al. (2009).

Loading of trace metals in Mary Ellen Gulch was substantially different from the loading of major ions. The first stream segment (163 m, indicated as “upstream” in Fig. 7) accounted for the Al and Cu that came from drainage of a fen, not from mine-related sources (samples of stream group 1; Table 4). Two other stream segments contributed the majority of metal loading (Fig. 7b). First, the segment containing the adit discharge of the Yankee #1 Mine (1,027–1,146 m) added substantial loads of Fe, Mn, and Zn (the mine discharge was inflow group 4; Table 1). In addition to the Yankee Mine inflow, the next downstream segment (1,294–1,354 m) contributed loading of the same constituents from mine-waste piles. The second substantial area of loading occurred downstream from the confluence with American Fork (4,713–5,030 m). The increases in load downstream from the confluence with American Fork were investigated in detail in 2000 because increasing metal concentrations were noted in 1999. These stream segments were the principal locations for the loading of Al, Cu, and Zn (Fig. 7b) and were distinguished as a separate stream group (group 5; Table 4). With no visible inflow, it is evident this loading was diffuse, groundwater discharge. Even without a sample of the groundwater discharge, a concentration of Zn, for example, can be calculated for that groundwater because of the detailed discharge values. This would be the concentration that is necessary to cause the observed increase in load. Total-recoverable Zn at 4,713 m was 0.034 mg/L and discharge was 148 L/s. At 5,030 m, the corresponding values were 0.044 mg/L and 154 L/s. Thus, the change in mass load of Zn was 1.74 mg/s. With a discharge increase of 6 L/s, the calculated Zn concentration would be 0.29 mg/L. Five inflows upstream in Mary Ellen Gulch had equal or greater Zn concentrations than 0.29 mg/L (Table 3 in Kimball et al. 2009), so similar

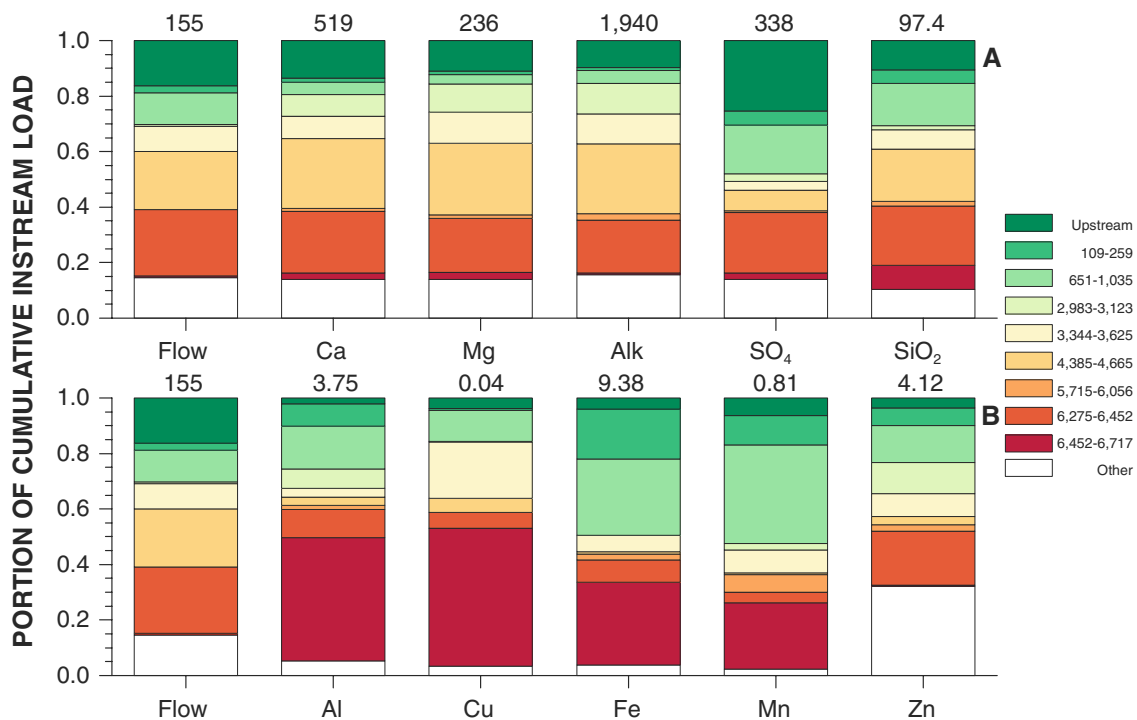


Fig. 6 Portions of loading from principal locations for **a** major-element and **b** trace-metal loading to American Fork, Utah, Oct. 1999; the absolute value of loading for each element is indicated in kg/day (or L/s for flow) above each bar

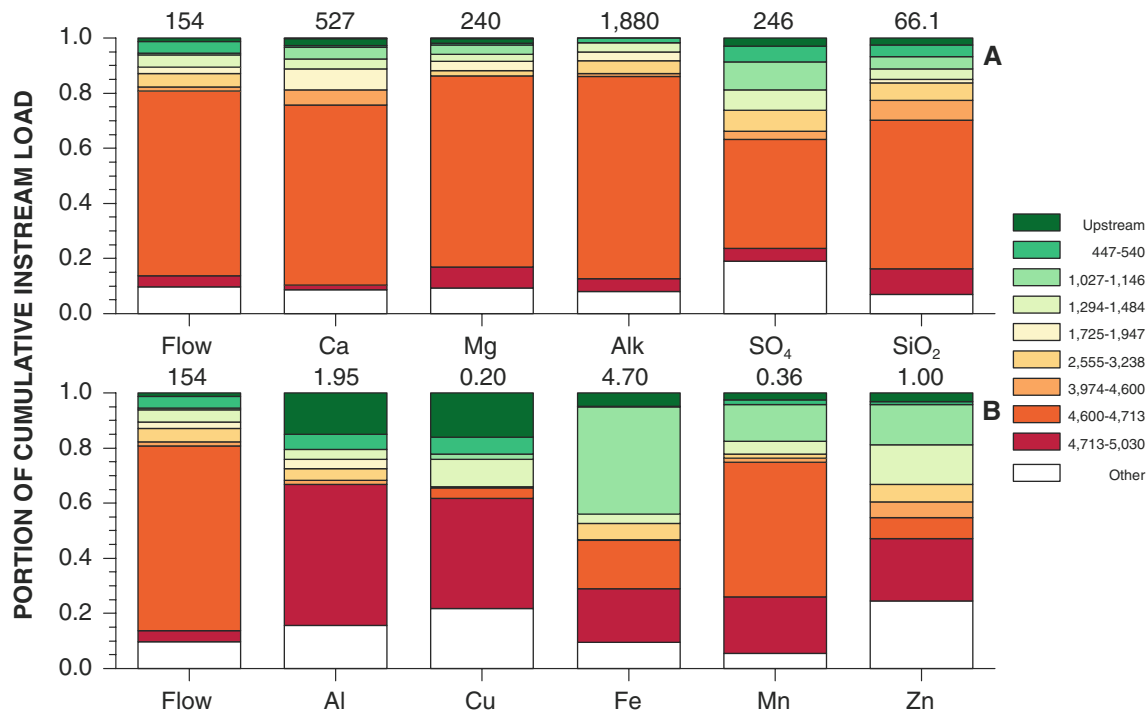


Fig. 7 Portions of loading from principal locations for **a** major-element and **b** trace-metal loading to Mary Ellen Gulch, Utah, Sept 2000

upstream water might be the source of metal-rich inflow to American Fork. These mass-loading studies do not provide information about the location and movement of

groundwater in Mary Ellen Gulch. The results only indicate the impact of a possible plume on American Fork. The Mary Ellen Gulch study is consistent with the increasing

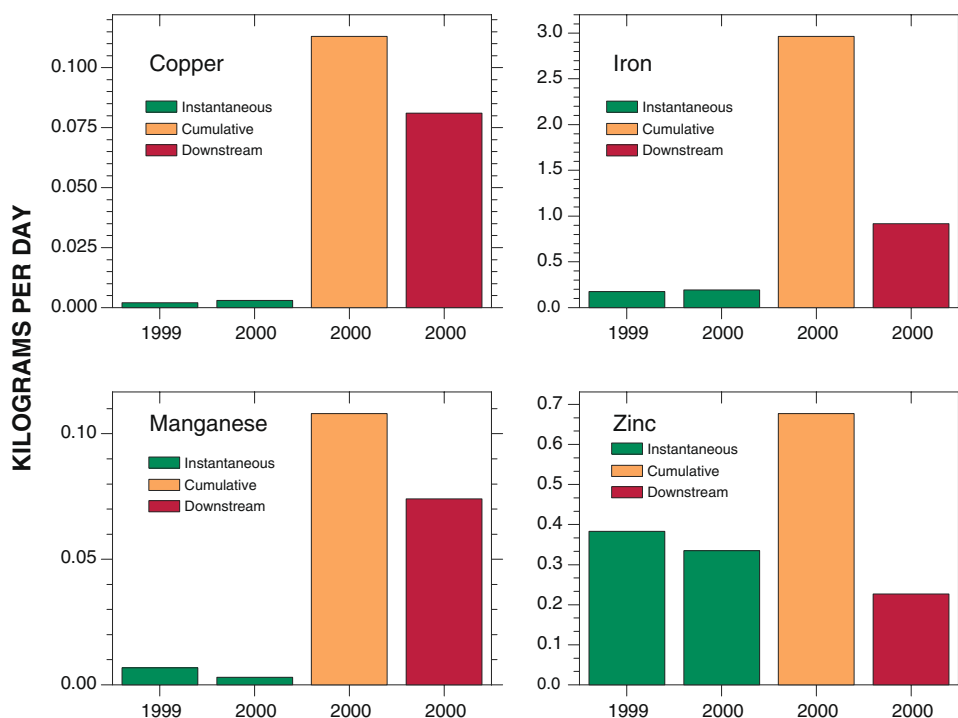
concentrations of metals downstream of the confluence, as was observed in 1999.

Comparison of Approaches for Calculating Loads

These two studies provide three quantitative measures of loading at the mouth of Mary Ellen Gulch and one measure of loading downstream from the confluence of American Fork and Mary Ellen Gulch (Fig. 8). In 1999, the inflow load of Mary Ellen Gulch (Kimball et al. 2009, Equation 3) was measured at the outlet as an inflow to American Fork. This included discharge calculated by tracer-dilution in American Fork and a chemical sample from Mary Ellen Gulch to calculate load. The second measure of load came from the in-stream load, measured at 4,600 m at the mouth of Mary Ellen Gulch in 2000 (Kimball et al. 2009, Equation 1). The load came from the tracer-dilution discharge and the chemical concentrations from the sample collected at 4,600 m during the synoptic sampling. Both of these calculations account for an instantaneous load at the mouth of Mary Ellen Gulch—a net load for Mary Ellen Gulch at that point (Fig. 8). A third measure of load at the mouth was the cumulative in-stream load from the mass-loading study in 2000 (Kimball et al. 2009, Equation 2 and discussion). This load determination accounted for all the positive increases in load to Mary Ellen Gulch upstream from 4,600 m. Finally, loading to American Fork, downstream from the mouth of Mary Ellen Gulch, was measured by the study in 2000.

These calculations of loading are illustrated for Cu, Fe, Mn, and Zn (Fig. 8). For each of these metals, the instantaneous loads measured in 1999 and 2000 were very comparable. The cumulative in-stream load measured in 2000 was substantially greater than either of the two instantaneous measurements for each metal. Decisions based on the instantaneous load measured at the mouth would not reflect upstream loading within the Mary Ellen Gulch catchment, and might result in underestimating the scale of remediation needs. This shows the importance of obtaining the detailed spatial information on loading within the catchment. The instantaneous, net loading at the mouth would equal the cumulative catchment loading only if there was no attenuation of load within the catchment. That circumstance would be unusual given the reactive nature of the metals. The extent of attenuation is illustrated by the example of the load profiles for Fe and Mn in Mary Ellen Gulch (Fig. 9). The total in-stream load (orange line, Fig. 9) at the vertical line, representing the confluence with upper American Fork, represents the net, instantaneous load. That measured load is less than the cumulative in-stream load (red line, Fig. 9), which accounts for all the contributions of loading along the study reach to a particular location. The greatest contributions to the 2.96 kg/day cumulative in-stream Fe load at the mouth of Mary Ellen Gulch occurred between 950 and 1,146 m (Yankee #1 inflow) and between 1,294 and 1,354 m (drainage from mine wastes). All but 9% of that cumulative in-stream load had been lost to attenuation during transport to the outlet of Mary Ellen Gulch at 4,600 m (Fig. 9a). Although the

Fig. 8 Comparison of outlet and catchment accounting of loading, Mary Ellen Gulch, Utah, Oct 1999 and Sept 2000; the outlet load quantifies the instantaneous load leaving the catchment at the site near the mouth and the catchment load quantifies the cumulative load to Mary Ellen Gulch upstream from that point



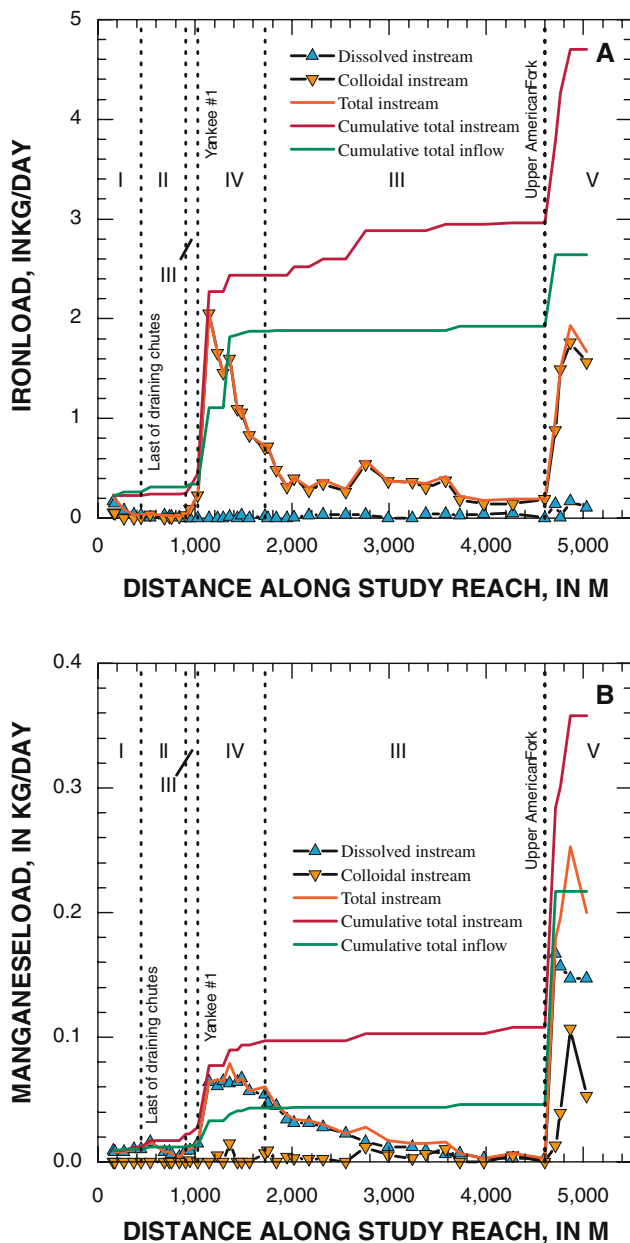


Fig. 9 Variation of **a** iron and **b** manganese loads with distance along the study reach, Mary Ellen Gulch, Utah, Sept 2000. Numbers 1–5 and vertical lines indicate the stream groups defined by cluster analysis

magnitude of Mn loading was smaller, a cumulative in-stream Mn load of 0.11 kg/day occurred at the outlet, and only 3% of that load remained after in-stream attenuation to the streambed (Fig. 9b). For both these metals, the net, instantaneous load would give no information about the most important sources within the catchment.

Although attenuation, as seen for Fe and Mn, removes metals from the water column, it does not provide natural remediation of the metals for two reasons. First, if removed

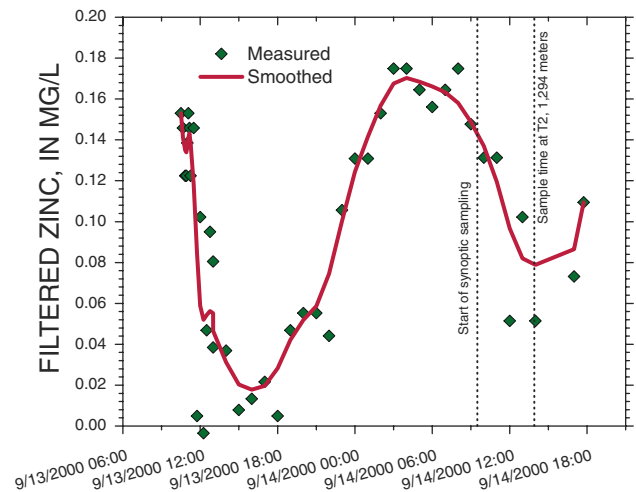


Fig. 10 Diel variation of zinc concentration with time, Mary Ellen Gulch, Utah, Sept 2000

to the streambed, metals will still be affecting the food web and can lead to chronic toxicity for benthic invertebrates and fish (Besser et al. 2001). Second, the removal is seasonal because snowmelt runoff will flush much of the metal mass back into the water column and transport it downstream (Church et al. 1997). An outlet approach combining discharge and concentration over time would be the way to quantify an annual flush of metals from snowmelt runoff. Thus, sources of metal loading upstream from where natural attenuation might occur must still be considered in remediation planning.

The net, instantaneous loads for Zn are much greater, relative to the cumulative in-stream load, than the net loads for Cu, Fe, or Mn. A possible reason for this may come from the diel variation of Zn concentrations in the stream. Hourly samples at 1,294 m were collected by an auto-sampler to monitor possible variations in tracer concentration, and these were also analyzed for filtered Mn and Zn concentrations (Fig. 10). The diel pattern for Zn was clear, but no similar pattern was observed for Mn in Mary Ellen Gulch. The consequence of this pattern is that a downstream-to-upstream sampling procedure will sample lower Zn concentrations in the upstream samples that are collected later in the day. For Zn, the sampled concentration at 13:55 hours was 0.092 $\mu\text{g/L}$, while the concentration at 09:30 hours at the beginning of synoptic sampling, was 0.14 $\mu\text{g/L}$, about 50% greater (note vertical lines in Fig. 10). Thus, the load of Zn was probably overestimated relative to the 24-h average load at the downstream sampling sites and underestimated at the upstream sites. This study did not address possible remedies to account for this process, but accurate loading profiles for metals affected by diel variation should be a topic of future study.

The measure of load downstream from the confluence represents positive values of load change (Kimball et al. 2009, Equation 2 and discussion). Only one stream segment was represented in 1999, but the same reach was divided into three stream segments in 2000. This downstream loading was substantial and would be significant in accounting for remediation needs because its magnitude was similar to the cumulative in-stream load for Cu, Fe, and Mn. Measuring only the instantaneous load at the mouth of Mary Ellen Gulch, and even the cumulative in-stream load to that same point, would miss this additional load. These results indicate the importance of studying the whole diffuse discharge of a catchment (Mayes et al. 2008).

Conclusions

Metal loading from a catchment affected by mining can be measured using two different approaches. Each approach provides different kinds of information to those who must make decisions about remediation. An *outlet approach* based on measures of concentration and discharge near the outlet of a catchment generally is used to account for temporal changes or total annual loading from a catchment. It provides fixed-point monitoring of trends and information for regulatory compliance. A *catchment approach* is based on a combination of spatially detailed synoptic sampling of stream and inflow sites within the catchment and discharge measured by tracer dilution. A catchment approach provides three important considerations that generally are needed for remediation planning.

First, detailed synoptic sampling of inflow sites provides the means to distinguish those sources affected by mining; with the aid of principal components and cluster analysis, this can help to differentiate the mine-affected inflows. Synoptic sampling of stream sites, also analyzed with cluster analysis, helps to identify where inflows, whether sampled or not, cause important changes in stream chemistry. For example, the profile of Pb in American Fork showed the effects of increased Pb downstream from the Pacific Mine area. Profiles of dissolved and colloidal Fe indicate which sections of the stream are most impacted by deposition of colloidal Fe on the streambed.

Second, the catchment approach allows the comparison of metal sources within the catchments. In American Fork, the importance of metal loading from the Lower Bog Mine, the Pacific Mine, and Mary Ellen Gulch was evident. In terms of relative contributions, however, the loading to American Fork from groundwater inflow downstream from Mary Ellen Gulch was obviously significant. When better quantified in 2000, this same groundwater contribution was

the most substantial metal loading in Mary Ellen Gulch for several metals.

Finally, the catchment approach gives the best estimate of total loading from a catchment, as represented by the cumulative in-stream load. Perhaps, the most important conclusion in this example of loading from Mary Ellen Gulch was that the principal impact was from groundwater inflow that occurred downstream from the outlet of the catchment. That loading would not have been accounted for by measuring the net load at the mouth of Mary Ellen Gulch.

This comparison of loads from Mary Ellen Gulch indicates that initial loading studies may have to be followed by selected mass-loading studies. Each inflow load from the American Fork study represented an instantaneous outlet load for tributary catchments. Because of the importance of the net load for the Mary Ellen Gulch catchment, and the knowledge that multiple sources were present in that tributary catchment, a subsequent catchment-approach study provided the detail needed to support remediation decisions. The catchment approach can characterize the sources of mine drainage within the catchment, provide a comparison of multiple sources within a catchment, and quantify the total catchment loading. The outlet approach can provide a temporal context for the catchment approach and indicate important seasonal changes in loading. Both give detailed information and are needed to make science-based decisions about remediation.

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