

NATURALLY OCCURRING ACID ROCK DRAINAGE IN COLORADO'S LAKE CREEK WATERSHED¹

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Abstract. The Lake Creek watershed in Colorado is an excellent, unique, natural outdoor laboratory for studying naturally occurring acid rock drainage (ARD) and other hydrogeochemical processes involving metal transport and deposition. ARD originates in Peekaboo Gulch, Sayres Gulch, and Sayres Bowl Stream, headwater tributaries of Lake Creek that drain low-grade Cu-Mo hydrothermal systems associated with the Grizzly Peak Caldera, host of an Oligocene, calc-alkaline porphyry. The watershed receives no visible contribution of ARD from mining or other anthropogenic disturbances. The pH in Peekaboo Gulch, Sayres Gulch, and Sayres Bowl Stream starts in the 2.5-3.0 range, but is naturally neutralized by freshwater tributaries to Lake Creek and ultimately attains a pH of 7.7 at the confluence with the Arkansas River, 37 kilometers downstream. Dissolved concentrations of 277 mg/L Al, 498 mg/L Fe, 10 mg/L Cu, and 1,180 µg/L Zn in the acidic headwaters are naturally attenuated downstream to 0.014 mg/L, <0.05 mg/L, 0.0016 mg/L, and 1.57 µg/L, respectively, at the confluence. However, suspended Al and Fe concentrations, which can exceed their dissolved counterparts by a factor of 100 locally, tend to increase along significant stream reaches even as dissolved concentrations are decreasing, resulting in gradually increasing total metal loads over most of the watershed. Many kilometers of streambed are coated with mineral precipitates caused by the neutralization of Lake Creek from freshwater inflow along its course. In low-pH regimes high in the watershed, Al and Fe precipitates consist primarily of sulfates, but grade into oxides and hydroxides as pH increases downstream. Trace metal concentrations tend to mimic Al and Fe concentrations, probably due to adsorption onto precipitated phases of Al and Fe. Concentrations of dissolved Al, Fe, and other metals are strongly pH dependent, and the system displays the ability of Al and Fe to shift rapidly from dissolved to suspended forms depending on pH.

Additional Keywords: Arkansas River, Peekaboo Gulch, Sayres Gulch, Grizzly Peak Caldera, aluminum, iron

¹Paper was presented at the 2005 National Meeting of the American Society of Mining and Reclamation, June 19-23, 2005. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2005 pp 71-97

DOI: 10.21000/JASMR05010071

<https://doi.org/10.21000/JASMR05010071>

Introduction

ARD receives much attention in the environmental community due to the impacts caused by anthropogenic disturbances such as mining. However an often-overlooked contributor to ARD is natural sources that cannot be directly attributed to anthropogenic disturbance. As this paper will demonstrate, natural ARD can be as extreme as anthropogenic ARD, with impacts to watersheds comparable to any anthropogenic source.

The Colorado Geological Survey (CGS) and several partners are conducting an investigation in Colorado's upper Arkansas River basin to determine the ability of remote sensing and spectroscopic methods in assessing the contribution of natural and anthropogenic acidic and metalliferous drainage to the watershed. Partners in the project include HENDCO Services of Nathrop, CO, Peters Geosciences of Golden, CO, Spectral International, Inc. of Arvada, CO, and Overhill Imaging of Golden, CO. Field sampling was done with the assistance of the Natural Resources Management Institute of the Colorado Mountain College in Leadville, CO.

The project area is approximately 150 kilometers southwest of Denver in the Upper Arkansas River and Lake Creek watersheds (Fig. 1). In the Lake Creek watershed, the focus of this paper, elevations range from about 2,804 m (9,200 ft) at the lowermost sample site on Lake Creek to about 4,023 m (13,200 ft) on Red Mountain at the head of Peekaboo Gulch. Topography is steep and rugged along most of the Lake Creek watershed. Lake Creek flows between two of Colorado's highest peaks, Mt. Elbert (Colorado's highest) to the north at 4,409m (14,466 ft), and La Plata Peak to the south, Colorado's 5th-highest, at 4,369 m (14,336 ft).

The primary objective of the project is to use hyperspectral remote sensing to map acid-generating minerals that indicate and affect water quality in the watershed. Greater detail on the project's remote sensing component can be found in Hauff et al. (2003a, 2003b) and Peters et al. (2004). Concurrently with the collection of spectral and mineral precipitate data, water samples were collected from both the Lake Creek and Arkansas River watersheds, and analyzed for dissolved and total recoverable metals, anions, and other constituents to compare with the streambed mineralogy. The focus of this paper is to present the findings of the water chemistry component of the project. The Lake Creek watershed was chosen for this study because it is an excellent example of naturally occurring ARD, and the effects that occur to an ARD system, as it is naturally diluted and attenuated along its course.

Project Organization

Fieldwork for the project was divided into two phases (Fig. 1) to accommodate the size of the project area and the amount of data to be collected. Phase 1, for which fieldwork was completed in 2002, consists of the Lake Creek watershed from its headwaters in Peekaboo Gulch down to the confluence of Lake Creek with the Arkansas River, a stream distance of 37 kilometers (22 miles). Phase 2, for which field work was completed in 2003, includes the Arkansas River from just north of Leadville downstream to the last sample location about 2.5 kilometers upstream from the railroad siding of Riverside, a stream distance of 48 kilometers. Both phases involved collection of spectral data, water samples, and precipitate samples under both high-flow and low-flow conditions. This paper presents the findings of the Phase 1 (Lake Creek) water quality investigation, as an example of a watershed affected by natural ARD and metalliferous drainage

with no known anthropogenic influence. Conversely, Phase 2 - the Arkansas River – investigated the effects of anthropogenic ARD.

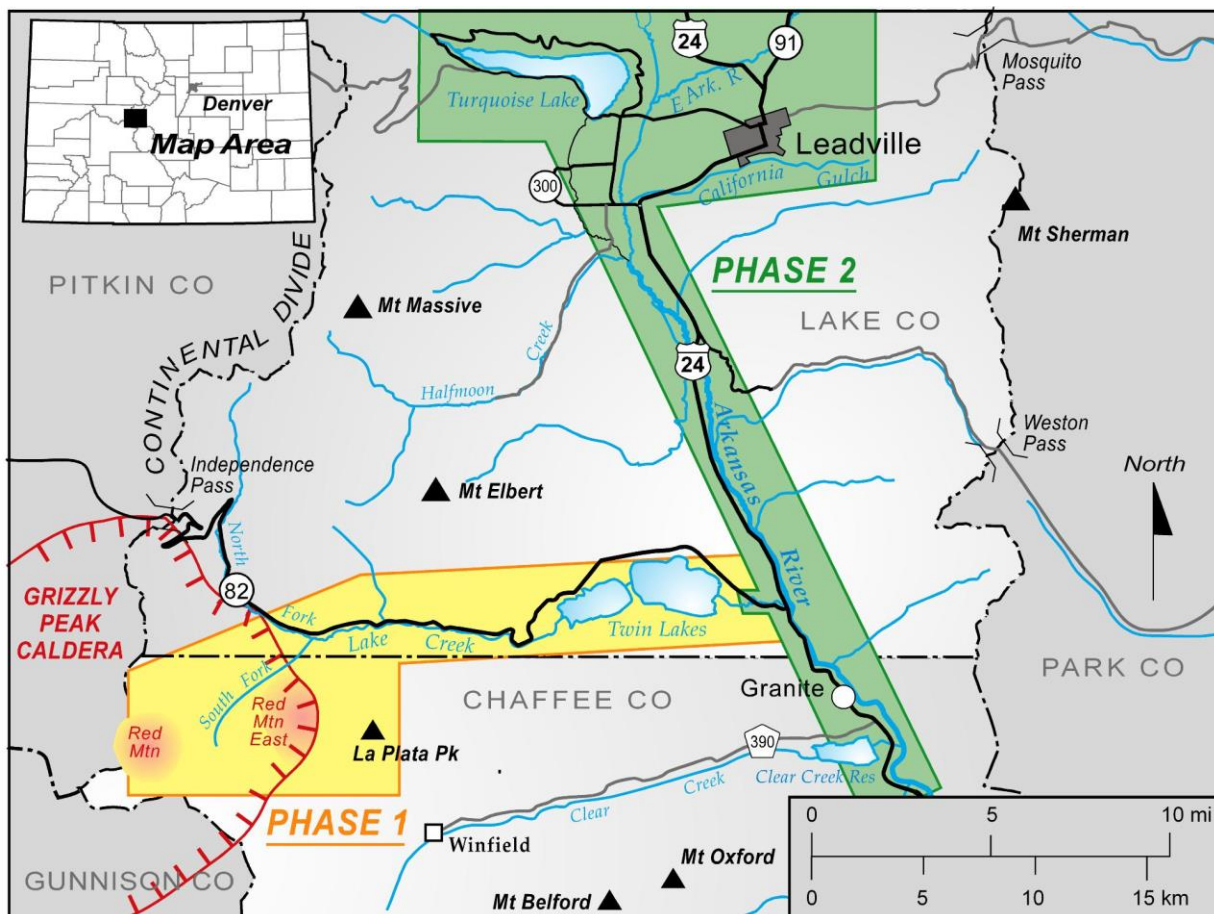


Figure 1. Location of project area.

The sampling programs were designed to evaluate the hydrogeochemical conditions within the Lake Creek mainstem, which originates in Peekaboo Gulch on the eastern flank of Red Mountain (Fig. 2), plus influences from major tributaries. Thus, sample points were spaced appropriately along the Lake Creek watershed, from Peekaboo Gulch (PG- samples) to South Fork Lake Creek (SF- samples) and finally to the mainstem of Lake Creek (LC- samples), to provide a representative downstream profile of water and precipitate chemistry (Figs. 3a, 3b, and 3c). Also, major tributaries to the mainstem that affect stream chemistry and mineral loadings were sampled at their mouths. These include Sayres Gulch (SG-14), Sayres Bowl Stream (SBS-1), McNasser Gulch (MG-1), North Fork Lake Creek (NF-1), and La Plata Gulch (LPG-1). Red Mountain East, located about 6.5 km east of Red Mountain at the headwaters of Sayres Gulch and Sayres Bowl (Fig. 4), is the second significant source of ARD in the Lake Creek system after Peekaboo Gulch.



Figure 2. Red Mountain.

Methods of Investigation

Each phase consisted of two sampling events – one during spring runoff to assess high flow conditions and one during low flow in the fall to assess as closely as possible base flow conditions. At each sample site, a composite sample was collected across the stream channel with the objective of obtaining a representative sample across the entire cross-section of the channel. At each location, samples were collected for the following analyses:

- 1) Dissolved metals (EPA methods 200.7 and 200.8) - nitric acid-preserved, filtered through a 0.45-micron in-line filter;
- 2) Total recoverable metals (EPA methods 200.7 and 200.8) – nitric acid-preserved, unfiltered;
- 3) Inorganic anions (EPA method 9056A) – unpreserved, unfiltered;
- 4) Total nitrate & nitrite as N (method 9056A), sulfuric acid-preserved, unfiltered.
- 5) Total suspended solids (EPA method 160.2) - unpreserved, unfiltered;

All samples were refrigerated upon collection until delivery to the laboratory. For each water sample collected, field measurements were made of pH, temperature, electrical conductivity, dissolved oxygen, total alkalinity, and acidity.

Geologic Setting

The Lake Creek watershed lies partially within the Grizzly Peak Caldera, which is estimated at 32 to 37 million years old, and is about 20 km long by 17 km wide with its northernmost boundary at Independence Pass. Formation of the Grizzly Peak Caldera was associated with eruption of the rhyolitic Grizzly Peak Tuff onto rocks largely Precambrian in age. Pre-caldera magmatism resulted in the emplacement of numerous rhyolitic stocks and dikes, and associated hydrothermal fluids produced widespread alteration and formed porphyry Cu-Mo deposits and gold-bearing quartz-pyrite veins (Cruson, 1973; Fridrich et al., 1991, 1998).

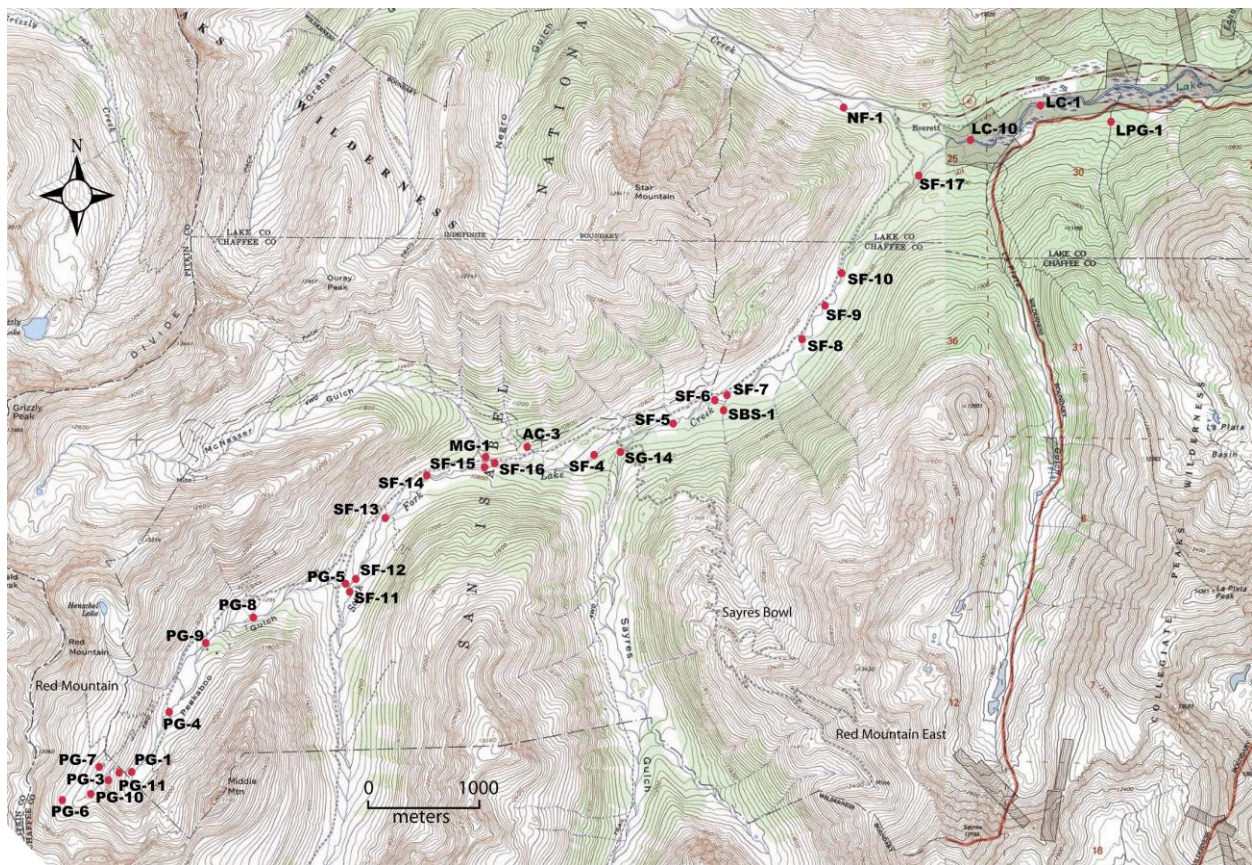


Figure 3a. Sample locations in Lake Creek watershed from Peekaboo Gulch to South Fork Lake Creek.

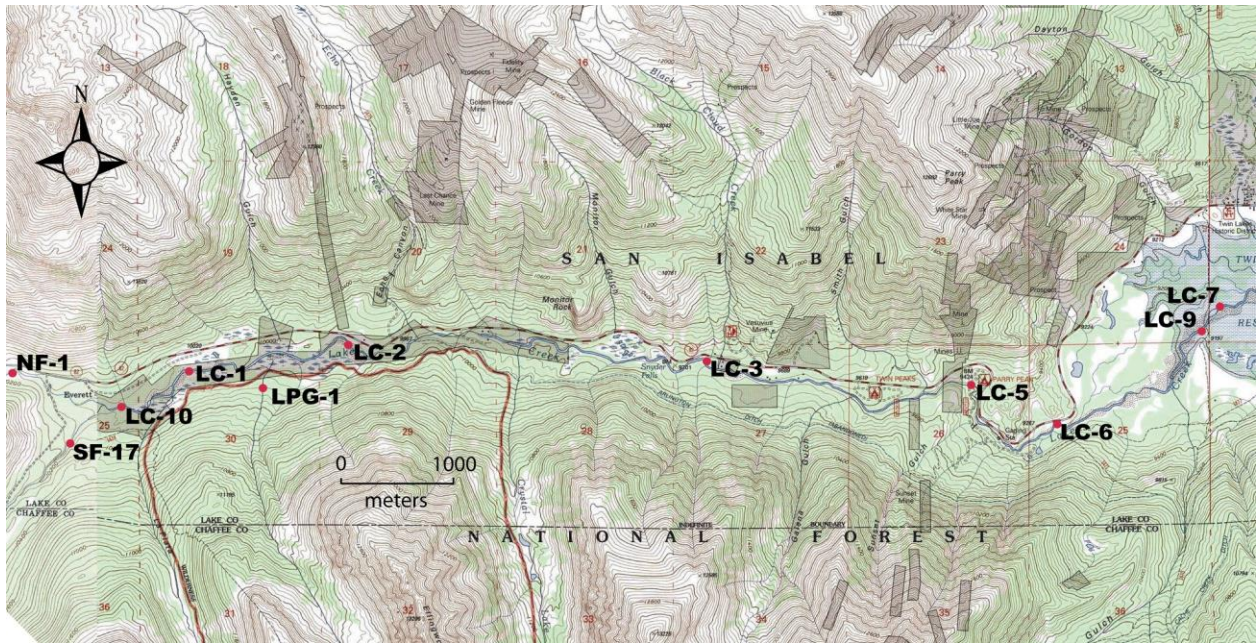


Figure 3b. Sample locations in mainstem Lake Creek above Twin Lakes Reservoir.

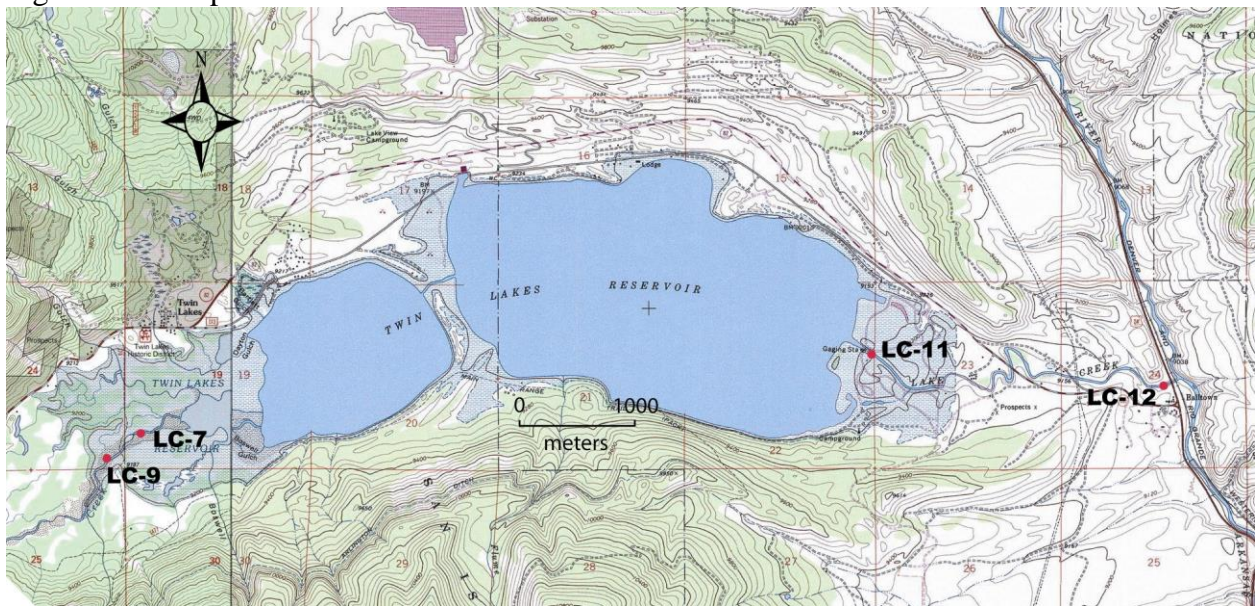


Figure 3c. Sample locations in lower Lake Creek.



Figure 4. Red Mountain East.

The dominant hydrothermal alteration on Red Mountain and Red Mountain East is acid-sulfate, characterized by quartz-sericite-alunite-pyrophyllite, quartz-sericite, and quartz-sericite-pyrite that have caused a distinct reddish coloration on the two mountains. A small, strongly hydrothermally-altered Tertiary quartz-lattice porphyry stock outcropping on the west side of Red Mountain contains quartz-molybdenite-pyrite stockwork veins in a quartz-sericite-pyrite matrix (Fridrich et al., 1998; Holtzclaw et al., 1973), and is the likely cause of the extensive alteration of the Red Mountain area and source for sulfide mineralization (Neubert et al., in press). Sulfides and other minerals associated with the hydrothermal event are the source of the ARD produced in Peekaboo Gulch, Sayres Gulch, and Sayres Bowl Stream.

Bedrock in the lower southwestern slope of Red Mountain East, along the two southern tributaries to East Sayres Gulch, is primarily unaltered, Precambrian, banded quartz-biotite gneiss. The principal altered rocks at Red Mountain East also appear to be Precambrian gneiss, but the intense alteration makes distinction of rock types difficult. Quartz-sericite alteration forms the core of the Red Mountain East area.

Historic mining production in the Red Mountain and Red Mountain East areas has been limited to exploitation of small veins (Howell, 1919). The only significant working in the area is the 365m-long Burge Tunnel located on the western flank of East Red Mountain. The few

workings and waste dumps developed in the Red Mountain and East Red Mountain area do not release any visible ARD to the watershed.

Stream Flows

The Lake Creek system drains a high mountain watershed that experiences significant annual snowfall and sub-freezing temperatures extending over a long winter season. The elevation difference between the Peekaboo Gulch headwaters (4,000+ m) and the Lake Creek - Arkansas River confluence (2,804m) is nearly 1,200 m. Thus, significantly different flow regimes occur in the watershed between snowmelt runoff in late spring and base flow conditions in winter. As Figure 5 shows, stream flows measured during this project at high flow were consistently about an order of magnitude greater than those measured at low flow.

Stream flows over the Lake Creek watershed varied from about 1 to 54 cfs at low flow, and from 8 to over 400 cfs at high flow (note: for this and all subsequent graphs, headwaters in Peekaboo Gulch are on the left edge of the graph, and the confluence with the Arkansas River is on the right edge of the graph). Some downstream locations were too treacherous for gauging at high flow, so the chart has some data gaps. The fluctuations in stream flow are accompanied by some dramatic effects on stream hydrochemistry, as explained in the following sections.

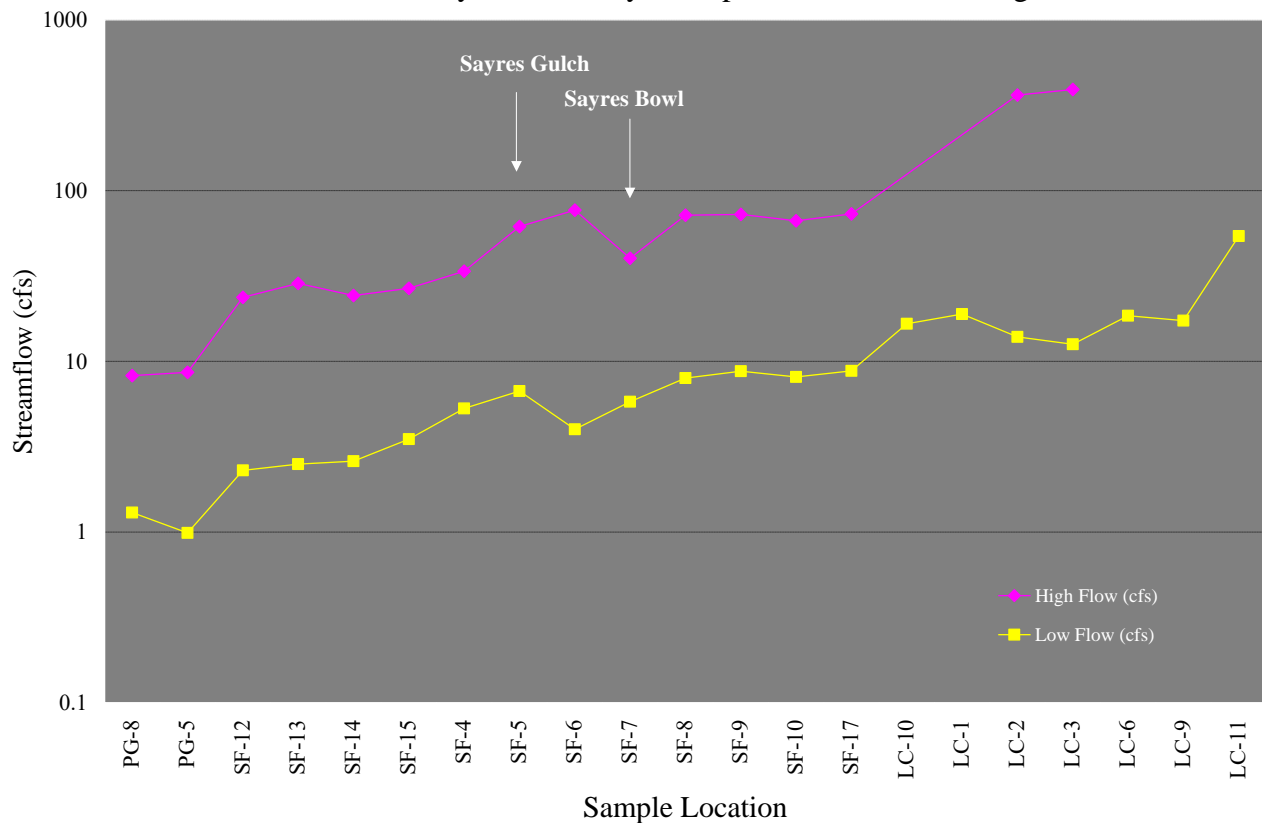


Figure 5. Stream flow profile in Lake Creek at high and low flow from Peekaboo Gulch to confluence with Arkansas River.

Hydrogeochemistry of Lake Creek

The Lake Creek Watershed offers an interesting hydrogeochemical profile from its source in Peekaboo Gulch down to its confluence with the Arkansas River. An example is the profile of total dissolved solids (TDS) down the watershed (Fig. 6). Where the water first emerges from a talus slope at the head of Peekaboo Gulch, the water is clean and clear with a pH of 6.6, a temperature of 2.2 °C, and total dissolved solids (TDS) of 78 mg/L at low flow and 13 mg/L at high flow. Within a few hundred meters, the stream receives discharge from two springs, informally named the red spring and the white spring (Fig. 7), which emerge from areas of intense hydrothermal alteration on the east flank of Red Mountain. The red and white springs (RWS) had pH of 2.74 and 4.97 respectively at low flow. The TDS of the red spring was 29,487 mg/L at high flow and 4,236 mg/L at low flow. A comparison of concentrations of selected constituents in the two springs is shown in Table 1. None of the ARD originating on the Peekaboo Gulch side of Red Mountain is associated with any anthropogenic disturbances such as mine adits, shafts, waste rock dumps, or tailings deposits.

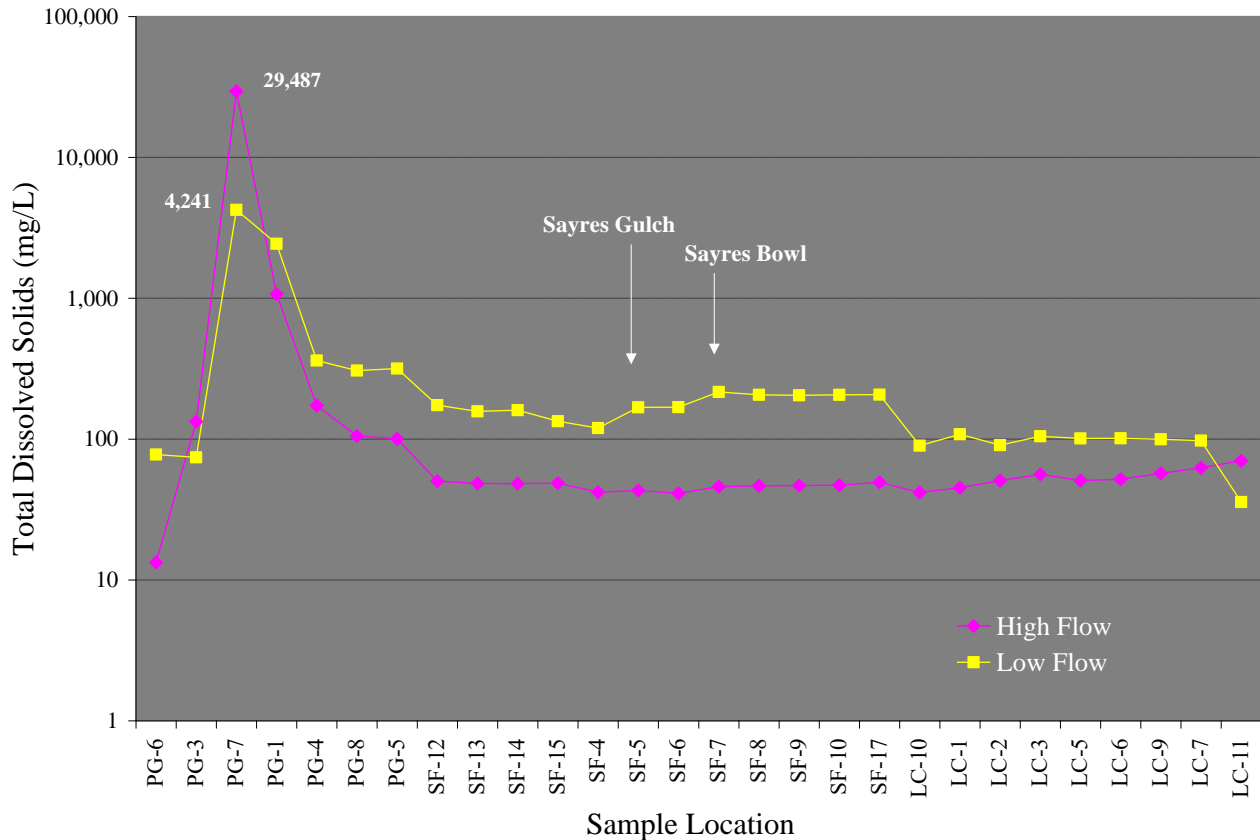


Figure 6. Total dissolved solids profile of Lake Creek at high and low flow from Peekaboo Gulch to confluence with Arkansas River.

The red spring has high Fe concentration and abundant Fe precipitates, and the acidic pH allows elevated concentrations of several trace metals. The white spring however, carries

elevated Al but very little Fe, despite its emergence only about 100 meters from the red spring. The white spring is near thermodynamic saturation with aqueous Al species, as shown by the abundant white precipitate. The pH of South Fork Lake Creek behaves quite differently depending on flow conditions (Fig. 8). Under both regimes, the pH at the headwater source is close to neutral, but plummets sharply to below 3 due to the influence from RWS (sample sites PG-3 and PG-7). At low flow, the pH stays acidic until the confluence of North and South Fork Lake Creek, at which point the pH is neutralized to around 7. However, at high flow, the influence of snowmelt high in the watershed causes neutralization of the pH to around 7 shortly after Peekaboo Gulch enters South Fork Lake Creek, and the pH stays neutral over the remainder of the Lake Creek reach.

The influx of acidic water at Sayres Gulch (pH = 4.29) and Sayres Bowl (pH = 3.17) has a notable effect on pH at low flow, but not at high flow. At low flow, the pH drops from 5.31 to 4.57 due to Sayres Gulch inflow at site SF-5, and again from 4.66 to 4.07 due to Sayres Bowl inflow at site SF-7. At high flow, the dilution provided by the additional flow from snowmelt is able to overcome the influx of acidity from Sayres Gulch and Sayres Bowl.

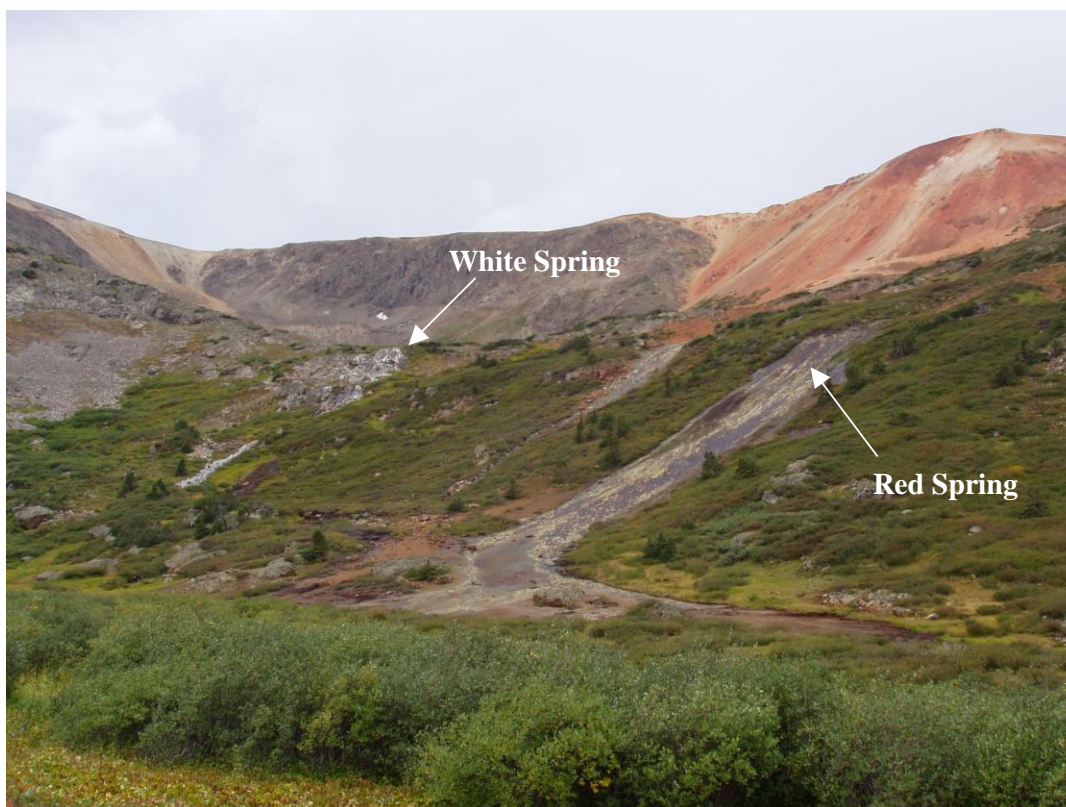


Figure 7. The red and white springs near the headwaters of Peekaboo Gulch.

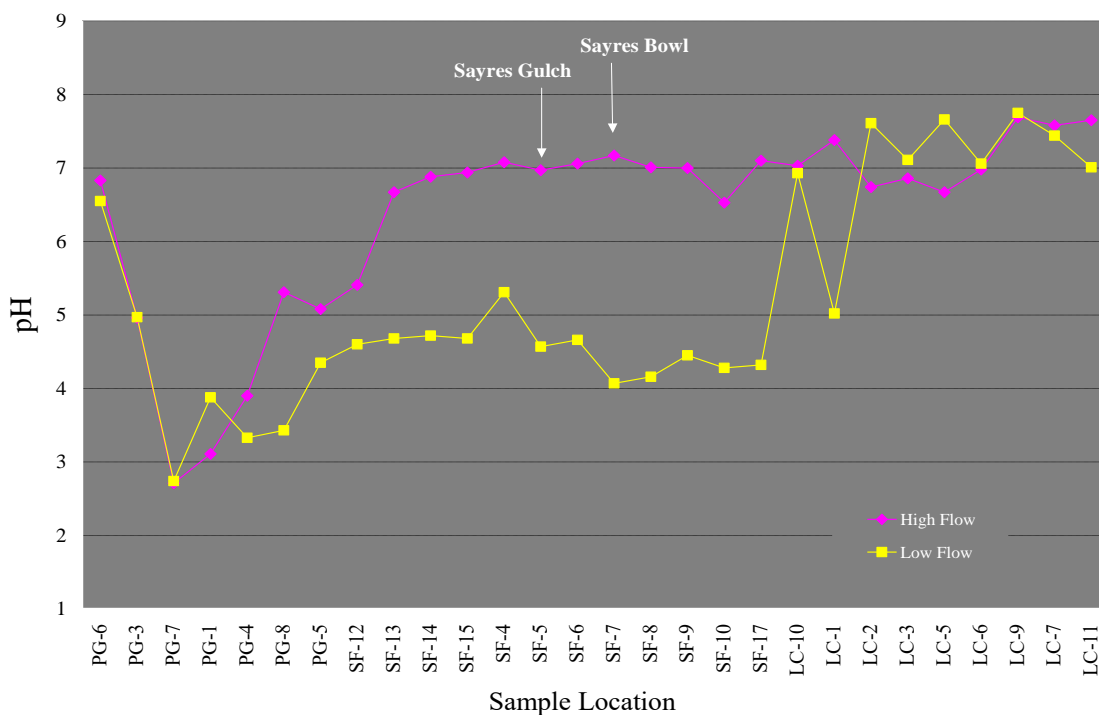


Figure 8. pH profile of Lake Creek at high and low flow from Peekaboo Gulch to confluence with Arkansas River.

Some interesting quality control issues are revealed in the measurement of pH at low flow. First, the pH of site LC-10 at low flow was apparently measured at a point before the two tributaries had mixed thoroughly, and the sample appears to be biased toward the more neutral pH of North Fork Lake Creek. Apparently, the stream is not fully mixed at this point and we should have sampled it farther downstream. Second, two different sample crews were leap-frogging their way upstream, and the disparity of the pH meters used by each crew is obvious in the measurements made along the Lake Creek reach (LC- samples). Although the two meters were calibrated at the same time each morning before fieldwork commenced, the meters apparently were not calibrated using the same pH buffers. Unfortunately, by the time this problem was discovered, the flow regime had changed to the extent that re-measuring pH would have been meaningless.

At the Peekaboo Gulch headwaters, most trace elements were undetectable, but at RWS the concentrations of trace metals increased sharply. From RWS downstream throughout the Lake Creek system, the dominant process becomes attenuation of dissolved and suspended constituents in the water column due to dilution, mineral precipitation and probably trace metal adsorption. The stream consequently is lined with a smorgasbord of different precipitates, primarily Al and Fe minerals that instill shades of red, orange, yellow and white to the streambed (Figs. 9 to 12).

Table 1. Chemical compositions of red and white springs at low flow.

Analyte	Red Spring	White Spring
pH	2.74	4.97
Total Dissolved Solids (mg/L)	4,236	74
Aluminum (mg/L dissolved)	277	1.6
Antimony ($\mu\text{g/L}$ total recoverable)	0.123	<0.15
Arsenic ($\mu\text{g/L}$ total recoverable)	51	0.15
Cadmium ($\mu\text{g/L}$ dissolved)	24	<0.2
Calcium (mg/L dissolved)	6.1	5.8
Copper ($\mu\text{g/L}$ dissolved)	10,000	160
Chromium ($\mu\text{g/L}$ dissolved)	21.7	<0.15
Fluoride (mg/L dissolved)	1.6	0.05
Iron (mg/L dissolved)	498	<50
Lead ($\mu\text{g/L}$ dissolved)	<0.1	0.18
Magnesium (mg/L dissolved)	5.9	1.4
Manganese ($\mu\text{g/L}$ dissolved)	446	63
Nickel ($\mu\text{g/L}$ dissolved)	75	1.87
Potassium (mg/L dissolved)	4.7	0.58
Silicon (mg/L dissolved)	28.4	3.6
Silver ($\mu\text{g/L}$ dissolved)	0.76	<0.1
Sodium (mg/L dissolved)	2.3	1.5
Sulfate (mg/L dissolved)	3,400	59
Thallium ($\mu\text{g/L}$ total recoverable)	0.388	<0.15
Uranium ($\mu\text{g/L}$ dissolved)	8.75	<1
Zinc ($\mu\text{g/L}$ dissolved)	1,180	32



Figure 9. Near sample site PG-4 in Peekaboo Gulch.



Figure 10. Near sample site SF-17 in South Fork Lake Creek.



Figure 11. Near sample site SF-6 in South Fork Lake Creek.



Figure 12. Near sample site SF-7 in South Fork Lake Creek.

Conservative Ions

Selected major ions that behave conservatively in this system under low flow conditions are shown on Figure 13. The behavior pattern is fairly consistent among the different ions. Concentrations are relatively low at the headwaters, but then increase sharply, typically about an order of magnitude, due to the RWS inflow (sample sites PG-3, PG-11, and PG-4). Sulfate increases by a factor of more than 30. Along the South Fork Lake Creek reach (SF- samples), the concentrations of all constituents stay fairly constant, but some experience a slight upward spike due to Sayres Gulch and Sayres Bowl. After the inflow from North Fork Lake Creek (LC- samples), most constituents show a decrease, with anions (sulfate, fluoride, and chloride) showing a pronounced decrease than cations. Below Twin Lakes Reservoir (sample sites LC-11 and LC-12), all constituents drop significantly.

Trace Elements

Aluminum and Iron. Samples were analyzed for both dissolved and total recoverable (trec) Al and Fe to compare the behaviors of the dissolved and suspended fractions of these very important elements that can control the mobility and dissolved concentrations of many other elements. The profiles of Al and Fe concentrations at low flow (Fig. 14) reveal some very interesting processes.

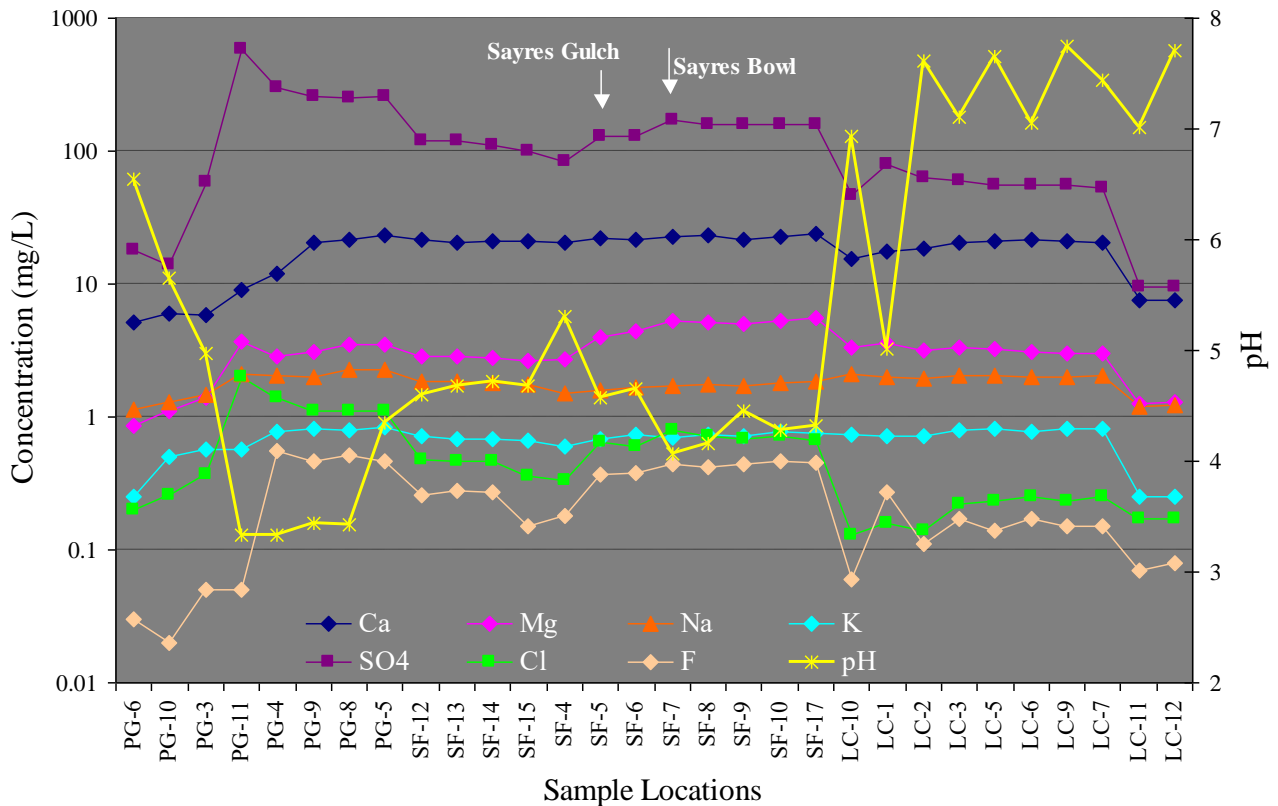


Figure 13. Concentration profile at low flow of selected major ions that behave conservatively in Lake Creek system.

The concentrations of both Al and Fe are well over 100 mg/L at the red spring (Table 1), and the impact to Peekaboo Gulch is an increase in the concentrations of Al and Fe (both total recoverable and dissolved) by more than two orders of magnitude (samples PG-3 and PG-11 on Fig. 14). Note also that the total recoverable and dissolved concentrations of both Al and Fe at PG-11 are nearly identical, indicating that Al and Fe exist almost entirely in the dissolved phase at this point. With increasing distance downstream, both total recoverable and dissolved Al and Fe are attenuated, but another interesting process occurs. A separation starts to form between the lines representing total recoverable and dissolved concentrations. This represents the concentration of the suspended fraction, which was not analyzed directly but presumably consists of amorphous flocs. The relative proportion of the suspended fraction gradually increases for both Al and Fe, except for some local aberrations, indicating that Al and Fe are flocculating and forming particles larger than the size of the sampling filter (0.45 μm). These particles are generally considered to be precursors to precipitation.

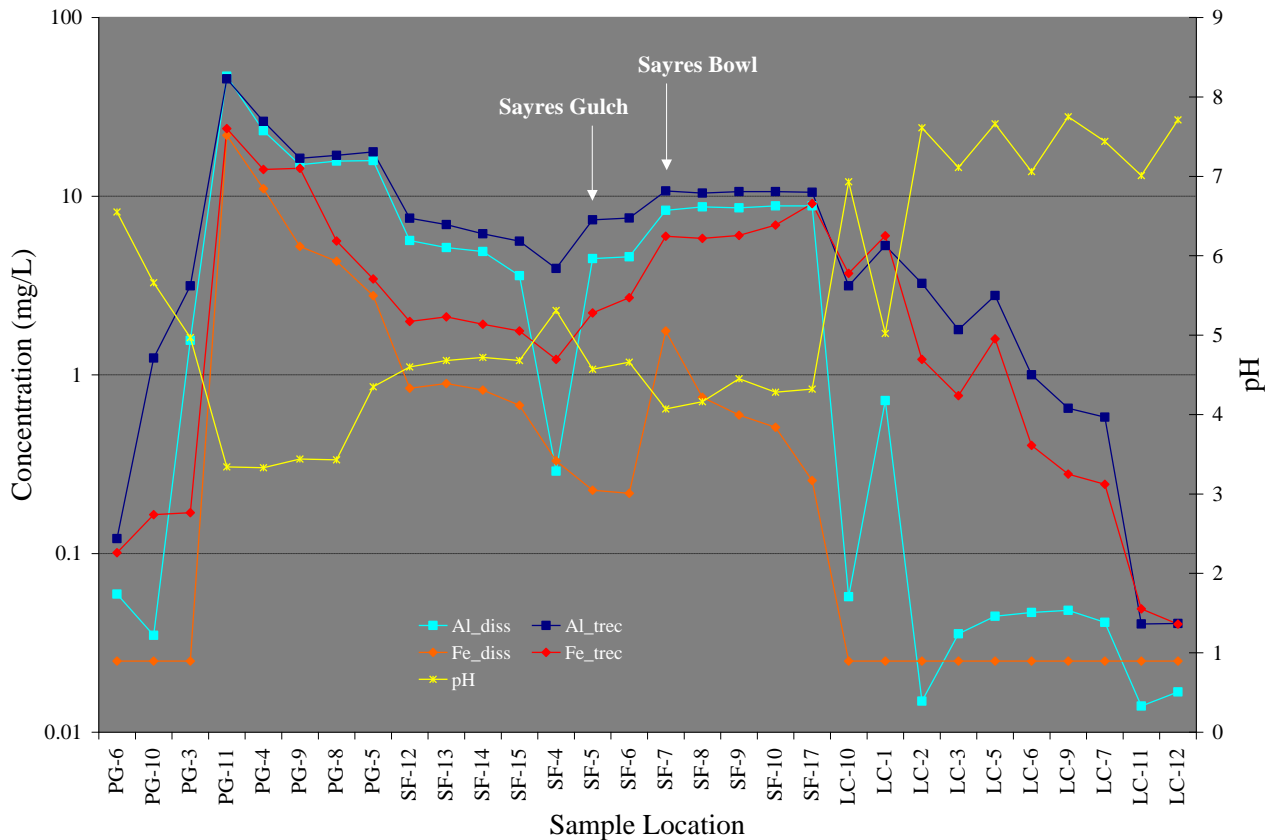


Figure 14. Profiles of dissolved and total recoverable Al and Fe in Lake Creek at low flow from Peekaboo Gulch to confluence with Arkansas River.

Moving downstream, the suspended Al fraction is relatively small until sample site SF-4. Here, a sudden pH increase from 4.68 to 5.31 accompanies a significant drop in dissolved Al from 3.6 mg/L at SF-15 to 0.29 mg/L at SF-4, and a more subtle drop in the Al-trec concentration. The next sample site demonstrates the ability of Al to quickly shift phases between dissolved and suspended due to sudden pH changes. The influx of 14.6 and 12.8 mg/L

respectively of Al-trec and Al-dissolved causes a proportionate increase in concentrations of these two components in South Fork Lake Creek. However, the pH drop in South Fork Lake Creek due to the Sayres Gulch inflow produces a temporarily more stable environment for dissolved Al, and hence a decrease in suspended Al from 3.7 to 2.9 mg/L, as shown by the closure in separation between Al-trec and Al-dissolved at sample point SF-5. As the pH drops below 5 downstream from site SF-4, Al solubility increases, and the separation closes as Al moves from the suspended to the dissolved phase. However, after the dilution caused by the large inflow from North Fork Lake Creek (LC-1), Al becomes less soluble and the separation greatly increases as Al minerals precipitate along the entire Lake Creek segment. Another interesting process is revealed at sample locations LC-10 and LC-1. The failure to properly composite the sample at LC-10, reflected in the erroneous upward pH spike, coincides with steep drops in the concentrations of Al-trec and Al-dissolved. The decrease in the dissolved fraction is proportionally greater, resulting in an increase in suspended Al in the sample. Al-trec and Al-dissolved both sharply increase at the next sample site, where the pH was correctly measured at 5.02, and the sample was properly composited.

Fe follows a somewhat similar pattern as Al, but Fe has a less direct pH dependence. Iron's redox dependency causes Fe(III) to become progressively more dominant than Fe(II) as the stream becomes more oxygenated along its course. Furthermore, since dissolved Fe(III) phases are unstable under oxidizing, neutral pH conditions, the Fe(III) compounds are removed by precipitation as the stream becomes progressively oxidized and neutralized. The separation between Fe-trec and Fe-dissolved tends to increase steadily downstream, indicating a steadily increasing suspended Fe fraction. The only exception occurs at SF-7 where the acidic, Fe-rich discharge from Sayres Bowl enters the Lake Creek system and dissolved Fe increases by about a factor of 10. Significant Fe precipitation is indicated along two reaches, where Fe-trec increases but Fe-dissolved decreases, from SF-4 to SF-6 and from SF-7 to SF-17. Dissolved Fe becomes undetectable starting at the North Fork Lake Creek confluence (LC-10), indicating that the entire Fe load is comprised of the suspended phase. However, Fe-trec eventually decreases to undetectable levels below Twin Lakes Reservoir, indicating that all Fe is ultimately removed by precipitation in Lake Creek and the reservoir.

Another interesting discovery is revealed in the South Fork Lake Creek reach where Fe-dissolved decreases even as Fe-trec is increasing, indicating significant shifting of Fe from the dissolved to the suspended phase. This occurs over two reaches – from SF-4 to SF-6 and from SF-7 to SF-17 (Figure 14). The suspended Fe fraction is obviously experiencing great increases through this section, in advance of the large-scale streambed precipitation that occurs downstream in the Lake Creek mainstem.

Other Trace Elements. The behavior of other trace elements (Fig. 15) generally mimics that of Al and Fe. The highest concentrations usually occur at the RWS, followed by gradual but steady attenuation downstream. The attenuation trend is interrupted briefly by increases in concentration caused by the inflow from Sayres Gulch and Sayres Bowl. The increases are significant for some trace metals (Ni, U) and less pronounced for others (Cd, Zn). Along the Lake Creek reach (LC- samples), all trace elements are greatly attenuated, and several drop to undetectable concentrations, coincident with the onset of sustained neutral pH conditions.

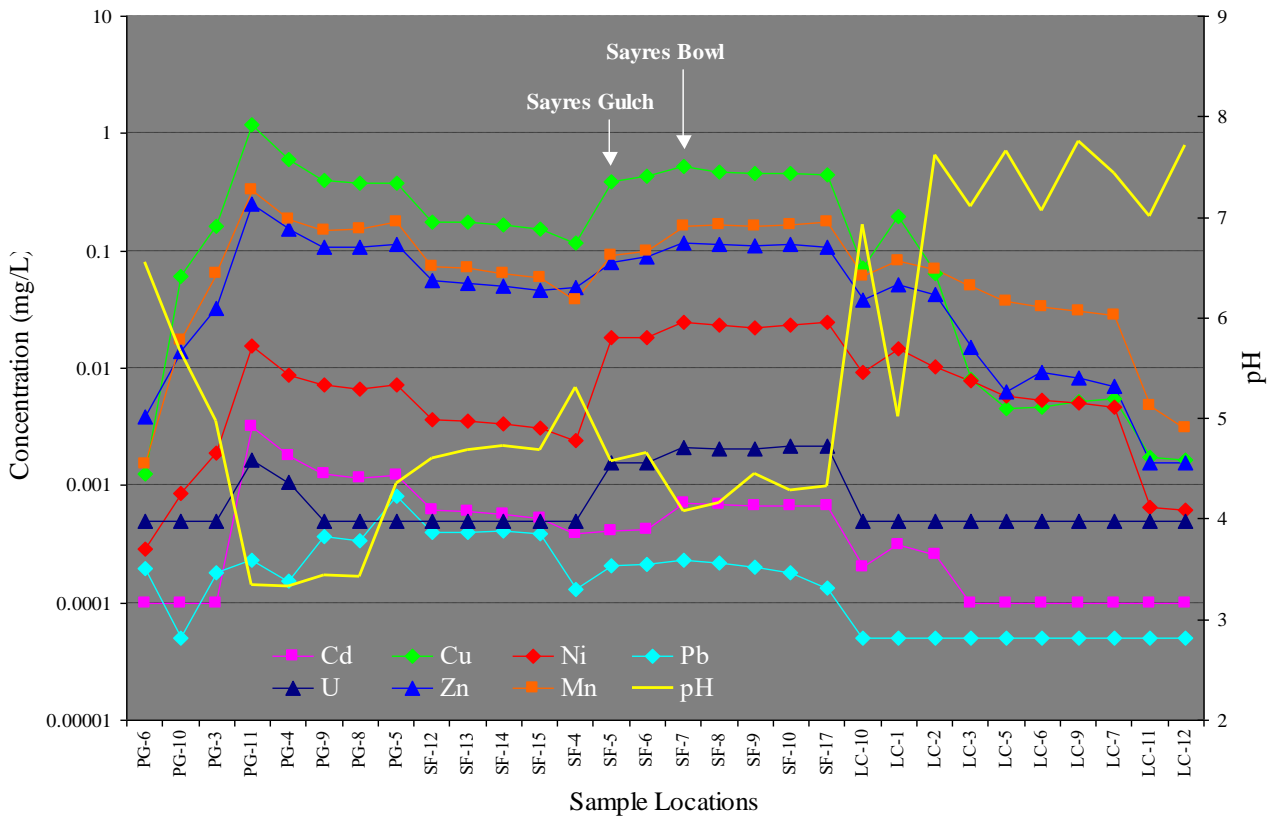


Figure 15. Profile of selected trace element concentrations in Lake Creek watershed at low flow from Peekaboo Gulch to confluence with Arkansas River.

Noting that dissolved Fe and Al drop to undetectable levels, yet Fe and Al remain in suspension until below Twin Lakes, it is reasonable to assume that the attenuation of dissolved trace metals could be due to adsorption onto Al and Fe suspensions and precipitates settling from the water column. However, XRF analyses that could confirm the presence of other trace elements with Al and Fe precipitates have not yet been completed.

One interesting discovery resulting from the unintentional bias introduced to sample LC-10 is the demonstration of the pH-dependence of trace metal concentrations. All elements depicted on Figure 15 show a sharp decrease at LC-10 coincident with the sharp upward spike of pH. However, all elements except Pb and U immediately rebound upward at sample LC-1, coincident with the sharp downward spike in pH. This dependence is presumably a function of the propensity of these trace elements to adsorb onto suspensions of Al and Fe, which can rapidly shift in size about the 0.45 μm filter size in response to pH changes.

Mass Loadings

Mass loading calculations incorporate flow data to calculate the mass of constituent per time, expressed as grams per day. Mass loadings provide a more complete indication of the

actual fate of constituents than do concentrations, and help to ascertain whether decreases in concentrations are due to actual attenuation of the constituent or simply dilution.

Conservative Ions. Figure 16 shows the mass loadings of various major ions that behave conservatively in this system. Most of these ions show a gradual, steady increase along the entire Lake Creek system, indicating that insoluble mineral phases containing these ions were not precipitating in the Lake Creek system, and other attenuation processes such as adsorption were not acting on these ions (note: for the purpose of these calculations non-detectable concentrations were adjusted to one-half the detection limit).

Aluminum and Iron. Al and Fe loadings (Fig. 17) increase sharply at the influx of RWS, but from that point downstream their behavior generally reflects their pH-dependence. Even though the streambed coatings suggest that precipitation of Al and Fe phases occurs throughout the Lake Creek system, the low flow mass loading data indicate only two reaches where the elements (based on the total recoverable fraction) are attenuated. The first is the reach that includes lower Peekaboo Gulch and upper South Fork Lake Creek; Al is removed from site PG-4 to site SF-14, and Fe is removed from site PG-9 to PG-5. The second reach is the mainstem of Lake Creek, where both Al-trec and Fe-trec are removed in significant quantity starting at site LC-1. This apparent discrepancy might be attributable to seasonal variations in stream chemistry that cause shifts in stability regimes of various Al and Fe precipitates.

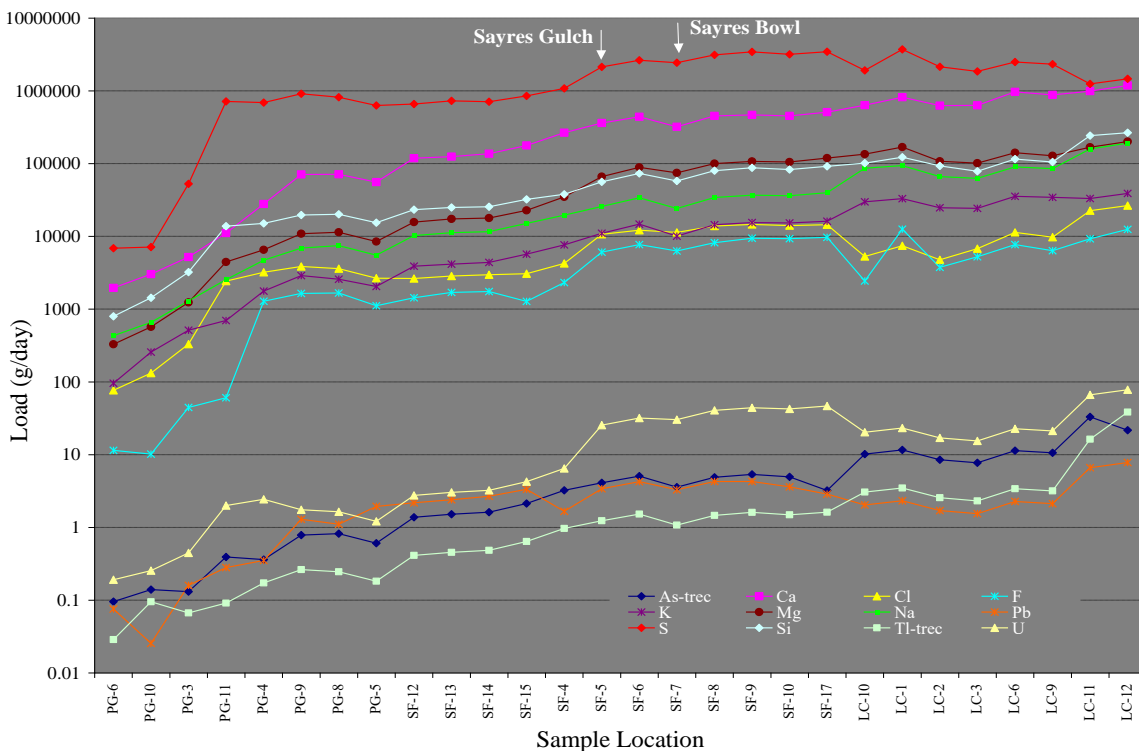


Figure 16. Profiles of mass loadings for selected conservative ions at low flow in Lake Creek watershed.

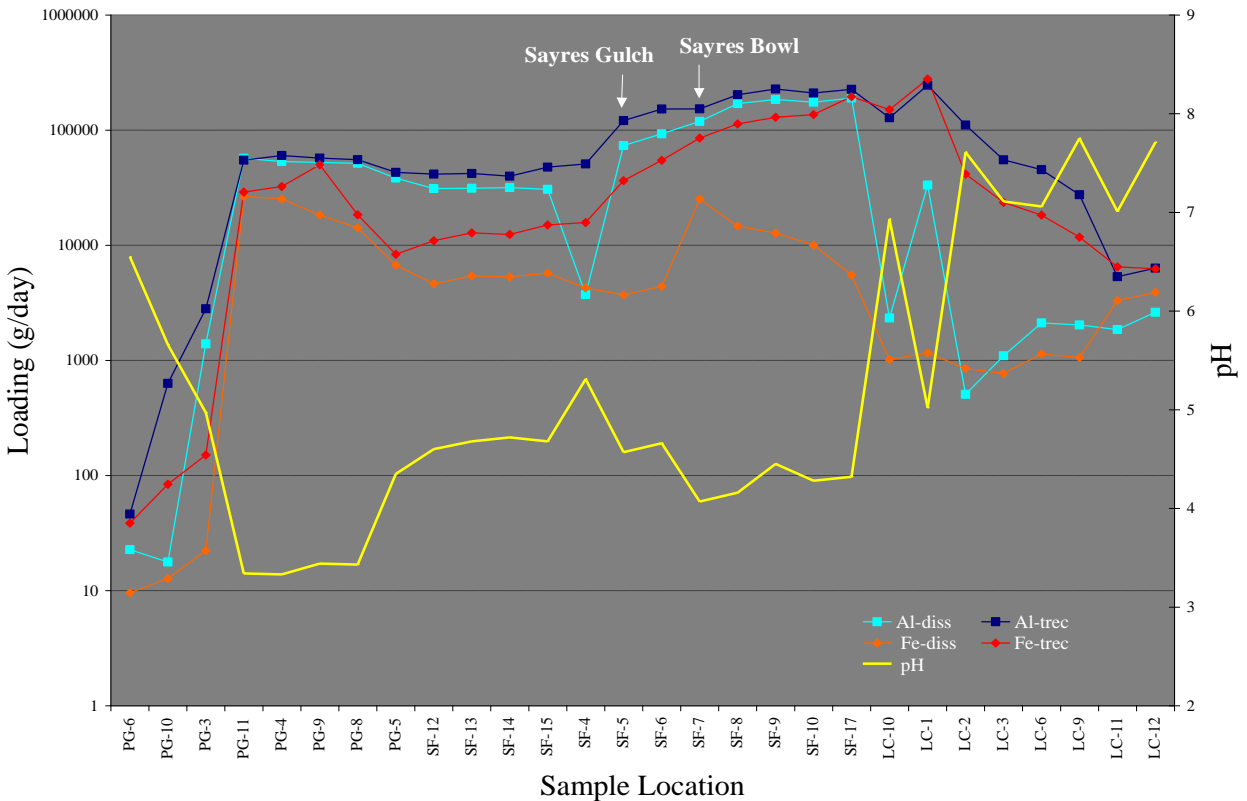


Figure 17. Profiles of mass loadings for Al and Fe at low flow in Lake Creek watershed.

Trace Elements. Most trace element mass loadings show a slightly different picture, as shown on Figure 18. All ions depicted on Figure 18 show a significant increase in upper Peekaboo Gulch due to the inflow from RWS. In the case of Cu, the increase is more than 1000-fold, and for Cd, Mn, and Zn the increase is over or close to 100-fold. However, most elements that show a steep increase (Cu, Mn, Zn, Ni, Cd, and U) suddenly plateau in lower Peekaboo Gulch and upper South Fork Lake Creek, as apparently the flux of these materials to the system suddenly ceases or, alternatively, addition is balanced by removal.

Trace element loads tend to swing upward again after the inflow from Red Mountain East. The four elements that started with the greatest increase at RWS (Cu, Mn, Ni, Zn) also showed the greatest removal in the lower LC system, suggesting that these ions are more strongly adsorbed to substrates in this system than the others. In the case of Mn, the thermodynamic data indicate that precipitation plays a significant role in its attenuation. It is worth noting that the increase in loading seen in As-trec, Cd, Cr, Pb, and Tl-trec downstream from LC-3 probably is not real. This is merely a reflection that undetectable concentrations were adjusted artificially to one-half of the detection limit and subsequently multiplied against a relatively high stream flow for calculation of mass loading.

Phase Solubilities

The USGS geochemical modeling computer code PHREEQC (Parkhurst and Appelo, 1999) was used to evaluate saturation indices of various mineral phases to corroborate the observations in the field regarding mineral solubility and precipitation. Two important elements, Al and Fe,

will be examined in this section to determine their fate along various reaches of the Lake Creek system.

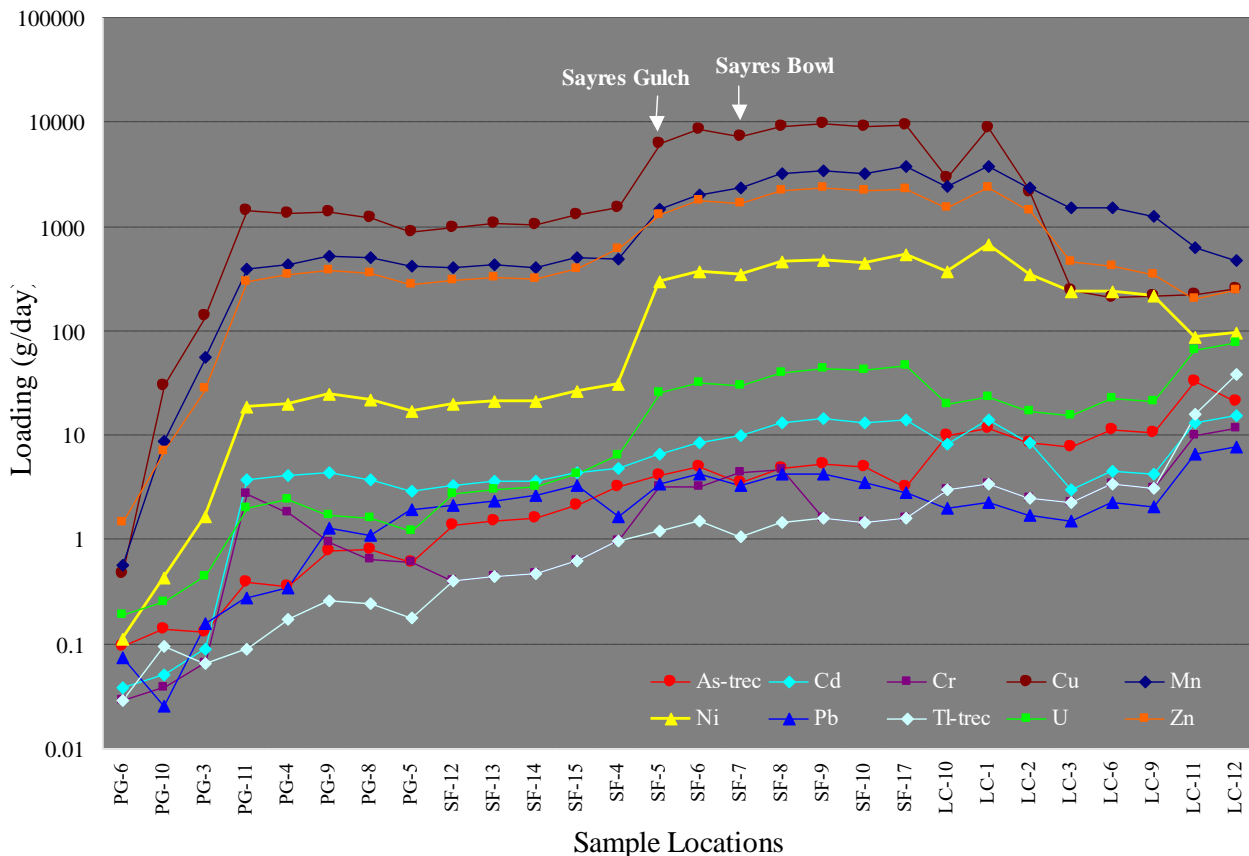


Figure 18. Profiles of mass loadings for selected trace elements at low flow in Lake Creek watershed.

Aluminum. Saturation indices of various Al minerals, plus the concentration profile of dissolved Al, are plotted on Figure 19. Several Al minerals are oversaturated over most of the Lake Creek system, indicating that precipitation of Al phases is thermodynamically possible at most sites throughout the watershed. However, influxes of acidic drainage that lower the pH (from RWS, Sayres Gulch, and Sayres Bowl) can instantaneously increase the solubility of Al species, and result in spikes in the Al concentration that coincide with reduced saturation indices of Al phases. With dilution comes neutralization, decreased Al solubility, gradual increases of saturation indices, and removal by precipitation. It is noteworthy that across four sample sites in lower Peekaboo Gulch (PG-11 to PG-8), none of the selected Al phases are oversaturated, suggesting that formation of Al flocs is thermodynamically improbable through this reach. However, settling of pre-existing suspended flocs to the streambed could still occur.

Iron. Saturation indices of selected Fe minerals, plus the concentration profile of dissolved Fe, are plotted on Figure 20. Several Fe minerals are oversaturated throughout the entire Lake Creek system. Hydroxide phases are unstable at acidic pH and are therefore typically undersaturated in these areas, but will approach and exceed saturation with dilution and neutralization in the lower

Lake Creek reach. The Fe-sulfate minerals schwertmannite and the jarosites are stable in acidic waters, so positive saturation indices of these minerals is common in acidic reaches, such as in Peekaboo Gulch and upper South Fork, and less common in neutral reaches.

Precipitate composition

Figure 21 shows minerals that have been identified by spectral means as precipitate coatings in the streambed of the Lake Creek watershed. These findings are in general agreement with the inferences made from the water chemistry. For instance, in the lower reaches of Peekaboo Gulch, the spectral data indicate the presence of Fe- and S-bearing precipitates such as jarosite ($K,NaFe_3[SO_4]_2[OH]_6$), schwertmannite ($Fe_8O_8[OH]_6[SO_4]$), melanterite ($FeSO_4 \cdot 7H_2O$), and copiapite ($Fe^{2+}Fe^{3+}_4[SO_4]_6[OH]_2 \cdot 20[H_2O]$). The mass loading calculations indicate that Al, Fe and S are removed and presumably are deposited on the streambed in this reach. No Al-bearing phases have been reported from the spectral processing on this reach, but this likely reflects the limitations of the spectral methods. There is a high probability that amorphous Al phases are present, but they have not been reported in the spectroscopy. Mass loadings of Al, Fe, and S decrease again in the lower reaches of Lake Creek, and the spectral findings reveal precipitates of goethite ($FeOOH$), lepidocrocite ($FeOOH$), green rust ($\{Fe[II]_{1-x}Fe[III]_x[O]_2\}^{+x}\{xOH\}$) and aluminum hydroxide ($Al(OH)_3$).

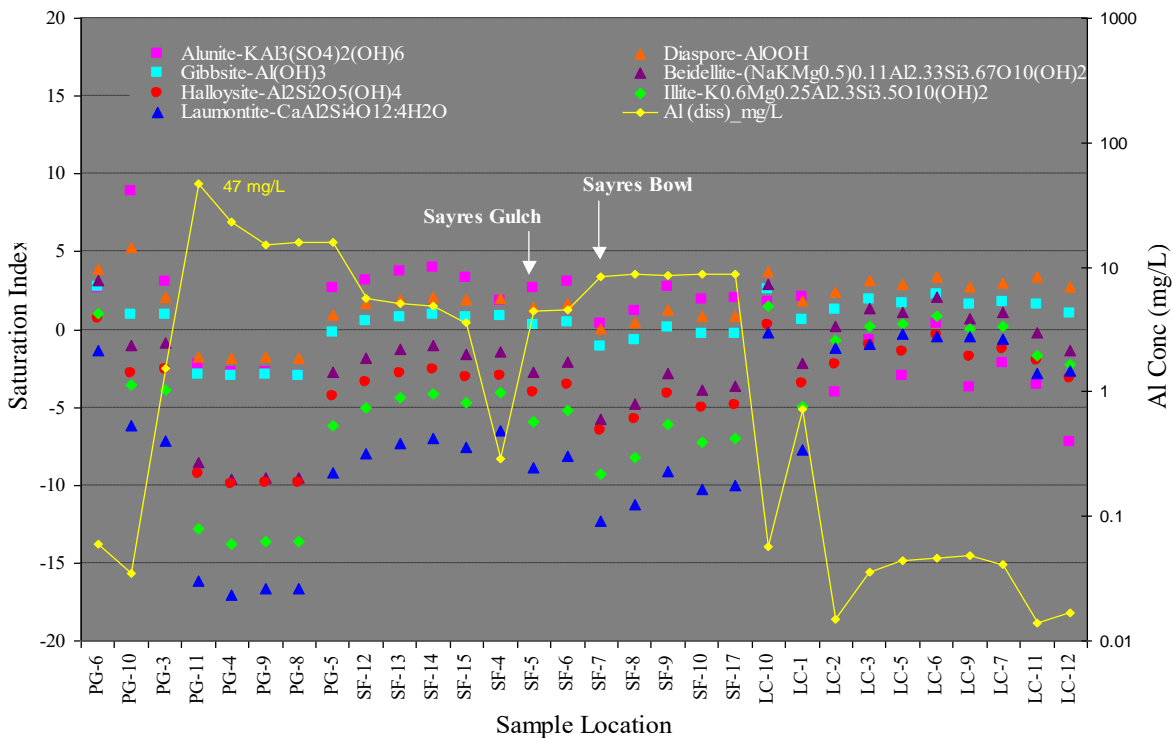


Figure 19. Profile of saturation indices of selected Al minerals, and concentration of dissolved Al, along Lake Creek watershed.

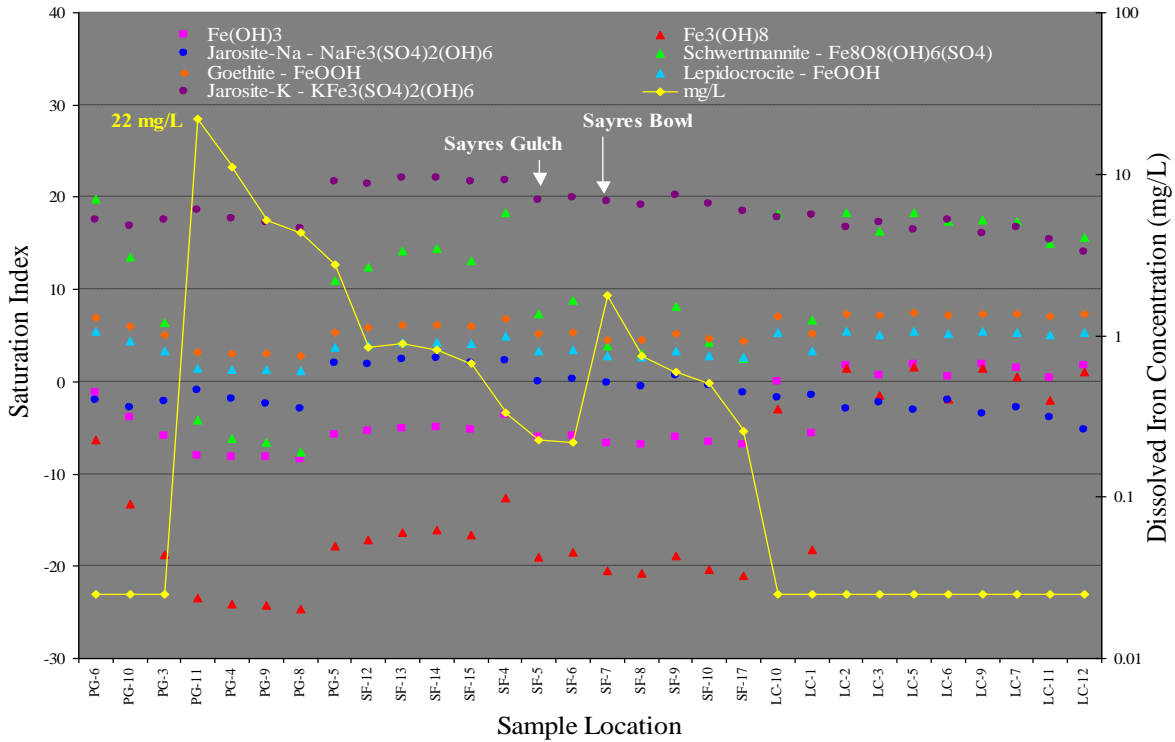


Figure 20. Profile of saturation indices of selected Fe minerals, and concentration of dissolved Fe, along Lake Creek system.

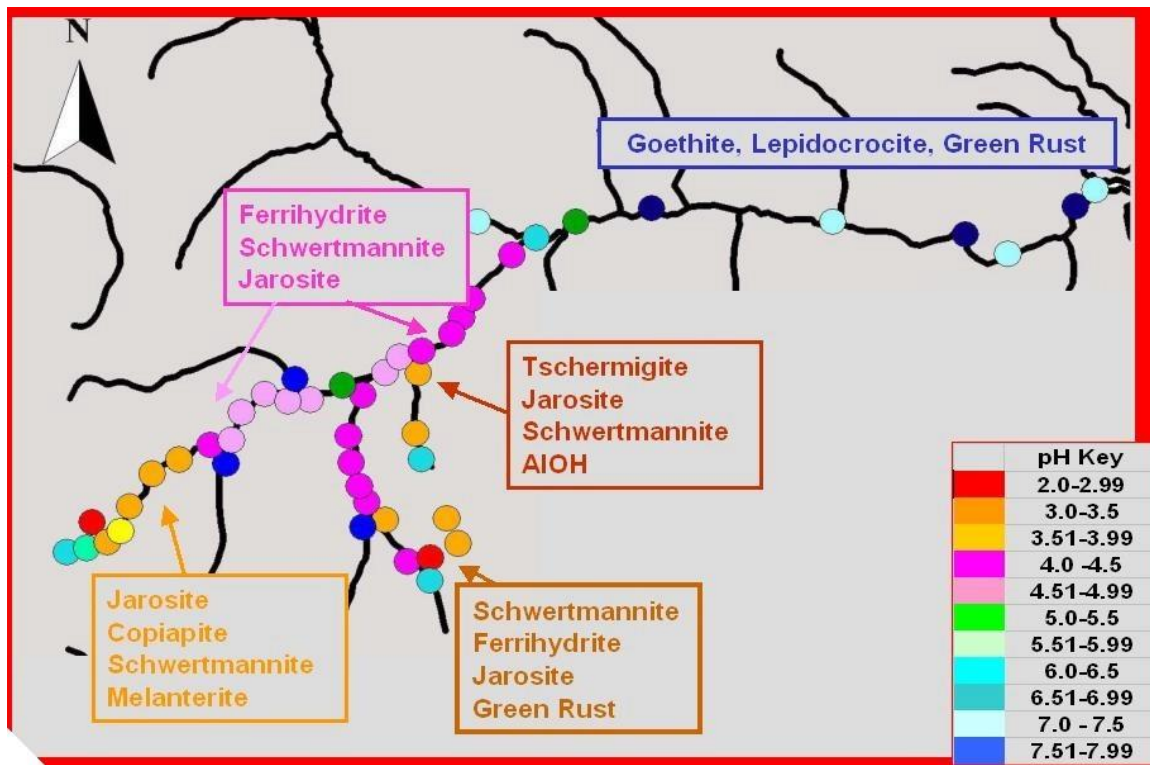


Figure 21. Mineral precipitates identified through spectroscopy in Lake Creek watershed.

Comparison to Water Quality Standards

As we would expect, the process of dilution influences the tendencies of several different constituents to exceed water quality standards. During low flow, some constituents exceeded the State water quality standards for aquatic life (<http://www.cdphe.state.co.us/regulate.asp>) over a greater reach than during high flow. Examples are seen in dissolved Al (Fig. 22), dissolved Fe (Fig. 23), and dissolved Zn (Fig. 24).

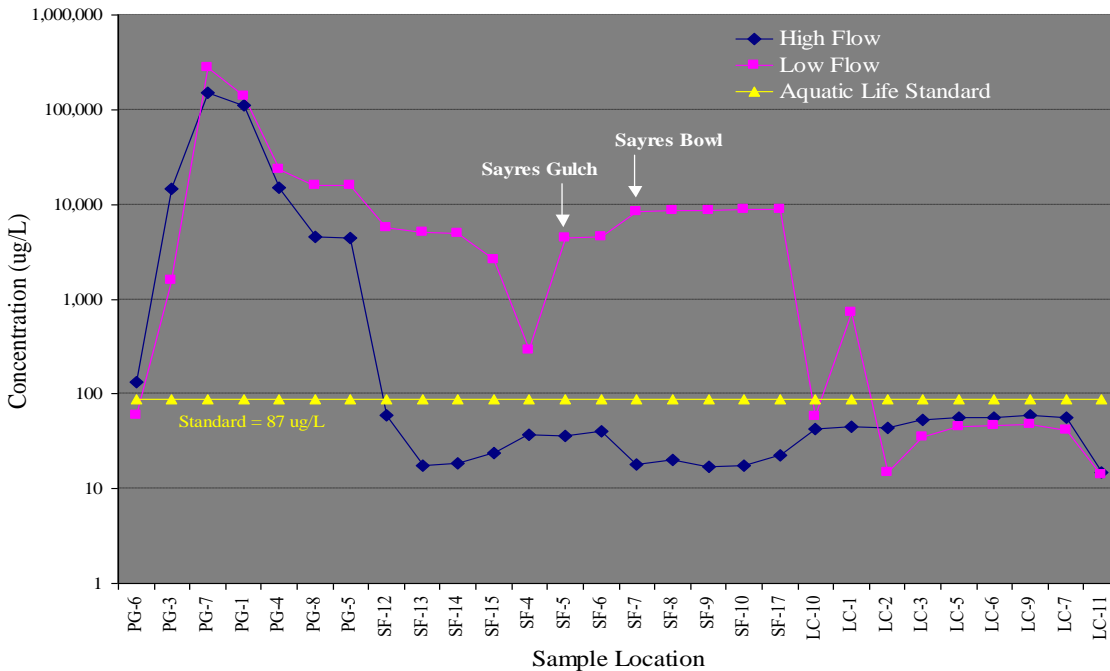


Figure 22. Profile of dissolved Al in Lake Creek watershed at high and low flow versus water quality standard of 87 $\mu\text{g/L}$.

As Figure 22 shows, dissolved Al exceeds the standard of 87 $\mu\text{g/l}$ at low flow over nearly the entire stream, with the only exception being the Lake Creek reach (LC- samples). At high flow, dilution lowers the concentration such that the standard was exceeded only in Peekaboo Gulch. The same is true for Fe (Fig. 23) and Zn (Fig. 24). At high flow, Fe and Zn exceeded their respective standards only in Peekaboo Gulch, whereas at low flow they exceeded the standards over reaches that extend well into South Fork Lake Creek (SF- samples).

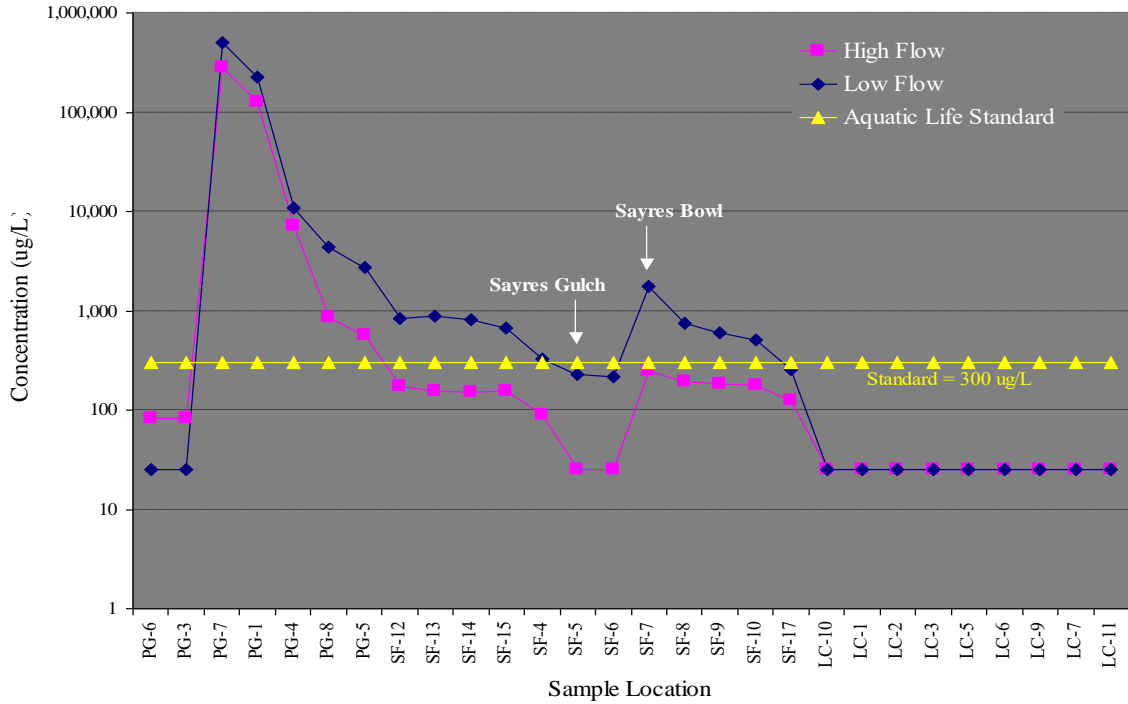


Figure 23. Profile of dissolved Fe in Lake Creek watershed at high and low flow versus water quality standard of 300 $\mu\text{g/L}$.

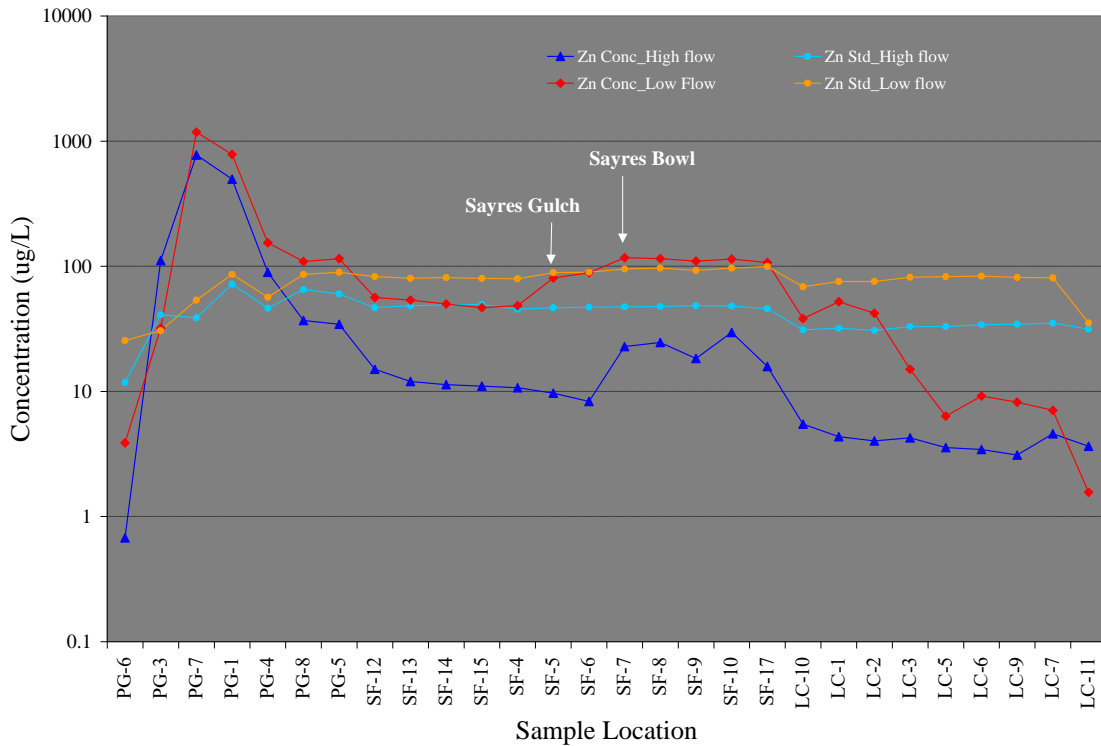


Figure 24. Profile of dissolved Zn in Lake Creek watershed versus hardness-based water quality standards.

Summary and Conclusions

This paper has presented findings from just one component in a multi-year, multi-disciplinary project. The water chemistry study in the Lake Creek watershed has been designated as Phase 1 of the overall project designed to evaluate the causes and effects of both natural and anthropogenic ARD in a watershed. This project has provided the opportunity to evaluate the effects of natural and anthropogenic ARD under both high and low flow conditions in an otherwise pristine high mountain watershed.

With pH as low as 2.74 and metals concentrations as great as 498 mg/L Fe, 277 mg/L Al, 10 mg/L Cu, 1.2 mg/L Zn, and 3,400 mg/L sulfate, this watershed demonstrates that natural ARD can produce water quality as severe, and with impacts that are as significant, as ARD from anthropogenic disturbances. The ferricrete/ferrosinter sources demonstrate that metal sulfides do not require exposure from anthropogenic activity to be a significant source of ARD with severe impacts.

The data reveal the strong pH dependency of metals concentrations and mass loadings in the aqueous environment. Low pH conditions allow high solubility and mobility of metals that are present in this system, such as Al, Fe, Cu, Mn, and Zn. With neutralization of pH, the system displays decreasing solubility of metals and eventual removal due to precipitation or adsorption.

The measurements of Al-trec and Fe-trec allow us to observe the relationship between suspended and dissolved forms of these elements. These data demonstrate that the kinetics of flocculation and dissolution about the 0.45 micron particle size are rapid in this system, as shown by the nearly instantaneous conversion between dissolved and suspended forms in response to relatively fast pH changes.

An interesting but predictable discovery has been the relationship between the hydrologic flow regime and the tendencies of constituents to exceed water quality standards. Under low flow conditions, there are more occurrences under which standards are exceeded. Under high flow conditions, dilution results in significantly fewer occurrences under which standards are exceeded.

The existence of such an extreme natural ARD situation has significant implications for the mining industry. Mining companies that conduct pre-mining baseline environmental investigations must be thorough in their inventory of natural sources of ARD in the vicinity of their operation, to reduce the probability of being held liable for environmental impacts arising from such sources.

Acknowledgment

The authors acknowledge the support of the National Aeronautics and Space Administration for this project through BAA Grant # NAG13-02026. The grant was a competitive award of the 2001 NASA Earth Science Enterprise Broad Agency Announcement for State, Local, and Tribal Uses of Remote Sensing and Geospatial Information, implemented out of the John C. Stennis Space Center in Mississippi. The authors would also like to thank Larry Scott and Jason Wilson of CGS for their work in preparing the illustrations for this report.

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