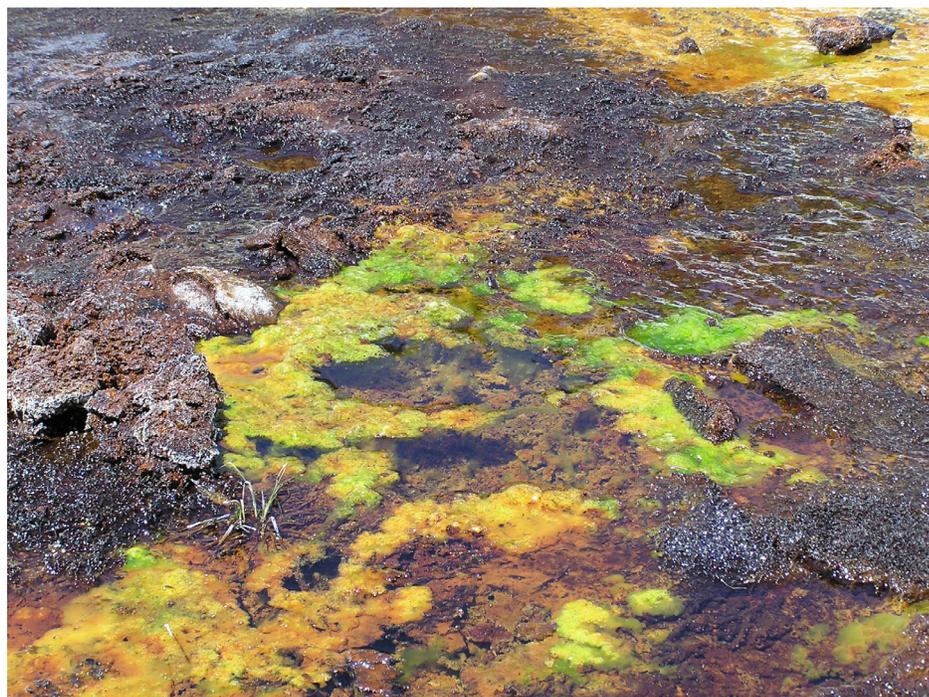




# Temporal Geochemistry Data from Five Springs in the Cement Creek Watershed, San Juan County, Colorado

By Raymond H. Johnson, Laurie Wirt, and Kenneth J. Leib



Photograph of Tiger Iron Spring by Douglas B. Yager

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A. Ferricrete master database.....	online file Ferricrete master database.xls
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# Temporal Geochemistry Data from Five Springs in the Cement Creek Watershed, San Juan County, Colorado

By Raymond H. Johnson<sup>1</sup>, Laurie Wirt<sup>2</sup>, and Kenneth J. Leib<sup>3</sup>

## Abstract

Temporal data from five springs in the Cement Creek watershed, San Juan County, Colorado provide seasonal geochemical data for further research in the formation of ferricretes. In addition, these data can be used to help understand the ground-water flow system. The resulting data demonstrate the difficulty in gathering reliable seasonal data from springs, show the unique geochemistry of each spring due to local geology, and provide seasonal trends in geochemistry for Tiger Iron Spring.

## Introduction

Five springs in the Cement Creek watershed (located within the upper Animas River watershed), San Juan County, Colorado (figs. 1 and 2) were sampled from November 13, 2003 through October 31, 2004. Red Spring in Prospect Gulch, the Upper Bog, Renoux Spring, Tiger Iron Spring, and Yager Spring were selected because of their active precipitation of iron oxyhydroxides. These springs were sampled as additional data in support of research on the formation of ferricretes. Ferricretes are iron cemented unconsolidated material that commonly host high contents of adsorbed trace metals. Previous research on ferricrete formation was completed by Wirt and others (2007). The goal of this additional sampling is to understand the seasonal nature of the spring geochemistry and its possible affects on ferricrete formation and metal adsorption. In addition, any temporal changes in ground-water geochemistry may help identify the ground-water flow system that feeds these springs.

## Methods

Every effort was made to collect water samples at the point where the spring emerged from the ground with the greatest flow, in an attempt to collect water before equilibration with the atmosphere. In areas of diffuse seepage, the sampling location was selected by surveying the spring with field meters to find areas with the lowest pH and lowest dissolved oxygen. Field parameters included pH, temperature, specific conductance, and dissolved oxygen. Field parameters and sample collection were completed following the protocols provided in the U.S. Geological

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<sup>1</sup> U.S. Geological Survey, Denver, Colorado

<sup>2</sup> deceased, last with the U.S. Geological Survey, Denver, Colorado

<sup>3</sup> U.S. Geological Survey, Grand Junction, Colorado

Survey's National Field Manual for the Collection of Water-Quality Data (Wilde and others, 1998). Three aliquots of water were collected: 1) an unfiltered sample stored in a glass bottle with a top cone to reduce air contamination for oxygen and hydrogen isotopic analyses, 2) a filtered sample stored in a plastic vial, which was acidified to a pH of less than 2 with ultra pure nitric acid, for elemental analyses, and 3) an unfiltered sample stored in a plastic vial for anion analyses. Water-quality samples were collected using either a small peristaltic pump or with a plastic syringe. Filtered pump samples were collected using an in-line Gelman 0.45  $\mu\text{m}$  capsule filter and filtered syringe samples were collected using a syringe-mounted Gelman 0.45  $\mu\text{m}$  Acro-disc filter.

The oxygen and hydrogen isotopic compositions of water ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) were determined by the USGS Crustal Imaging Team Laboratory in Denver, Colo. Oxygen isotopic compositions were determined using a Micromass Optima, with an automated  $\text{CO}_2$  equilibration technique adapted from Epstein and Mayeda (1953). Water samples were prepared for hydrogen-isotopic analyses using the Zn-reduction technique (Kendall and Coplen, 1985). The hydrogen analyses were performed on a Finnigan MAT 252 mass spectrometer. Values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are relative to VSMOW (Vienna Standard Mean Ocean Water) and have a reproducibility of approximately 0.2 and 1.0 per mil, respectively. Analyses for major and minor cations and anions were completed at the USGS Mineral Resources Laboratory in Denver, Colo. Major and minor cations plus sulfate were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Lamothe and others, 1999). Analyses for major cations were also completed using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Briggs and Fey, 1996). Anion analyses were completed using ion chromatography (IC, d'Angelo and Ficklin, 1996). Measurements of alkalinity were not required, as all pH values were less than 4.5, giving an alkalinity of zero mg/L as calcium carbonate. Reproducibility of the ICP-MS, ICP-AES, and IC data are generally within 5 percent (Lamothe, P., personal communication, 2007). Two field blanks were collected to identify contamination during sampling (no significant contamination was found).

## **Resulting Data and Discussion**

### **Data Format**

The resulting data are in appendix A in a Microsoft Excel compatible spreadsheet with multiple worksheets. These worksheets have already been formatted to be print ready. Separate worksheets have the field parameters, oxygen isotopes, hydrogen isotopes (deuterium), ICP-MS, ICP-AES, and IC data. Sample identification is as follows: Red Spring = CC29, Renoux Spring = RENO1, Tiger Iron Spring = GT2, Upper Bog = UB1, and Yager Spring = YSLB, with numbers to indicate the sampling date (for example, 0408 = August 2004).

### **Spring Sampling Reliability**

In areas of diffuse seepage and in springs with very low flow (such as the Red Spring and Renoux Spring), identifying a sample point that represented active ground-water discharge to the spring was difficult. Each sampling location was selected by surveying the spring with field meters to find areas with the lowest pH and lowest dissolved oxygen. However, in times of high surface flow during the spring melt and just after heavy rain events, these springs can be dominated by interflow (lateral flow through the unsaturated soil zone). Interflow does not reach the ground-water table, but remains in the unsaturated zone (Fetter, 1994) and discharges within weeks to local springs and streams. This interflow is not considered to be representative of the ground-water flow

that feeds the springs, and it is identified by low specific conductance values and high dissolved oxygen (due to limited contact time in the subsurface).

Of the five springs, the low flows of Red Spring and Renoux Spring make them prone to the influence of interflow. This is observed in the May 2004 samples from the Red Spring, during spring snow melt, where these samples have much lower specific conductance values and higher dissolved oxygen values than any other samples. Renoux Spring does not show a great difference in specific conductance or dissolved oxygen values, but does show a large variation in temperature. This may be due to the influence of interflow or may just represent a larger component of shallow ground-water flow with varying temperature.

The Upper Bog shows possible evidence of a larger component of interflow and (or) shallow ground-water flow in the November and December 2003 samples because of low specific conductance, high dissolved oxygen, and low temperature readings. Interflow is not as likely during winter conditions and these samples may represent shallow ground-water flow. The Upper Bog is a larger area (approximately 200 square meters) than the other springs (on the order of 10 square meters) and field parameters in the Upper Bog show a variation in values at different seep locations. A piezometer installed at the edge of the Upper Bog (UBSP, Johnson and others, 2007) indicates geochemistry that is more consistent with shallow ground-water flow (higher pH, lower specific conductance, and greater dissolved oxygen). Although an effort was made to sample at the same location within the Upper Bog, assurance of consistently sampling a “deeper” ground-water component is difficult in an area with many seeps, some of which may shift in ground-water source throughout the year. The geochemistry of the November and December 2003 samples for the Upper Bog shows distinctly lower calcium and strontium values, which is generally an indicator of the deeper ground-water flow in this area (Johnson and others, 2007).

Field parameters and geochemistry for Tiger Iron Spring appear to be quite consistent and any variations appear to be due to variations in ground-water flow geochemistry. Only two samples were collected from Yager Spring, which is not sufficient to establish seasonal variations.

## **Comparison of Spring Geochemistry**

For all five springs, an average of the temporal data for representative field parameters, isotopes, and elements are presented in table 1. Anion data (sulfate and fluoride) are from IC analyses and cation data are from ICP-AES analyses. As discussed above, the data from the Red Spring in May 2004 and the data from the Upper Bog in November and December 2003 may not be representative of the more consistent ground-water flow and were not included in calculating the averages for table 1.

In comparing the five springs, Red Spring is at the highest elevation, and Yager Spring is at the lowest elevation (fig. 2). In general,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are more depleted for ground water recharged at higher elevations. Altitude can deplete  $\delta^{18}\text{O}$  by  $-0.1\text{‰}$  to  $-0.5\text{‰}$  per 100 m (Appelo and Postma, 2005). This is consistent with the data for these two springs with the higher Red Spring having slightly more depleted  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values than Yager Spring. The intermediate elevation springs are Renoux Spring, the Upper Bog, and Tiger Iron Spring, which show  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values between the Red Spring and Yager Spring. The Upper Bog and Tiger Iron Springs stand out as having the highest temperature, specific conductance, sulfate, calcium, strontium, iron, and manganese concentrations. Because they have higher temperatures, these two springs presumably are fed by ground water that has flowed to greater depths and possibly had longer rock/water interaction times. The Red Spring has the lowest concentration of sulfate and fluoride, yet it has the highest concentration of aluminum. Overall, ground-water flow to each spring represents water that

has contacted slightly different geology and the resulting rock/water interaction has produced unique geochemical signatures.

## **Seasonal Trend for Tiger Iron Spring**

Because Tiger Iron Spring had the best sampling reliability and consistently observable flow, graphs of temporal changes in element concentrations are shown only for this spring (figs. 3 and 4). Data for the other springs are listed in temporal order in appendix A. The understanding of seasonal signatures in geochemistry is important in identifying flow paths of ground water to these springs and the possible influence on ferricrete formation. However, a more detailed discussion of these processes is beyond the scope of this data report.

The temporal trends in Tiger Iron Spring for strontium, zinc, sulfate, calcium, and iron are presented because they were present in relatively high concentrations and are most representative of the overall temporal trends (data are from ICP-MS analyses, which appeared to be more consistently representative for this spring). Concentrations of sulfate, calcium and iron show similar seasonal trends, with lower concentrations occurring in August 2004. Strontium shows a reduction in concentration in May 2004 with concentrations remaining somewhat lower through the end of September 2004. Zinc concentrations show a slight reduction in early spring through summer, but are relatively unchanged throughout the year. These data appear to indicate a seasonal variation that is influenced by spring snow melt along with a late summer effect. Tiger Iron Spring is located on an alluvial fan at the base of Tiger Gulch (fig. 2). The early spring reduction in metal concentrations (seen to some degree in all elements) may be influenced by shallower ground water in the alluvial fan reaching Tiger Iron Spring soon after snow melt occurs. The delayed reduction in concentrations for iron, calcium, and sulfate may represent an intermediate depth for ground-water flow. This intermediate flow may be influenced by snow melt recharge, yet takes a longer flow path, with greater time to reach Tiger Iron Springs. The majority of the flow presumably comes from the deepest ground water that maintains the elevated temperatures and total dissolved solids (specific conductance). In this case, shallow, intermediate, and deep are all relative depths that cannot be quantified without further research.

The observations in Tiger Iron Spring are also found in the other springs (appendix A), but are more difficult to identify due to the sampling variabilities discussed above. The data from Tiger Iron Spring compare well with the observations of Johnson and others (2007) in this same general area, where iron concentrations were representative of deeper ground-water flow. Calcium, strontium, zinc, and sulfate were less conclusive in representing a distinct flow depth since these constituents were found in both shallow and deep ground water. In Tiger Iron Spring, calcium and sulfate do appear to be good indicators of deeper ground-water flow and strontium appears to be more representative of shallow ground-water flow (zinc is still less conclusive). Johnson and others (2007) concluded that barium, copper, and lead were representative of the shallowest ground-water flow. Whereas the concentrations of these elements in Tiger Iron Spring was consistently quite low, the samples in the Upper Bog from November and December 2003 were identified as possibly representing interflow and (or) more shallow ground-water flow. The Upper Bog samples had distinctly elevated barium, copper, and lead concentrations, but most other elements had lower concentrations.

## **Conclusion**

The data in this report provide temporal geochemistry from five springs in the Cement Creek watershed in San Juan County, Colorado. These temporal data: 1) demonstrate the difficulty in gathering reliable seasonal data from springs, 2) show the unique geochemistry that exists in

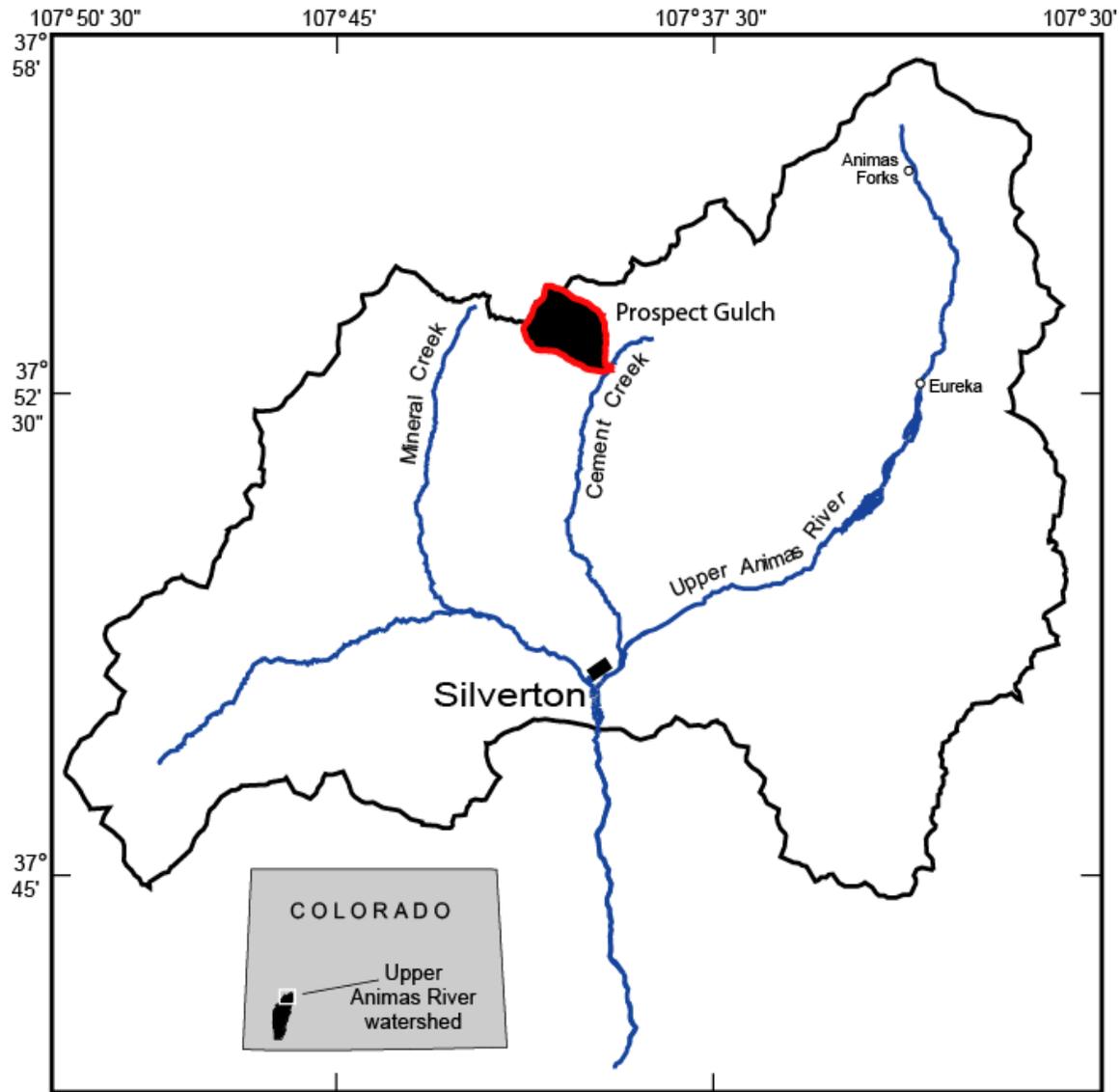
each spring due to local geology, and 3) provide evidence for a seasonal trend in geochemistry for Tiger Iron Spring. This seasonal trend with lower metal concentrations in the spring and summer may represent shallow ground-water flow to the springs initially, with a delayed response in ground water of intermediate depths reaching the spring a few months later. The majority of the geochemical signature is provided by deep ground-water flow. A similar trend may occur in the other springs, but is not as conclusive due to sampling reliability.

For future research, the data presented in this report can be used for geochemical modeling of reactions that form ferricrete within these springs. In addition, the seasonal geochemical signature will be useful in understanding the overall ground-water flow system in this area.

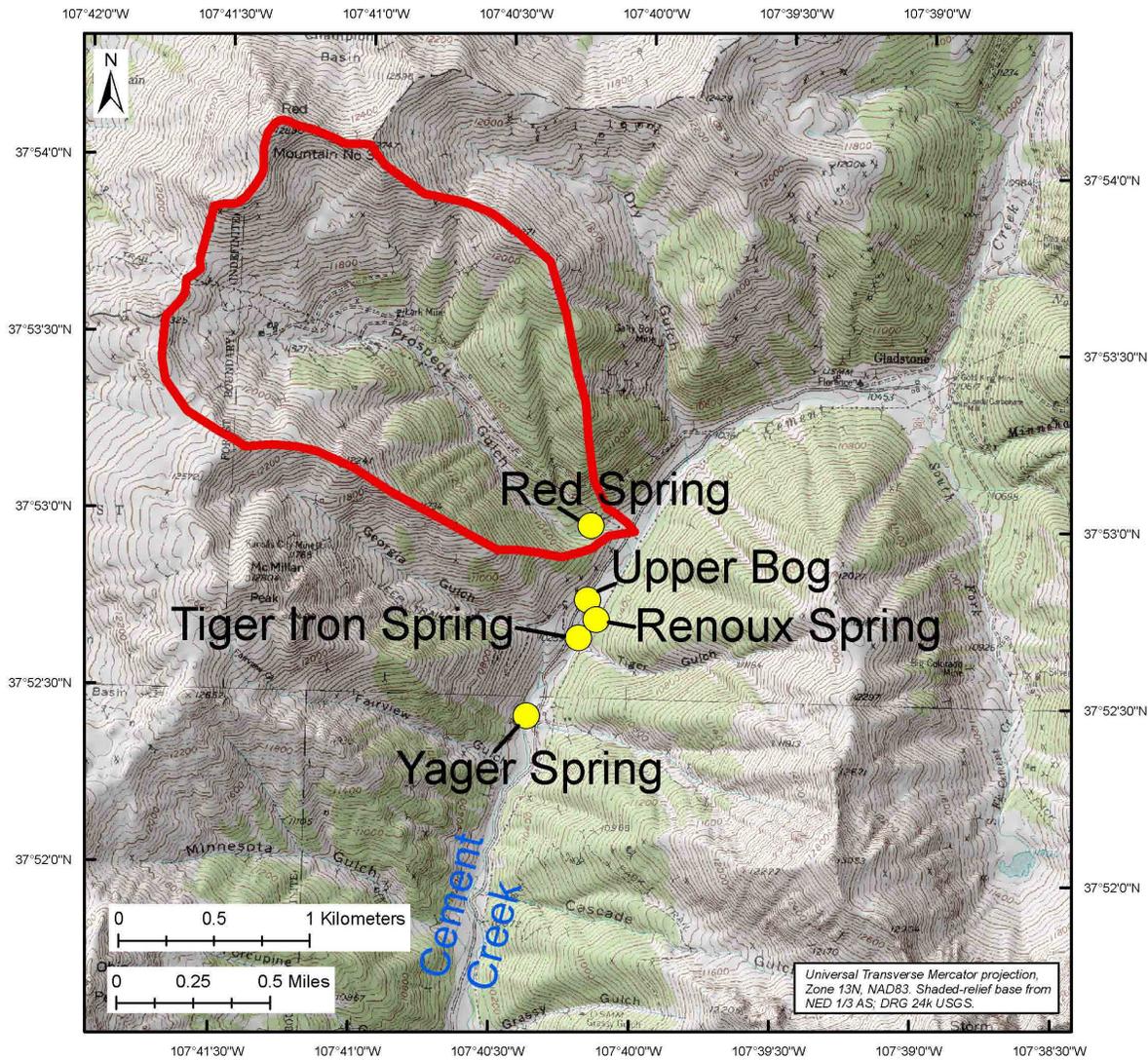
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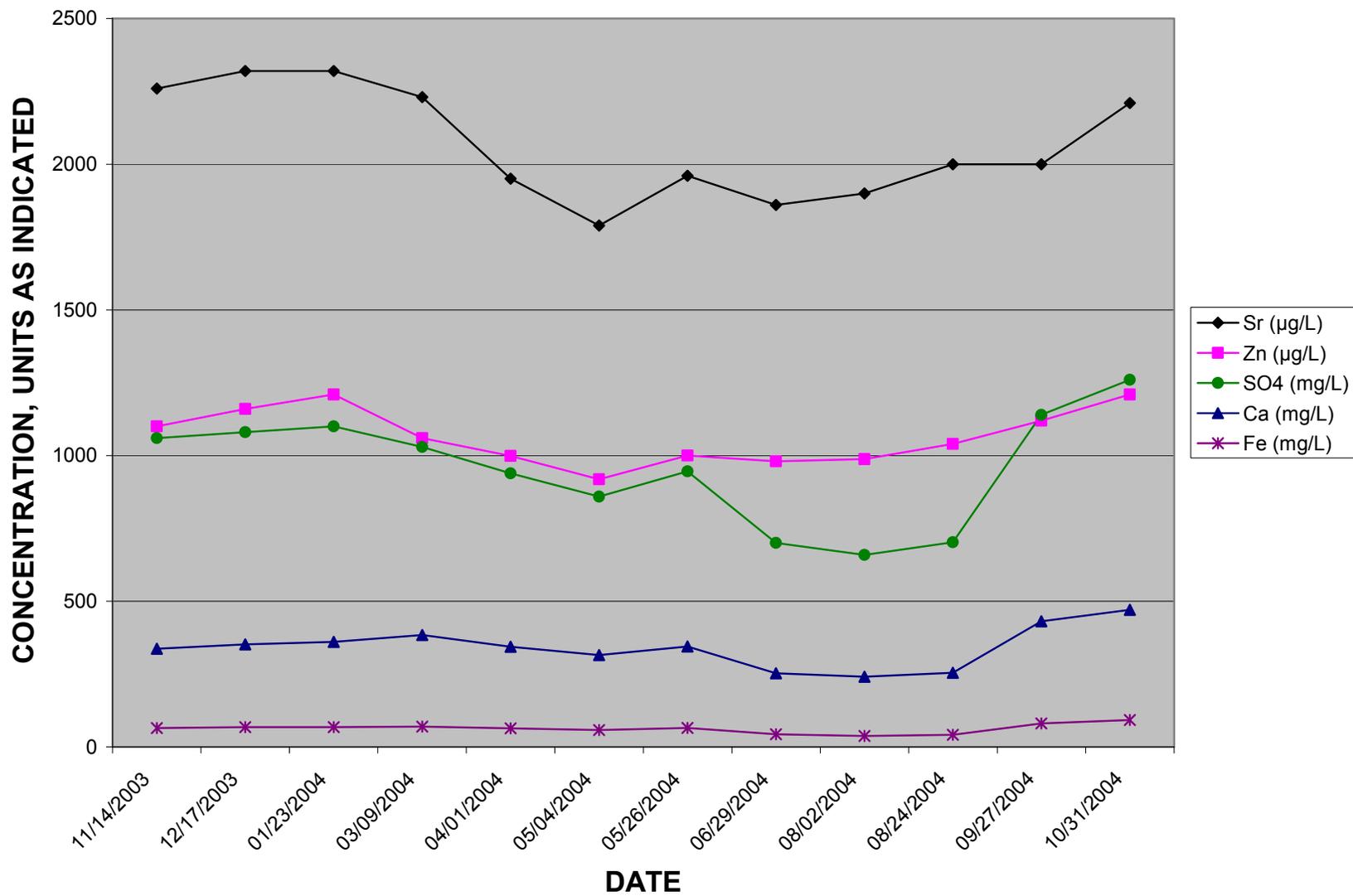
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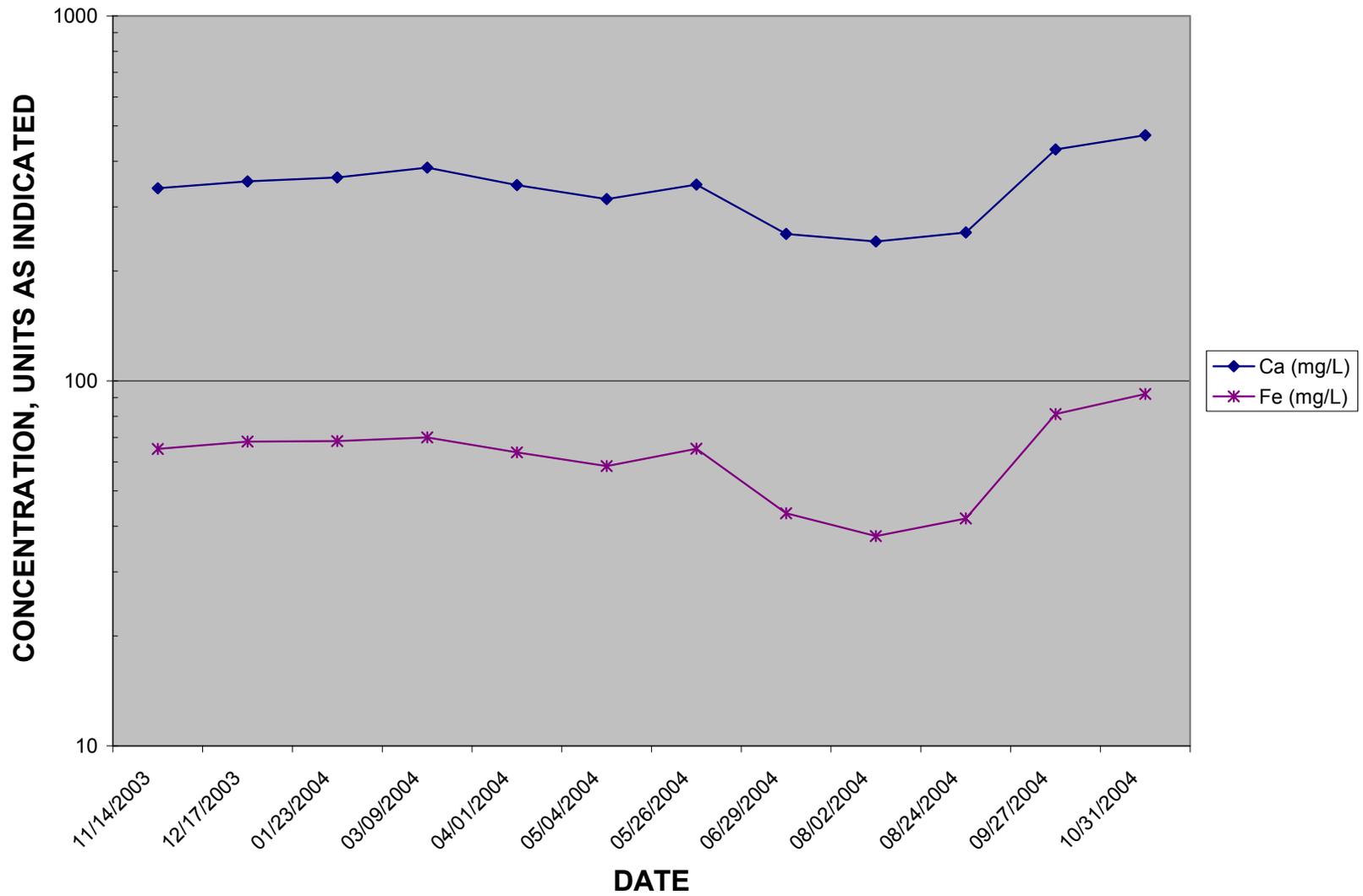
**Figure 1.** Location of the Cement Creek watershed within the upper Animas River watershed, San Juan County, Colorado. Prospect Gulch, outlined in red, is located for reference.



**Figure 2.** Location of the five sampled springs in the Cement Creek watershed. Prospect Gulch is outlined in red for reference.



**Figure 3.** Temporal concentrations of strontium, zinc, sulfate, calcium, and iron in Tiger Iron Spring.



**Figure 4.** Temporal concentrations of calcium and iron in Tiger Iron Spring. Note log scale.

**Table 1.** Comparison of geochemistry between springs.  
 [Temp. = temperature and SC = specific conductance]

Spring	SC ( $\mu\text{S}/\text{cm}$ )	pH	Temp. ( $^{\circ}\text{C}$ )	$\delta^{18}\text{O}$ (per mil)	$\delta\text{D}$ (per mil)	$\text{SO}_4$ (mg/L)	F (mg/L)	Ca (mg/L)	Sr ( $\mu\text{g}/\text{L}$ )	Fe (mg/L)	Al (mg/L)	Mn ( $\mu\text{g}/\text{L}$ )	Zn ( $\mu\text{g}/\text{L}$ )
Red Spring	582	3.66	6.1	-16.6	119	296	0.86	30	371	22.7	26.6	713	1,380
Renoux Spring	875	4.08	6.4	-16.2	118	428	1.63	144	550	25.4	6.4	697	135
Upper Bog	1,280	3.56	10.0	-16.4	118	737	1.87	208	1,480	65.3	19.2	2,010	1,640
Tiger Iron Spring	1,800	3.88	13.6	-16.2	118	1,060	2.13	358	1,980	67.6	9.9	2,860	1,260
Yager Spring	865	3.70	1.5	-15.7	114	390	1.87	142	932	26.7	10.6	964	295