



Water Chemistry of Surface Waters Affected by the Fourmile Canyon Wildfire, Colorado, 2010–2011

By R. Blaine McCleskey, Jeffrey H. Writer, and Sheila F. Murphy



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Photo caption: Fourmile Canyon fire photographed from Bear Peak, Boulder County, Colo., on September 6, 2010. Photographer, Brian A. Ebel (U.S. Geological Survey).

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Conversion Factors

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch (in.)
meter (m)	1.094	yard (yd)
kilometer	0.6214	mile (mi)
Volume		
milliliter (ml)	0.0338	ounce (oz)
liter (L)	1.057	quart (qt)
Density		
kilogram per cubic meter (kg/m ³)	0.06242	pound per cubic foot (lb/ft ³)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Abbreviations Used in This Report

°C	degrees Celsius
µm	micrometer
µS/cm	microsiemens per centimeter
meq/L	milliequivalents per liter
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
DOC	dissolved organic carbon
H ₂ SO ₄	sulfuric acid
HNO ₃	nitric acid
ICP–OES	inductively couple plasma–optical emission spectroscopy
K ₂ Cr ₂ O ₇	potassium dichromate
NTU	nephelometric turbidity units
SRWS	standard reference water sample
SUVA	specific ultraviolet absorbance
UV–254	ultraviolet absorbance at 254 nanometers

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Abstract

In September 2010, the Fourmile Canyon fire burned about 23 percent of the Fourmile Creek watershed in Boulder County, Colo. Water-quality sampling of Fourmile Creek began within a month after the wildfire to assess its effects on surface-water chemistry. Water samples were collected from five sites along Fourmile Creek (above, within, and below the burned area) monthly during base flow, twice weekly during snowmelt runoff, and at higher frequencies during storm events. Stream discharge was also monitored. Water-quality samples were collected less frequently from an additional 6 sites on Fourmile Creek, from 11 tributaries or other inputs, and from 3 sites along Boulder Creek. The pH, electrical conductivity, temperature, specific ultraviolet absorbance, total suspended solids, and concentrations (dissolved and total) of major cations (calcium, magnesium, sodium, and potassium), anions (chloride, sulfate, alkalinity, fluoride, and bromide), nutrients (nitrate, ammonium, and phosphorus), trace metals (aluminum, arsenic, boron, barium, beryllium, cadmium, cobalt, chromium, copper, iron, mercury, lithium, manganese, molybdenum, nickel, lead, rubidium, antimony, selenium, strontium, vanadium, and zinc), and dissolved organic carbon are here reported for 436 samples collected during 2010 and 2011.

Introduction

The Fourmile Canyon fire burned more than 26 square kilometers and destroyed more than 160 homes in Boulder County, Colorado, in September 2010 (U.S. Department of Agriculture Forest Service, 2011). This wildfire burned mostly within the Fourmile Creek watershed; about 23 percent of this watershed was burned (fig. 1). The Fourmile Creek watershed is 63.2 square kilometers in area and ranges in elevation from 1,746 to 3,515 meters, with a mean elevation of 2,435 meters. Fourmile Creek discharges to Boulder Creek about 3 kilometers upstream from the city of Boulder, Colorado. Stream discharge is dominated by snowmelt in the spring and transient high flows during summer convective storms. Base-flow conditions occur in the fall and winter months. The Fourmile Creek watershed is similar in climate, topography, and geology to many other Colorado Front Range watersheds. Although these forested montane watersheds are periodically subject to wildfire, limited information exists on postwildfire effects on surface-water quality.

An investigation was initiated less than one month after the Fourmile Canyon fire to better understand how wildfire affects surface-water quality. Water-quality samples were collected monthly during base-flow conditions, biweekly during spring snowmelt, and at frequent intervals (20 minutes to 4 hours) during selected storm events. The purpose of this report is to (1) provide water-quality data collected primarily during the 2011 water year, (2) describe the methods used to collect and analyze the samples, (3) describe quality-control procedures, and (4) supplement interpretive reports (Murphy and others, 2012; Writer and others, 2012).

Sample Locations

Primary monitoring sites on Fourmile Creek are two sites upstream of the burned area (FCCR and FCLG), two sites within the burned area (FCWM and FCLM), and one site downstream of the burned area (FCBC) (figure 1, table 1). Samples were collected from 6 additional sites on Fourmile Creek, 3 sites on Boulder Creek (2 upstream and 1 downstream of the Fourmile Creek confluence), and 11 tributaries or other contributors to Fourmile Creek (table 1).

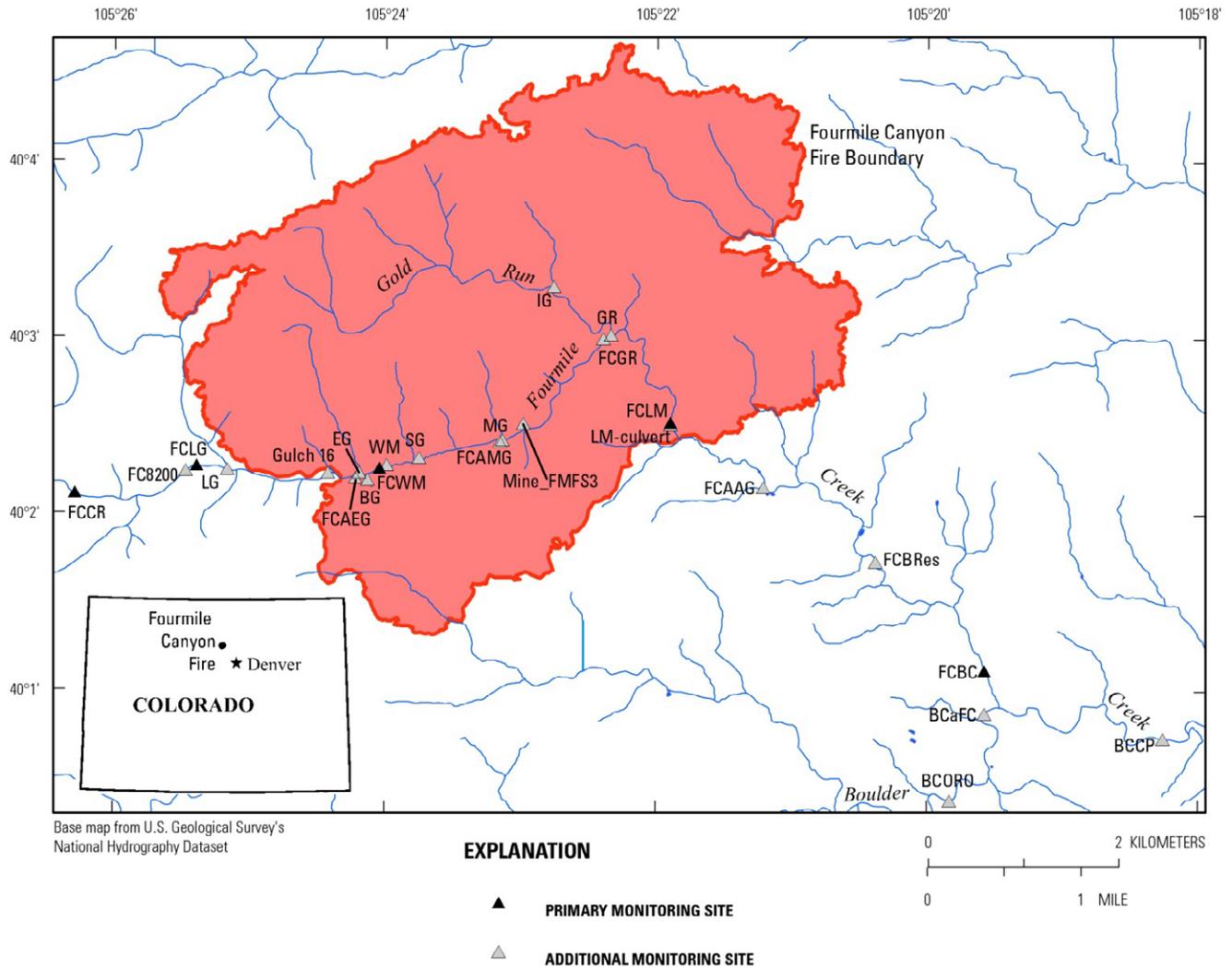


Figure 1. Sites in Fourmile Creek watershed, Colo., sampled for this report.

Table 1. Sample site locations, Fourmile Creek watershed, Colo.

[Sample sites listed upstream to downstream within categories. ID, identifier; m, meter]

Location ID	Site name	Latitude	Longitude	Elevation (m)
Primary monitoring sites				
FCCR	Fourmile Creek at Copper Rock	40.03526	-105.43811	2,256
FCLG	Fourmile Creek upstream of Long Gulch	40.03788	-105.42320	2,210
FCWM	Fourmile Creek upstream of Wood Mine	40.03766	-105.40068	2,120
FCLM*	Fourmile Creek upstream of Logan Mill Road	40.04203	-105.36492	1,935
FCBC	Fourmile Creek upstream of Boulder Creek	40.01861	-105.32631	1,760
Other monitoring sites on Fourmile Creek or Boulder Creek				
FC8200	Fourmile Creek near 8200 Fourmile Canyon Drive	40.03738	-105.42451	2,207
FCAEG	Fourmile Creek upstream of Emerson Gulch	40.03675	-105.40368	2,131
FCAMG	Fourmile Creek upstream of Melvina Gulch	40.04019	-105.38591	2,072
FCGR	Fourmile Creek upstream of Gold Run	40.04994	-105.37323	2,108
FCAAG	Fourmile Creek upstream of Arkansas Gulch	40.03592	-105.35351	1,882
FCBRes	Fourmile Creek downstream of reservoir	40.02889	-105.33970	1,816
BCORO	Boulder Creek at Orodell	40.00639	-105.33053	1,794
BCaFC	Boulder Creek upstream of Fourmile Creek	40.01458	-105.32629	1,750
BCCP	Boulder Creek at 100 Canon Park	40.01228	-105.30437	1,689
Monitoring sites on tributaries or other water sources				
LG	Long Gulch	40.03754	-105.41942	2,216
Gulch 16	Culvert at Emerson Gulch Road and Fourmile Creek	40.03722	-105.40701	2,149
EG	Emerson Gulch	40.03721	-105.40318	2,131
BG	“Banana” Gulch	40.03657	-105.40216	2,139
WM	Discharge from Wood Mine	40.03796	-105.39981	2,135
SG	Schoolhouse Gulch	40.03863	-105.39586	2,105
MG	Melvina Gulch	40.04036	-105.38558	2,071
Mine_ FMFS3	Mine discharging across from Fourmile fire station 3	40.04192	-105.38303	2,076
IG	Ingram Gulch (tributary to Gold Run)	40.05485	-105.37930	2,108
GR	Gold Run	40.05030	-105.37230	2,011
LM -culvert	Culvert downstream of Logan Mill Road	40.04181	-105.36493	1,934

* October 2010 samples collected approximately 20 meters downstream (downstream of Logan Mill Road).

Methods

Field Methods

Stream Discharge

Stream discharge was periodically measured with a pygmy meter using standard U.S. Geological Survey protocols (Rantz and others, 1982). Stream discharge at two sites (FCBC and FCLM) was obtained from U.S. Geological Survey stream-gaging stations (06727500 and 06727410; U.S. Geological Survey, 2011), which operated from April 1 to September 30, 2011. Vented water level loggers (Global Water, model WL16U) were deployed to monitor stage at sites FCCR and FCWM and at FCLM and FCBC before installation of streamgages. Before deployment, the water level loggers were calibrated by measuring instrument response at 0.10-meter intervals for water depths from 0 to 1.1 meter. The water level loggers were contained within 1.5-meter-long sections of 5-centimeter-diameter perforated polyvinyl chloride pipe anchored to the streambed with rebar. Data were downloaded from the loggers at approximately 30-day intervals. Discharge measurements and stage were used to generate a rating curve for each site and subsequently to estimate stream discharge at each monitoring site during the course of the study.

Collection of Water-Quality Samples

Grab samples were collected monthly during base-flow conditions and biweekly during snowmelt runoff. Electrical conductivity (Amber Science, Model 2052) and pH and temperature (Orion, 3-Star pH/temperature meter) were measured in the field. Water samples were collected in precleaned 1-liter (L) Teflon[®] bottles and returned immediately (within 4 hours) to the U.S. Geological Survey National Research Program laboratory in Boulder, Colo., for filtering, preservation, and measurement of turbidity. Samples were collected at more frequent intervals (between 20 minutes and 4 hours) during and after precipitation events by using automatic samplers (ISCO, models 6700 and 6712), which contained precleaned 1-L polyethylene sampling bottles. Within 24 hours of sample collection, samples were removed from the automatic sampler and delivered to the U.S. Geological Survey National Research Program laboratory in Boulder, Colo., where electrical conductivity and turbidity were measured and samples were filtered, split, and preserved within 48 hours according to U.S. Geological Survey water-quality sampling and measurement techniques (U.S. Geological Survey, 2012a).

Laboratory Methods

All laboratory measurements were made at the U.S. Geological Survey National Research Program laboratory in Boulder, Colo. All reagents were equal to reagent-grade standards of the American Chemical Society or higher purity. Deionized water and redistilled or trace-metal-grade acids were used in all preparations. Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. Detection limits were equal to three times the standard deviation of several dozen measurements of the constituent in a blank solution analyzed as a sample. Estimated precision values were for analyte concentrations greater than 10 times the detection limit and were based on multiple determinations of a laboratory standard or U.S. Geological Survey standard reference water samples (SRWS). Details on the instrumentation, techniques, general conditions, and variants from standard procedures are discussed in following sections.

Filtration and Preservation

Samples were processed by filtration under pressure (nitrogen, less than 140 kilopascals) in a 500-milliliter (mL) Teflon[®] column through a 0.4-micrometer (µm) membrane filter, unless otherwise noted in electronic database. Types of sample splits collected, constituents determined in each split, and sample treatments are provided in table 2. Processed water was collected in precleaned separate bottles: 125-mL high-density polyethylene bottles for cations and anions, 40-mL amber glass vials (heated to 500°C for 4 hours) for dissolved organic carbon (DOC) and specific ultraviolet (UV)-absorbance at 254 nanometers (UV-254), 20-mL glass bottles for ammonium, and for a small number of samples, 125-mL glass for mercury (table 2). For quality assurance, approximately 10 percent of the processed samples were replicates and blank samples. Cation (filtered-acidified HNO₃) samples were preserved with 1 percent (volume per volume) concentrated trace-metal grade HNO₃. Anion, DOC, and UV-254 samples were refrigerated at 4°C until analysis (within 2 weeks), and ammonia samples preserved with 1 percent (volume per volume) concentrated trace-metal grade H₂SO₄ and refrigerated at 4°C until analysis. A subset of 67 unfiltered samples were acidified with 1 percent (volume per volume) concentrated trace-metal grade HNO₃ (unfiltered-acidified HNO₃) to determine total recoverable cations.

Table 2. Sample-split preservation, constituents, and sample treatment, Fourmile Creek, Colo., postfire water samples.

[DOC, dissolved organic carbon; FA, filtered-acidified; FU, filtered, unacidified; HNO₃, nitric acid; H₂SO₄, sulfuric acid; K₂Cr₂O₇, potassium dichromate; RA, unfiltered-acidified; v/v, volume per volume; °C, degrees Celsius]

Sample-split preservation	Constituent	Sample treatment
RA - HNO ₃	Total recoverable major cations and trace metals	Unfiltered, 1 percent (v/v) concentrated trace-metal grade HNO ₃ added; samples not chilled.
FA - HNO ₃	Dissolved major cations and trace metals	Filtered, 1 percent (v/v) concentrated trace-metal grade HNO ₃ added; samples not chilled.
FU	Anions and alkalinity	Filtered, no preservation added; chilled at 4°C.
FA - H ₂ SO ₄	Ammonium	Filtered, 1 percent (v/v) 1:9 H ₂ SO ₄ added; chilled at 4°C.
DOC	Dissolved organic carbon and specific ultraviolet absorption	Filtered, no preservation added; chilled at 4°C.
FA - HNO ₃ , K ₂ Cr ₂ O ₇	Total dissolved mercury	Filtered, 4 percent (v/v) concentrated redistilled HNO ₃ and 0.04 percent (w/v) K ₂ Cr ₂ O ₇ added; samples not chilled.

Turbidity and Total Suspended Solids

Turbidity of unfiltered samples was measured within 4 hours of collection for grab samples and 48 hours of collection for automatic-sampler samples by using a HACH 2100Q portable turbidimeter, which is capable of measuring turbidity from 0 to 1,000 nephelometric turbidity units (NTU). The turbidimeter was calibrated with 20, 100, and 800 NTU formazin standards. Samples were inverted three times and turbidity was recorded immediately. If the sample exceeded 1,000 NTU, it was diluted with deionized water, agitated, and analyzed. Total suspended solids were measured for a subset of

samples. Masses of filters and sample bottles containing water samples were recorded before filtration. Samples were agitated and a portion of each sample was poured into a filtration column. After each sample was filtered, the sample bottle and any remaining sample not filtered were weighed. Filters were dried for 1 to 2 hours at 105°C, allowed to cool, and then weighed. Total suspended solids was calculated from the mass on the filter and the mass of sample passed through the filter. The volume of sample passed through the filter was determined by converting the mass of sample filtered to a volume by assuming a density of 1 milligram per liter (mg/L). Samples with large amounts of sediment may have densities greater than 1 mg/L, but the maximum error using this approach was determined to be less than 7 percent.

Major Cation, Trace Metal, Ammonium, and Mercury Determinations

Concentrations of total recoverable metals (unfiltered-acidified HNO₃) and dissolved major cations and trace metals (filtered-acidified HNO₃) were determined using inductively coupled plasma–optical emission spectrometry (ICP–OES, PerkinElmer 7300 DV). All cations and trace metals, except for potassium, were determined by using the axial plasma viewing orientation. The radial plasma viewing orientation was used for potassium. A cesium chloride ionization buffer was added in-line before sample nebulization to suppress the ionization of potassium and lithium in the plasma. Before ICP–OES analysis, the unfiltered-acidified HNO₃ sample splits were filtered through a 25-millimeter (mm)-diameter syringe filter (0.45-micrometer (µm) Supor Membrane, PALL). The ICP–OES method detection limits are reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet.

Concentrations of ammonium (filtered-acidified H₂SO₄) were determined by ion chromatography (Dionex DX 300) with suppressed electrical conductivity detection. An IonPac AS12A Analytical Column (4 millimeter (mm)), AG12A Guard Column, and a Cation Self-Regenerating Suppressor (CSRS 300 (4 mm)) were used. A gradient pump was used to pump sulfuric acid (H₂SO₄) eluent through the system. The method detection limit was 0.04 milligrams per liter (mg/L), a value that is also reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet.

Total dissolved mercury (Hg) concentrations (filtered-acidified HNO₃/K₂Cr₂O₇) for a subset of samples were determined by direct cold-vapor atomic fluorescence spectroscopy following oxidation with chromate and reduction by stannous chloride (Roth and others, 2001). The method detection limit was 0.4 nanograms per liter; it is also reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet.

Anion and Alkalinity Determinations

Concentrations of bromide, chloride, fluoride, nitrate, and sulfate were determined by ion chromatography (Dionex DX 600) with suppressed electrical conductivity detection (Brinton and others, 1995). An IonPac AS18 Analytical Column (4 mm), AG18 Guard Column, and an Anion Self-Regenerating Suppressor (ASRS ULTRA II (4 mm)) were used. Thirty-millimolar sodium hydroxide (NaOH) eluent was pumped through the columns at 1 milliliter per minute. Analytical errors for these constituents are typically less than 5 percent. The ion chromatography method detection limits are reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet.

Alkalinity was determined by automated titration (Thermo, 940-960 autotitrator) by using standardized sulfuric acid (Barringer and Johnsson, 1996). Fifteen milliliters of sample was titrated with 0.01 normal (N) sulfuric acid to the bicarbonate end-point. The analytical error in alkalinity concentrations is less than 3 percent. The alkalinity method detection limit is reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet.

Dissolved Organic Carbon and Specific Ultraviolet Absorption Determinations

Dissolved organic carbon (DOC) concentrations were measured by using the wet oxidation method (Aiken, 1992) with an Oceanography International Model 700 TOC Analyzer. Potassium biphthalate was used to calibrate the instrument, and sodium benzoate was used as a different organic carbon source to check the calibration. The absorbance was measured at 254 nanometers (UV-254) by a Hewlett-Packard model 8452A diode array spectrometer. The method detection limit for DOC and UV-254 was 0.4 mg/L and 0.001 per centimeter, respectively, and are reported in the accompanying Microsoft Excel spreadsheet in the Analytical worksheet. Specific ultraviolet absorption (SUVA) was determined by dividing the UV-254 absorbance by the DOC concentration (Weishaar and others, 2003).

Quality Assurance and Quality Control

Several techniques were used to assure the quality of the ionic analytical data. These techniques included calculation of charge imbalance, electrical conductivity imbalance, analysis of U.S. Geological Survey SRWS, analysis of blanks, and analysis of replicate samples.

The charge-imbalance calculation is a common quality-assurance/quality-control procedure to check the accuracy of a water analysis (American Public Health Association, 1971). For samples that were analyzed for major cations and anions, the accuracy of the analyses were checked for charge imbalance using the geochemical code WATEQ4F (Ball and Nordstrom, 1991). WATEQ4F uses equation 1 to calculate charge imbalance:

$$\text{Charge imbalance (percent)} = \frac{100 \times (\text{sum cations} - \text{sum anions})}{(\text{sum cations} + \text{sum anions}) \div 2} \quad (1)$$

where sum cations and sum anions are in milliequivalents per liter (meq/L). The charge balance calculation is discussed in more detail by Ball and others (2006). However, charge imbalance does not indicate whether the error is caused by a cation or an anion. Therefore, a second constraint is needed to identify the constituent most likely in error. By coupling charge imbalance and electrical conductivity imbalance, the measurement most likely in error can be identified or narrowed down to a few possibilities (McCleskey and others, 2012). This approach led to several reanalyses and identification of transcription errors.

The charge imbalance, sum cations (meq/L), and sum anions (meq/L) are reported for all samples having major cation and anion determinations. For samples not having a measured pH, a value of 7.7 (the median pH of all Fourmile Creek samples) was used to calculate charge imbalance. A frequency plot of charge imbalance for all samples with complete analyses is shown in figure 2. The mean charge imbalance is 0.6 percent with a standard deviation of 3.6 percent, and the range was -13.9 to 13.7 percent. Analyses having a charge imbalance less than ± 10 percent are considered reliable for speciation calculations (Nordstrom and Munoz, 1994). Seven sample analyses out of 436 had a charge imbalance greater than ± 10 percent. A plot of electrical conductivity imbalance against charge imbalance for all samples shows that the electrical conductivity imbalance was within ± 10 percent for all but seven samples (fig. 3).

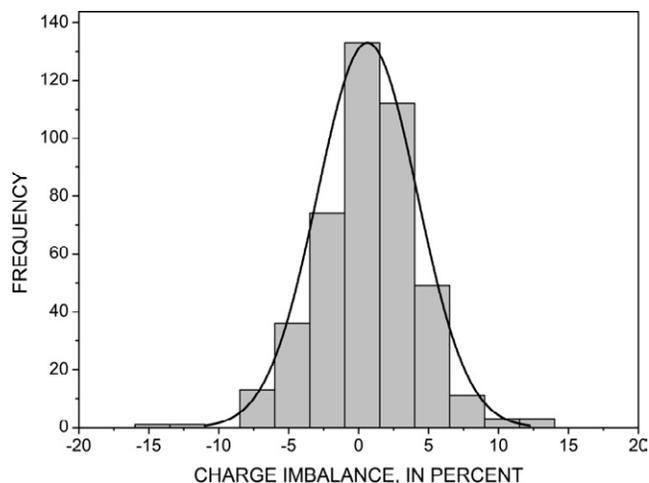


Figure 2. Frequency distribution of charge imbalance in Fourmile Creek, Colo., postfire water samples having major cation and anion determinations.

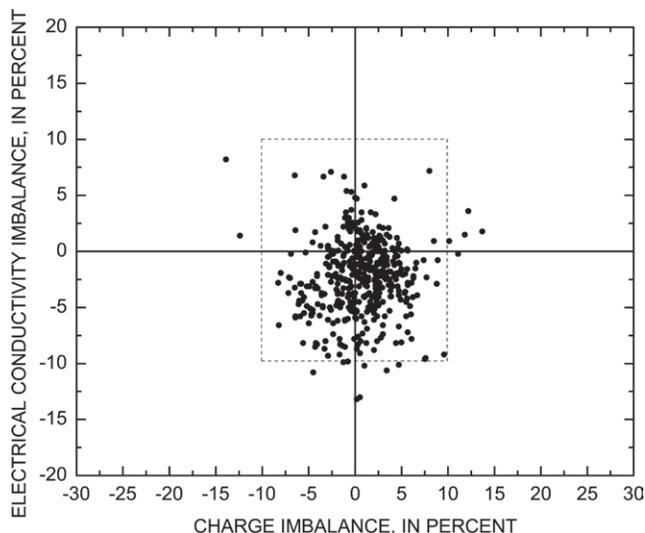


Figure 3. Electrical conductivity imbalance compared with charge imbalance, Fourmile Creek, Colo., postfire water samples.

U.S. Geological Survey SRWS (U.S. Geological Survey, 2012b) were analyzed as unknowns several times during each analytical run to check for accuracy. Standard reference water samples M186, M188, M196, M198, N104, N107, N108, N109, N110, T197, T201, T203, and T205 were used to check the analytical methods for major and trace metals, ammonium, and anions. The SRWSs were analyzed several times during each analytical run. For each SRWS constituent, the analytical result, the most probable value, and the percentage difference are presented in the accompanying Microsoft Excel spreadsheet in the SRWS worksheet.

Water analyses are reported for 22 blanks in the Blanks worksheet in the accompanying Microsoft Excel spreadsheet. Eighteen blanks were process blanks where deionized water was filtered and preserved in the same manner as the samples. Constituents were below detection in almost all

blanks. Chloride was detected in 10 blanks (highest concentration, 0.8 mg/L), most likely because the filter apparatus had been washed with hydrochloric acid. Sulfate was detected in 10 blanks (highest concentration, 1.4 mg/L) most likely because of small amounts of contamination within the ion chromatography columns. Dissolved organic carbon was detected in five blanks (highest concentration, 0.5 mg/L), most likely because of organic carbon in the deionized blank water. In addition, four blanks (12FW 101–104) were specifically run to determine if any DOC had been leached from the ISCO and Teflon bottles used to collect samples in the field. For these blanks, deionized water was left in sample bottles for 48 hours before filtering; in each of the blanks the DOC concentrations were below or at the method detection limit.

Several duplicate samples (Site ID column, -DUP) were collected and analyzed and are reported in the Water Chemistry worksheet in the accompanying Microsoft Excel spreadsheet. For analytes with concentrations greater than 20 times the detection limit, the average difference was –0.6 percent with a standard deviation of 4. The worst agreement was for a couple of low-level sulfate and nitrate duplicate samples. Overall, the agreement between duplicate samples is acceptable to very good.

Digital Data Contents

The Microsoft Excel data file accompanying this report contains five worksheets: locations, water-chemistry data, analytical details, and standard reference water sample.

Water Chemistry Worksheet

The Water Chemistry worksheet (appendix 1) contains the following information for each of the water-quality samples: location ID, site description, sample ID, collection date and time, filtration information, type (grab or ISCO), discharge, electrical conductivity (EC), pH, temperature, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), alkalinity (as bicarbonate, HCO_3), sulfate (SO_4), chloride (Cl), fluoride (F), bromide (Br), silica (SiO_2), ammonium (NH_4), nitrate (NO_3), phosphorus (P), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), rubidium (Rb), antimony (Sb), selenium (Se), strontium (Sr), vanadium (V), zinc (Zn), dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA), absorbance at 254 nanometers (UV–254), turbidity, total suspended solids, sum cation, sum anions, speciated charge imbalance, and electrical conductivity imbalance. Duplicate samples are labeled -DUP in the location ID column, and total recoverable samples are labeled TR in the sample ID column.

Analytical Worksheet

The Analytical worksheet (appendix 2) contains the following analytical information: constituent, analytical technique, detection limit, typical relative standard deviation (RSD), analytical wavelength, and plasma view orientation.

Standard Reference Water Sample (SRWS) Worksheet

The Standard Reference Water Sample (SRWS) tab (appendix 3) contains the following summary information for the U.S. Geological Survey SRWS analyzed as part of this study: constituent, analytical method, U.S. Geological Survey SRWS, number of analyses (n), mean concentration measured, relative standard deviation (RSD), reported most probable value and range (\pm), and the percent difference between the measured value and the most probable value.

Blanks Worksheet

The Blanks tab (appendix 4) contains the following summary information for field and laboratory blanks: sample type, sample ID, collection date, filtration information, Ca, Mg, Na, K, alkalinity (HCO₃), SO₄, Cl, F, Br, SiO₂, NH₄, NO₃, P, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, V, Zn, DOC, SUVA, and UV-254.

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