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Natural Resource Stewardship and Science

Evaluation of Quality-Control Data and Quality Assurance for Routine Water Quality Monitoring

Bryce Canyon, Capitol Reef, and Zion National Parks, Water Years 2006–2013

Natural Resource Report NPS/NCPN/NRR—2016/1154



ON THE COVER

Taking a flow measurement, Oak Creek, Capitol Reef National Park. NPS photo.

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Prepared by
Rebecca H. Weissinger
Northern Colorado Plateau Network
National Park Service
P.O. Box 848
Moab, UT 84532

Editing and Design
Alice Wondrak Biel
Northern Colorado Plateau Network
National Park Service
P.O. Box 848
Moab, UT 84532

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Executive Summary

To track long-term trends in water quality of stream water at Bryce Canyon, Capitol Reef, and Zion national parks, the Northern Colorado Plateau Network submits monthly water-quality samples to the Utah Public Health Laboratory (in cooperation with the Utah Division of Water Quality). Water-quality sampling began in September 2005. Quality-assurance procedures and quality-control samples are essential for determining the quality of data and our ability to use those data for trend analysis.

The majority of water-quality data reported from WY2006 to WY2013 met data-quality objectives for long-term trend monitoring. Variability in sulfate, total suspended solids, Kjeldahl nitrogen, and dissolved nitrite + nitrate was higher than expected, and may affect our ability to detect temporal trends in these constituents. A low bias for sulfate and sum of anions, and a high bias for total dissolved solids, seen from 2011 to 2013, could cause spurious short-term trends in the data. In addition, because of potential bias in sample handling, it is recommended that total suspended solids not be used for trend analyses.

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1 Introduction

1.1 Background

The overall mission of the National Park Service (NPS) is "to conserve the scenery, natural and historic objects, and wild life in the System units and to provide for the enjoyment of the scenery, natural and historic objects, and wild life in such manner and by such means as will leave them unimpaired for the enjoyment of future generations" (54 USC §100101). Maintaining unimpaired water quality is a high priority for park managers. The Northern Colorado Plateau Network (NCPN) is charged with tracking indicators of park ecosystem health, including water quality, at 16 park sites in Utah, Colorado, Wyoming, and Arizona. NCPN staff began routinely collecting water-quality data in September 2005, as part of an initiative to provide long-term monitoring of natural resources for parks.

The purpose of NCPN's water-quality program can be framed in a series of general questions that can be answered quantitatively via the following measurable objectives.

1. What are existing ranges in water-quality parameters within selected waters of NCPN parks?
2. What are the status and long-term trends in selected water-quality parameters at selected sites on selected NCPN water bodies?
3. Are selected NCPN water bodies in compliance with beneficial uses designated by state regulations?

Quality-assessment plans are essential for documenting the quality of environmental data. The NCPN published a quality-assessment plan as part of its water-quality monitoring protocol (Thoma et al. 2009). Quality assessment includes both quality control (QC) and quality assurance (QA) practices.

QC samples are collected to quantify the bias and variability in water-quality measurements introduced by field and laboratory methods, as compared to environmental factors (Pirkey and Glodt 1998). Bias is a consistent deviation from a true value over time. Field blanks are typically used to evaluate bias introduced by contamination of samples during collection, processing, and analysis. Bias introduced by analytical equipment or procedures can be assessed through proficiency testing of reference samples of known concentrations. Variability, as used in this report, is random error introduced by analytical or field procedures or by natural variation in the stream. Replicate samples are used to evaluate variability.

QA procedures are used to evaluate water-quality data for internal consistency and consistency over time. Procedures include checks that determine whether individual samples are compatible with chemical constraints. For instance, such checks might ensure that samples are neutrally charged, or that dissolved concentrations are lower than total concentrations (Friedman and Erdmann 1983; Hem 1985). QA procedures also require network staff to review the history of results for each site and parameter to identify unusual values. QA procedures are also useful for identifying outliers and potential errors in the dataset, such as reporting errors or mislabeling of sample bottles.

1.2 Purpose and scope

The purpose of this report is to describe the data quality for major constituents, nutrients, and trace elements in stream samples collected by the NCPN water-quality monitoring program at Bryce Canyon, Capitol Reef, and Zion national parks during water years (WY) 2006–2013 (Table 1-1, Figure 1-1; figures begin on page 4). Water-quality samples were collected approximately monthly. Some sites were sampled every year, while others were sampled on a rotating panel of two years of sampling followed by 2–5 years of rest. Monitoring was conducted at three sites at Bryce Canyon National Park (NP; Figure 1-2), five sites at Capitol Reef NP (Figure 1-3), and three sites at Zion NP (Figure 1-4).

Data collected during WY2006–2013 included major constituents, nutrients, and trace elements for 580 water-quality samples and 58 QC replicate samples. No blanks were collected during the study period. QA review procedures included the following:

Table 1-1. NCPN water-quality monitoring locations at Bryce Canyon, Capitol Reef, and Zion national parks, WY2006–2013.

Park[1]	STORET ID	STORET Station Name	Panel[2]	Established	End Date
BRCA	4951855	Sheep Ck bl Spring in Bryce Cyn NP	A	9/30/2005	Ongoing
BRCA	4951857	Yellow Ck bl Spring in Bryce Cyn NP	R	11/15/2005	Ongoing
BRCA	4951915	Mossy Cave Spring NW of Tropic	R	7/23/2008	Ongoing
CARE	4954770	Sulphur Ck ab Cnfl/Fremont R in Picnic Area	R	7/22/2008	Ongoing
CARE	4954775	Sulphur Ck bl road to Goosenecks Overlook In CRNP	R	7/22/2008	Ongoing
CARE	4954780	Pleasant Ck S of Sleeping Rainbow Ranch	R	7/22/2008	Ongoing
CARE	4954795	Oak Creek above Sands Ranch Dam	R	10/27/2010	Ongoing
CARE	4954812	Halls Ck bl Narrows	R	11/20/2005	Ongoing
ZION	4950800	La Verkin Ck at Lee Pass Trail	A	9/29/2005	Ongoing
ZION	4950920	North Ck at planned gage in park	A	11/17/2005	Ongoing
ZION	4951260	North Fk Virgin R at North Fork Rd	A	11/17/2005	6/20/2008[3]
ZION	4951265	N Fk Virgin R at WSA bndry	A	7/24/2008	Ongoing

[1] BRCA=Bryce Canyon NP; CARE=Capitol Reef NP; ZION=Zion NP

[2] A=annual; R=rotating

[3] Site discontinued to move sampling location downstream of potential development.

- performing a charge-balance analysis of major ions,
- plotting analyte concentrations over time,
- performing an outlier analysis, and
- comparing relative concentrations of related analytes, such as total and dissolved phosphorus.

Environmental and QC samples were submitted to the Utah Public Health Laboratory in Taylorsville, Utah. Constituents measured during the WY2006–2013 study period were:

- Major constituents: alkalinity, calcium, chloride, magnesium, potassium, sodium, sulfate, total dissolved solids (TDS), total suspended solids (TSS),
- Nutrients: ammonia, Kjeldahl nitrogen, dissolved nitrate + nitrite, total nitrate + nitrite, dissolved phosphorus, total phosphorus,
- Trace elements: aluminum, arsenic, barium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc.

Additional calculated values, such as hardness and bicarbonate, were included in results provided by the laboratory, but calculated values were not evaluated for this report. Measurements from replicate samples were used to assess variability by calculating the relative percent difference (RPD) between samples. Data used for testing laboratory proficiency, and charge-balance calculations based on major ions, were plotted over time to assess bias and variability in analytical results. For each site and constituent, individual results were compared to the range of concentrations over time. Outlier concentrations that fell outside of three standard deviations of the mean were further evaluated for potential errors.

1.3 Sample-collection methods

Sample-collection methods are documented in the NCPN water-quality monitoring protocol (Thoma et al. 2009). During each sampling event, streamflow measurements were made using an AquaCalc Pro™ and Pygmy meter, a Sontek Flowtracker™ acoustic Doppler velocity meter, an 8" Baski cut-throat flume, or a portable v-notch weir, as appropriate. Water temperature, pH, specific conductance, and dissolved oxygen were measured in the field using a field-calibrated In-Situ TROLL™ 9000 or 9500 multiparameter water-quality probe. Turbidity was measured in the field using a calibrated Hach

2100P™ turbidimeter. Fecal indicator bacteria (*Escherichia coli*) samples were collected, held on ice, and processed within eight hours using the IDEXX Colilert 2000™ method (IDEXX undated).

Water-quality grab samples were collected just below the surface, near the center of the channel, in a well-mixed portion of the stream. Samples consisted of (1) an unfiltered sample for alkalinity, TDS, TSS, and anions (unpreserved) and (2) an unfiltered and acidified sample for nutrients (preserved with sulfuric acid), processed stream-side. A bulk sample was collected and processed into two aliquots (subsamples) within five hours: a 0.45-µm, filtered and acidified aliquot for dissolved nutrients (preserved with sulfuric acid), and a 0.45-µm, filtered and acidified aliquot for dissolved metals (preserved with nitric acid). Samples were kept on ice and shipped to the Utah Public Health Laboratory within five days of sample collection.

From September 2006 to September 2011, water-quality samples were collected monthly at all sites. From October 2011 to October 2013, due to budget constraints, samples were collected monthly for 10 months of the year, with only one sample collected during the winter months of December–February. Gaps in data collection occurred during May 2011–August 2011, due to staff turnover.

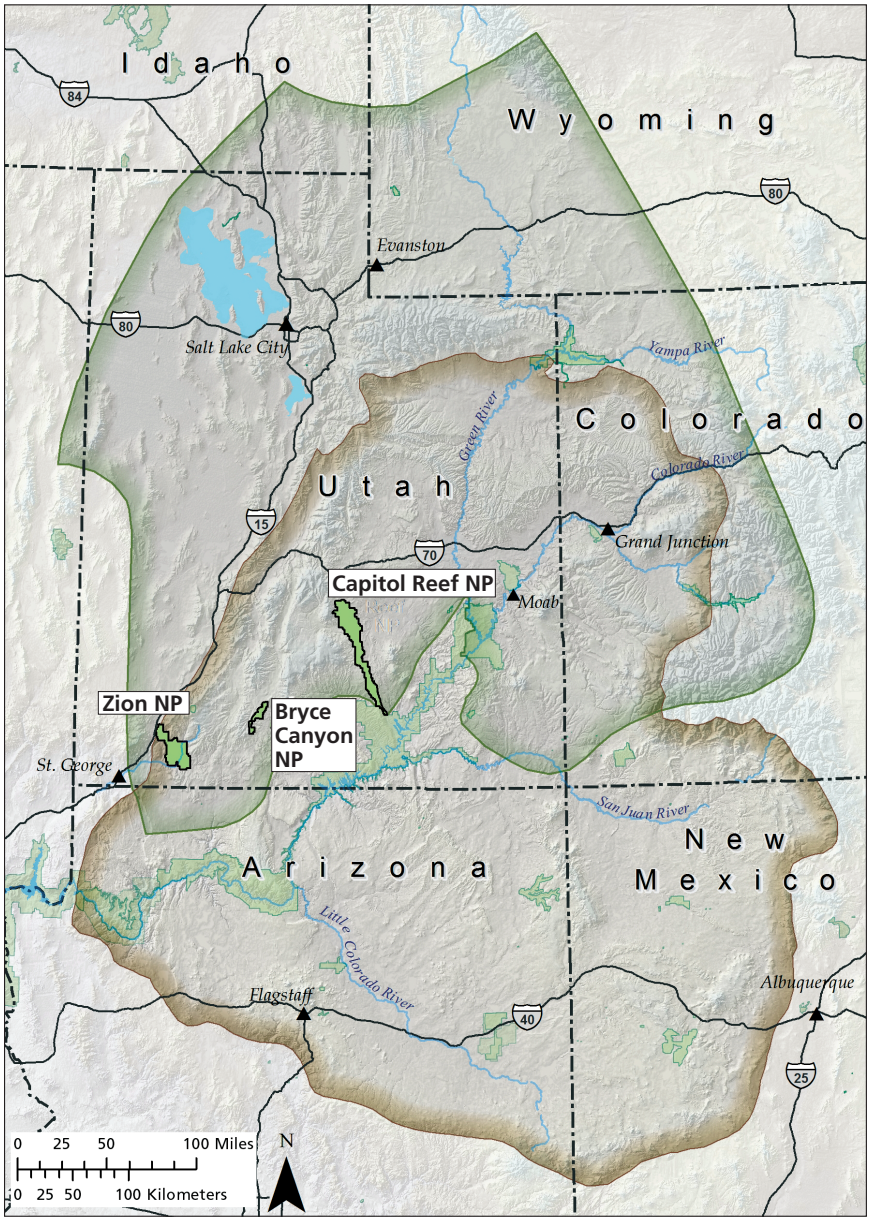


Figure 1-1. Location of Bryce Canyon, Capitol Reef, and Zion national parks in the Northern Colorado Plateau Network.

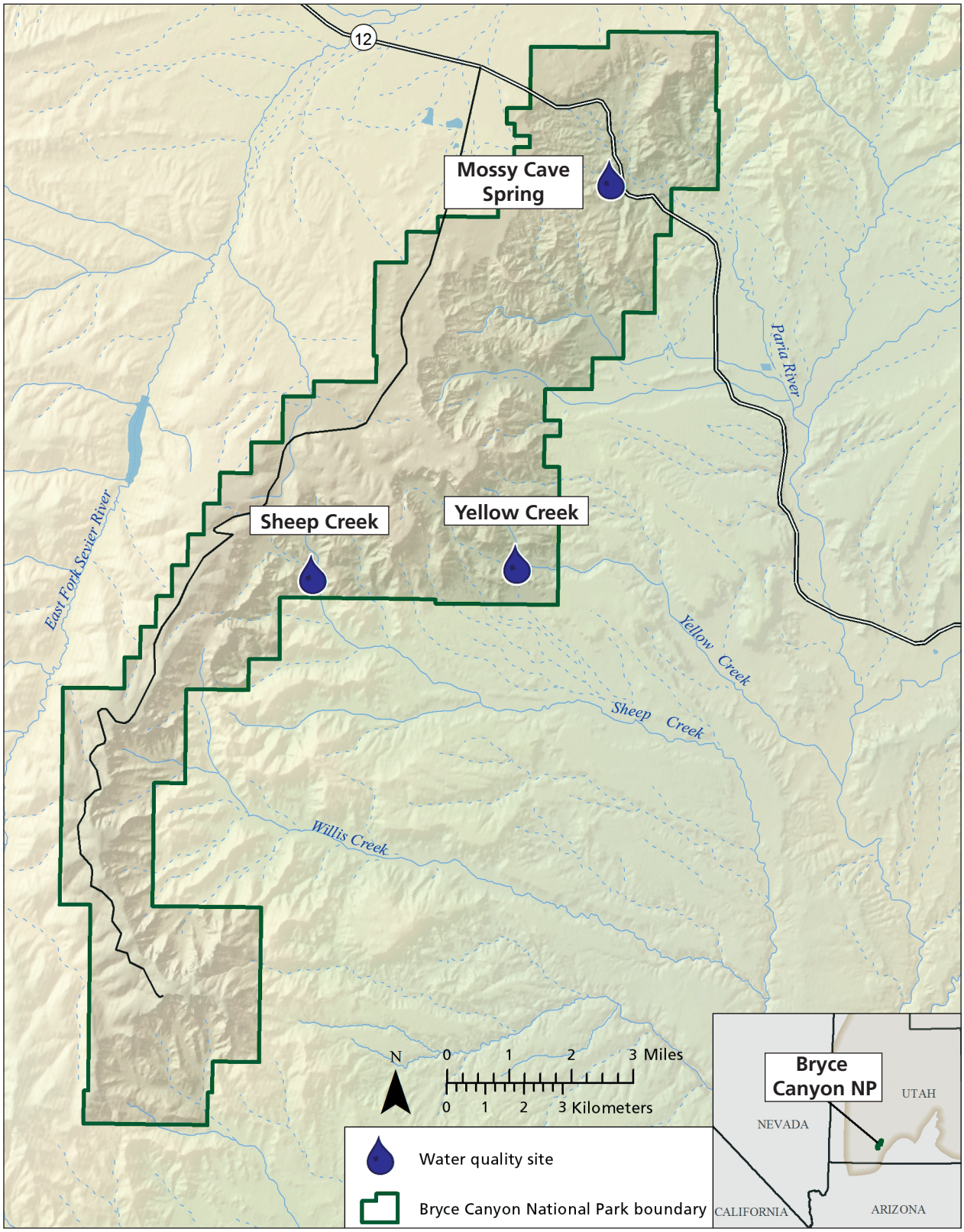


Figure 1-2. Water-quality monitoring locations at Bryce Canyon National Park, WY2006–2013.

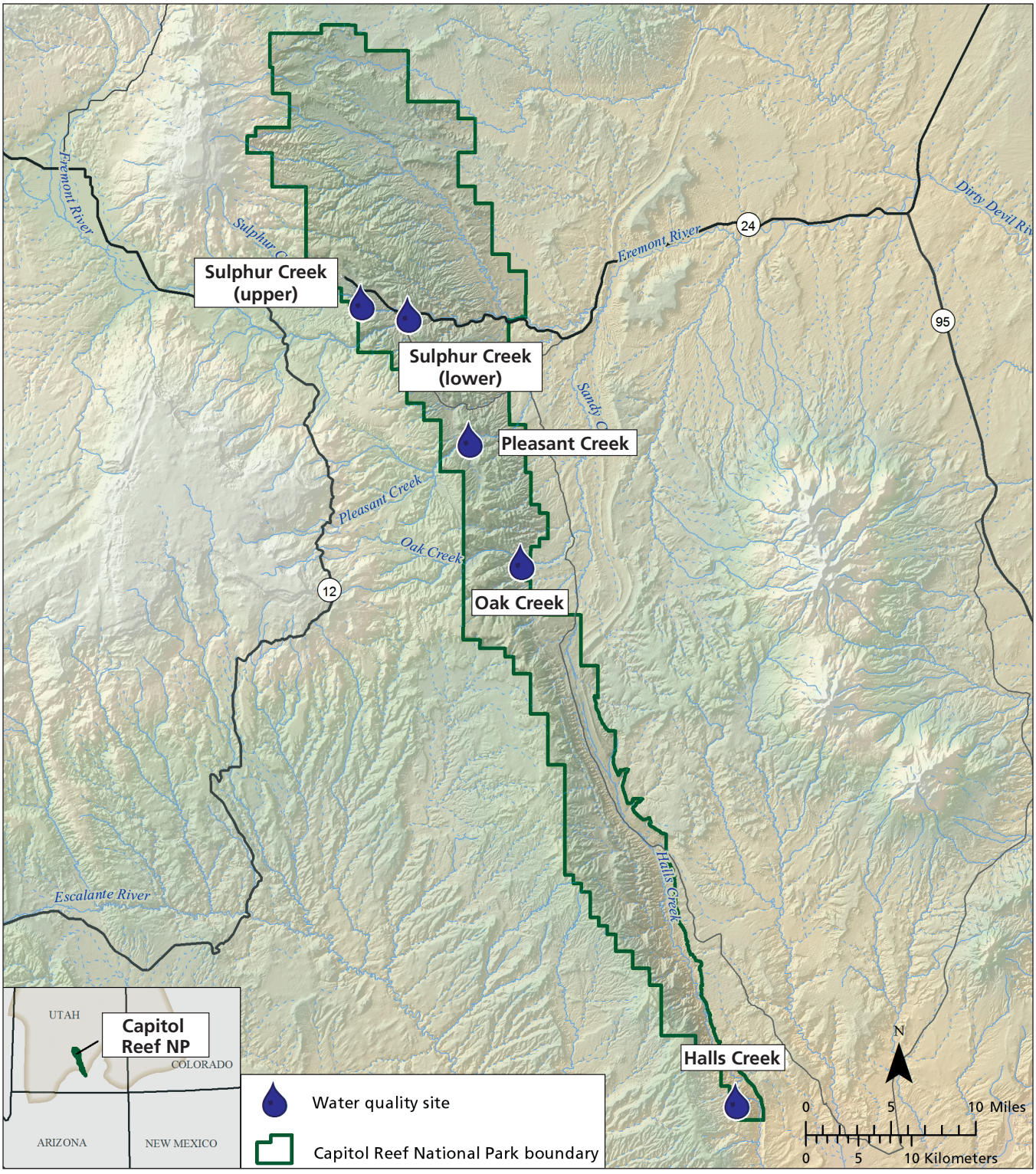


Figure 1-3. Water-quality monitoring locations at Capitol Reef National Park, WY2006–2013.

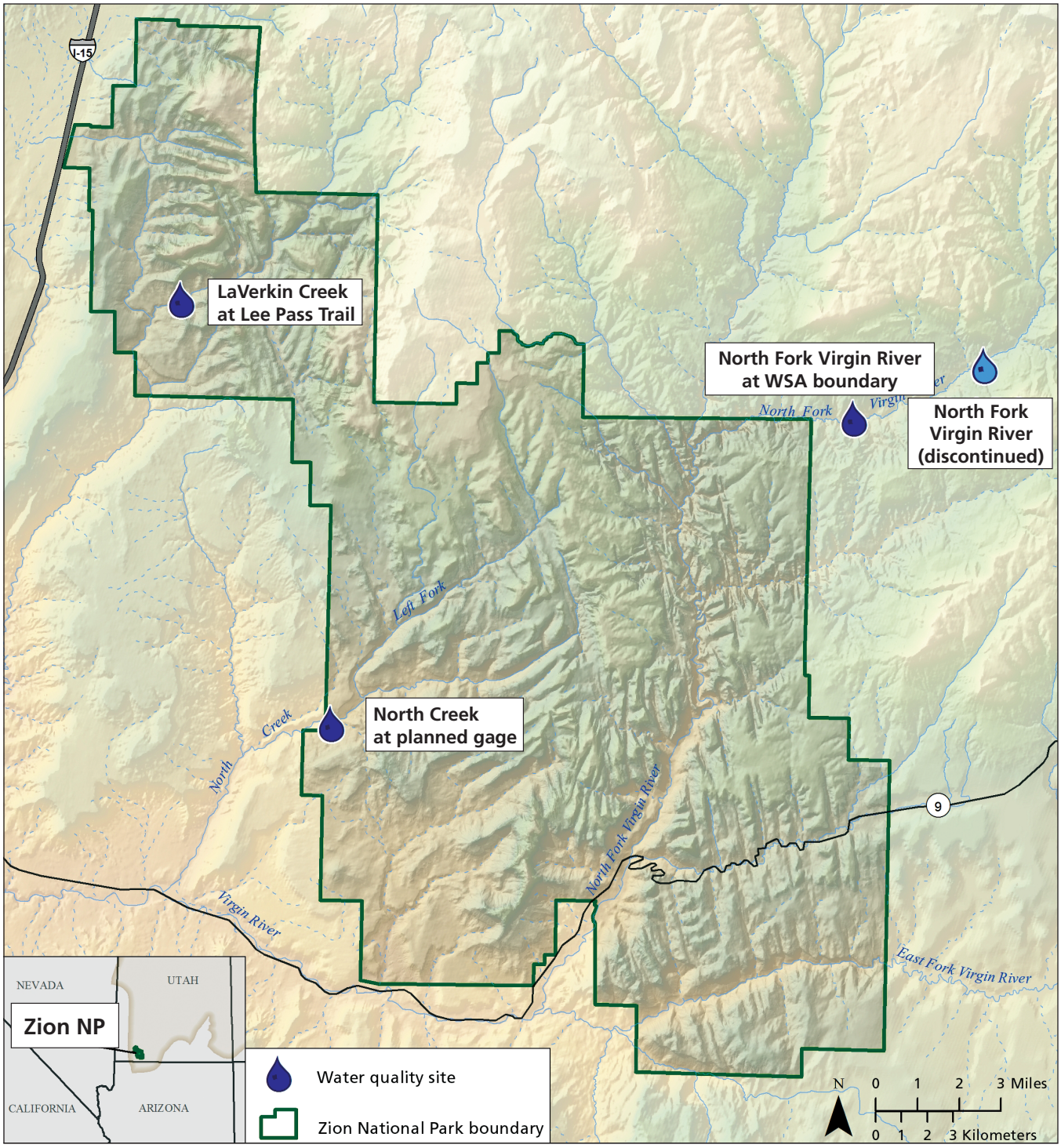


Figure 1-4. Water-quality monitoring locations at Zion National Park, WY2006–2013.

2 Quality Control

2.1 Variability

Variability was calculated from replicate water samples, and includes total variability introduced from field procedures (sample collection, processing, preservation, storage, and shipping), laboratory procedures (sample storage, preparation, and analysis), and natural variability in the stream. From WY2006 to WY2013, replicate water samples were collected at the North Fork Virgin River sampling site in Zion NP during every site visit. Environmental and replicate samples were collected in an identical manner, and replicates were collected as sequential samples with less than one minute between samples.

Variability was calculated as an RPD between replicate and environmental samples using the formula:

$$RPD = \left[\frac{S_1 - S_2}{(S_1 + S_2)/2}\right] \times 100$$

Where:

S_1 = concentration in the environmental sample

S_2 = concentration in the replicate sample

Major constituents were evaluated for an RPD of less than 15%. Trace elements and nutrients are often detected at very low concentrations, increasing uncertainty about precision and accuracy (Hem 1985). For this reason, trace elements and nutrients were evaluated for an RPD of less than 30% (Thoma et al. 2009). Measurements also were considered to be acceptable if replicate pairs both fell below the reporting limit (values censored), or if one measurement was below the reporting limit and the other was within two times the reporting limit. Analytes with better than 90% of replicates within the desired RPD from WY2006 to WY2013 were considered acceptable. Analytes that failed to meet that threshold were investigated more thoroughly.

2.1.1 Major constituents

Of 518 comparisons of major constituent measurements, 486 (94%) were within the target range of less than 15% RPD. Data for alkalinity, calcium, chloride, magnesium, potassium, sodium, and TDS were more than 90% acceptable (Table 2-1). Unacceptable pairs (sample and replicate) for these analytes clustered on two dates: alkalinity, chloride, and TDS were highly variable for September 2007, and calcium, magnesium, potassium, and sodium were highly variable for November 2008.

Sulfate and TSS did not meet the quality goal (i.e., more than 90% of pairs acceptable). An examination of RPD over time for both analytes indicated some overlap in dates with high variability, but dates were not always the same (Figures 2-1 and 2-2). Variability was

Table 2-1. Number of replicate pairs meeting acceptance criteria for major constituent analyses.

Analyte	Number of replicate pairs	Pairs with both values censored	Pairs with one value censored	Percent one or more censored	Number of pairs acceptable	Percent acceptable
Alkalinity	58	0	0	0	58	100.0
Calcium	57	0	0	0	56	98.2
Chloride	58	40	1	70.7	56	96.6
Magnesium	57	0	0	0	57	100.0
Potassium	57	8	1	15.8	56	98.2
Sodium	57	0	0	0	56	98.2
Sulfate	58	4	0	6.9	50	86.2
Total dissolved solids	58	0	0	0	56	96.6
Total suspended solids	58	4	1	8.6	41	70.7

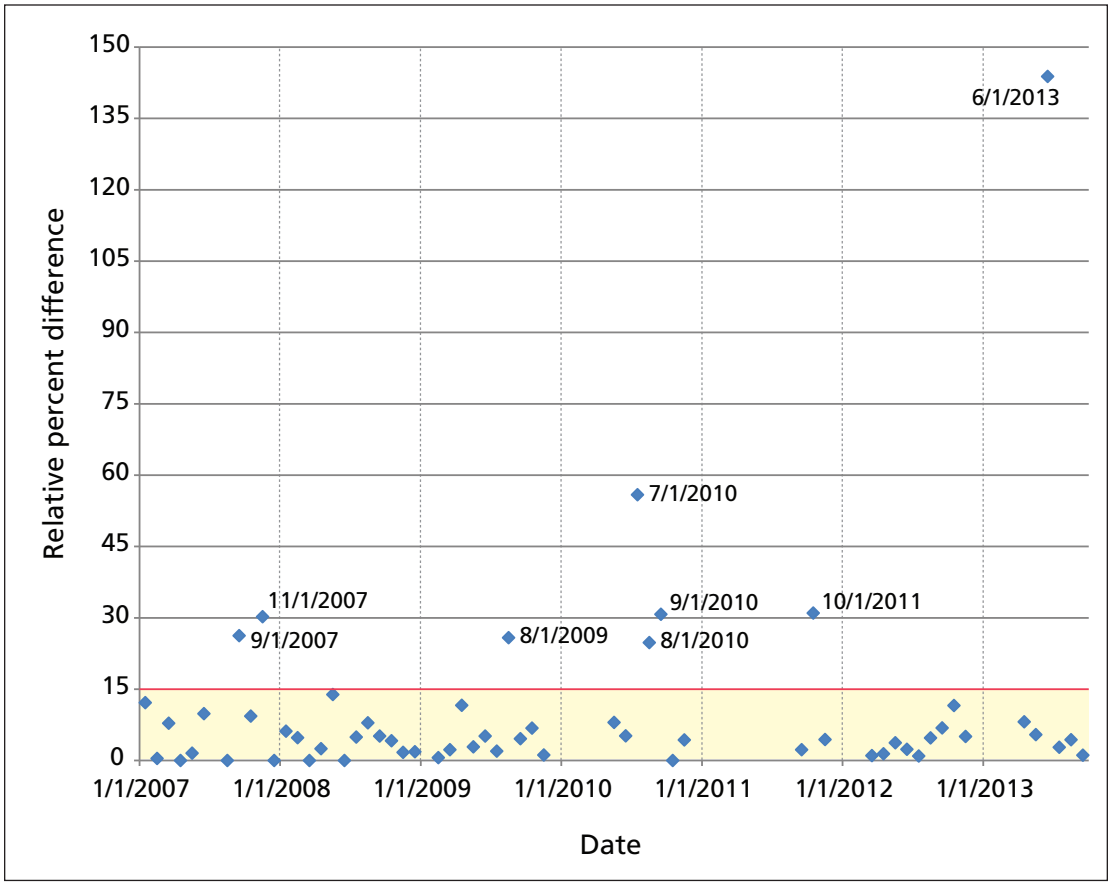


Figure 2-1. Relative percent difference in sulfate concentrations between environmental and replicate samples over time. Labeled sample dates had an RPD of greater than 15%.

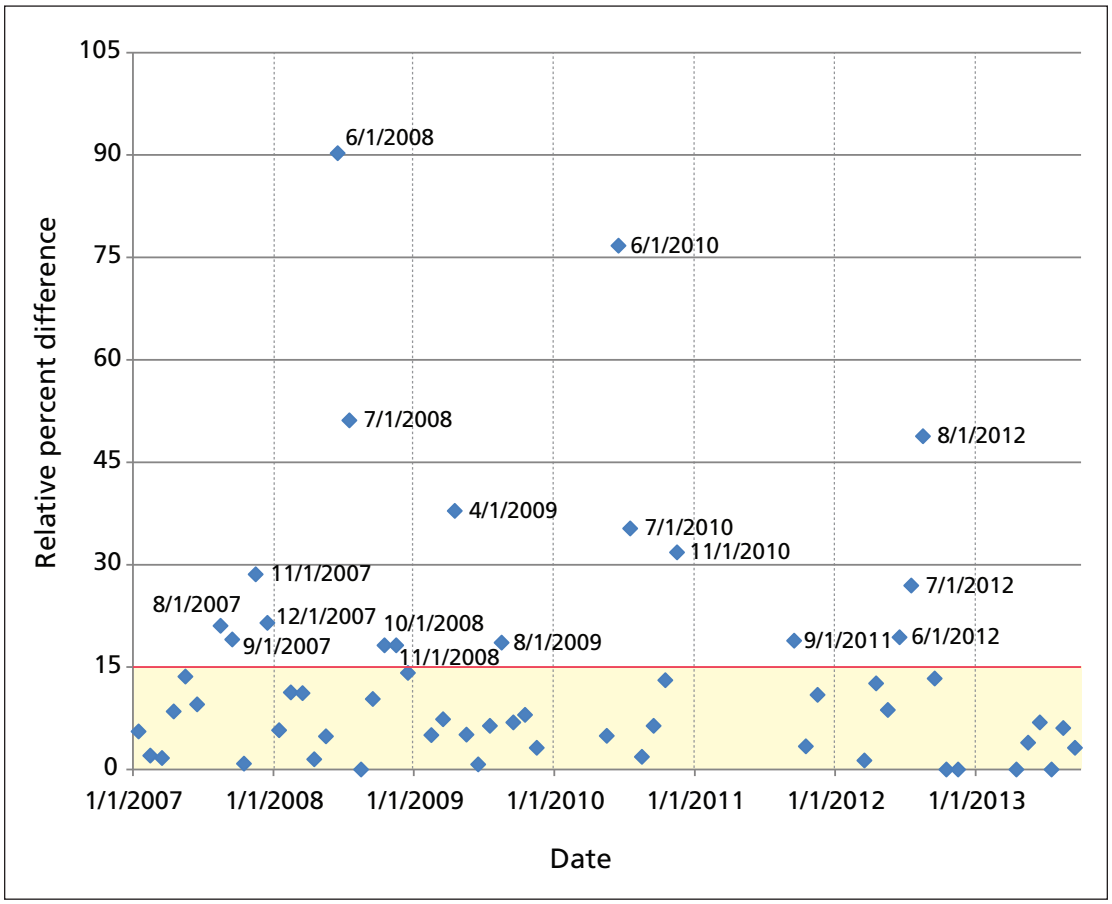


Figure 2-2. Relative percent difference in total suspended solid concentrations between environmental and replicate samples over time. Labeled sample dates had an RPD of greater than 15%.

greater than expected throughout the period of record. The Utah Public Health Laboratory used a partial bottle for TSS analysis, and if the bottle was not adequately mixed prior to pouring, variability in sample handling could occur (Gray et al. 2000). For this dataset, field turbidity might be a more reliable indicator of suspended solids in a stream.

2.1.2 Nutrients

Of 236 comparisons of nutrient measurements, 215 (91%) were within the target range of less than 30% RPD, or within two times the reporting limit if one value was below the reporting limit. Estimated values reported below the reporting limit were also accepted if the difference was within one reporting limit. For all nutrients except dissolved nitrite + nitrate, at least half of measurements fell below the reporting limits for both samples (Table 2-2). Data for ammonia, total nitrite + nitrate, dissolved phosphorus, and total phosphorus were more than 90% acceptable. Kjeldahl nitrogen and dissolved nitrite + nitrate did not meet quality goals for variability (i.e., more than 90% of pairs acceptable) (Figures 2-3 and 2-4). Variability for both was greater than expected early in the record (2008–2009).

Table 2-2. Number of replicate pairs meeting acceptance criteria for nutrient analyses.

Analyte	Number of replicate pairs	Pairs with both values censored	Pairs with one value censored	Percent one or more censored	Number of pairs acceptable	Percent acceptable
Ammonia as N	41	38	3	100	41	100.0
Kjeldahl nitrogen	40	20	7	67.5	35	87.5
Dissolved nitrite + nitrate	40	17	5	55.0	35	87.5
Total nitrite + nitrate	17	17	0	100	17	100.0
Dissolved phosphorus	40	27	5	80.0	36	90.0
Total phosphorus	58	29	5	58.6	55	94.8

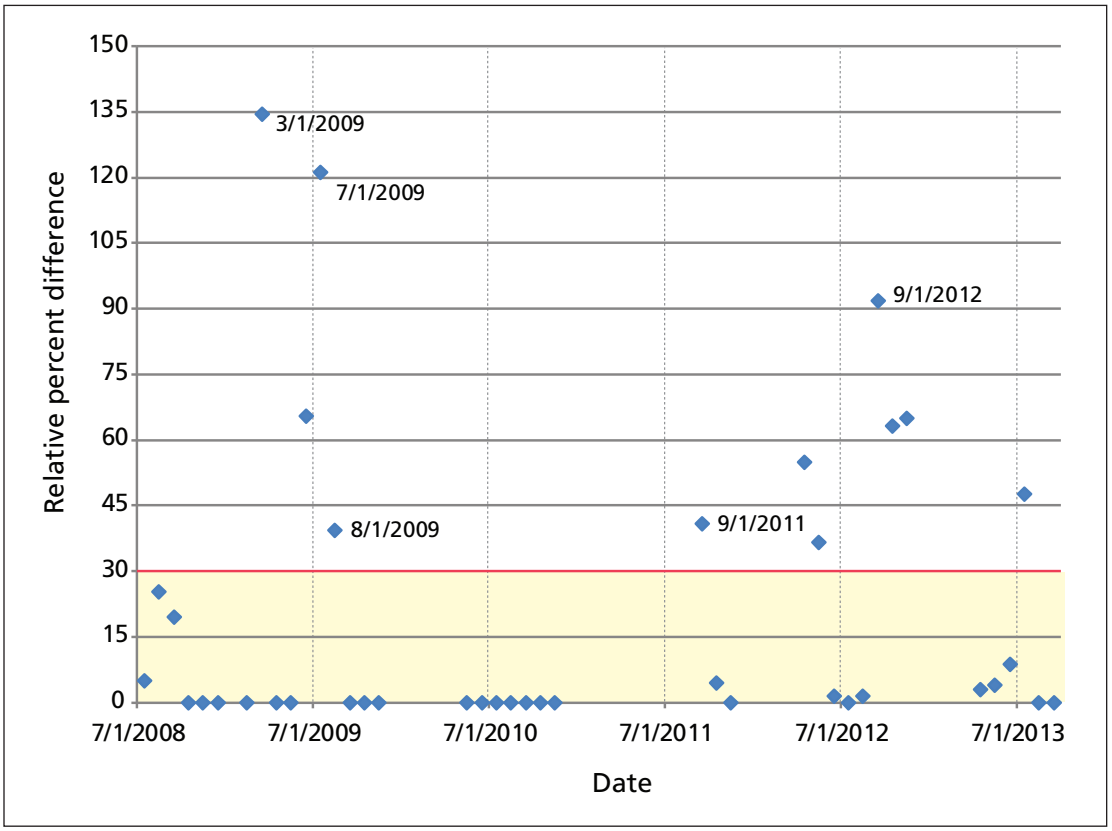


Figure 2-3. Relative percent difference in Kjeldahl nitrogen concentrations between environmental and replicate samples over time. Samples with RPD >30% that are not labelled with a date represent samples where at least one sample was below the reporting limit and the second sample was within two times the reporting limit.

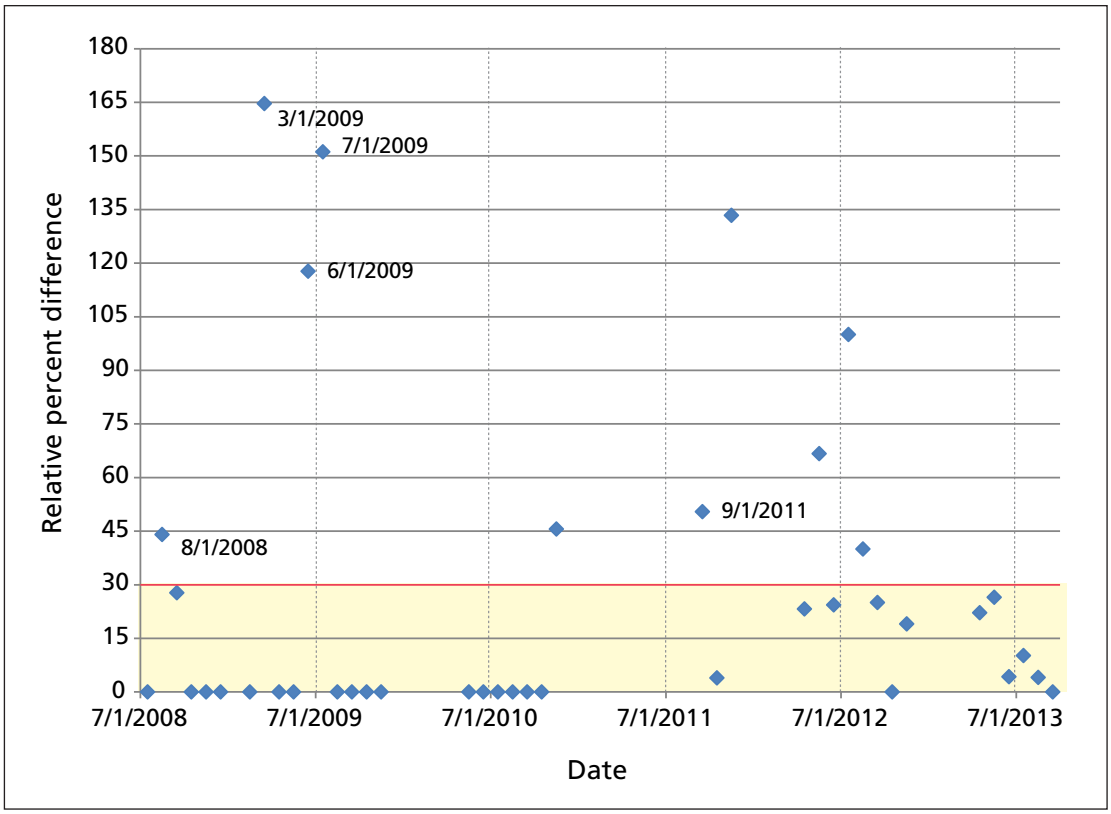


Figure 2-4. Relative percent difference in dissolved nitrite + nitrate concentrations between environmental and replicate samples over time. Samples with RPD >30% that are not labelled with a date represent samples where at least one sample was below the reporting limit and the second sample was within two times the reporting limit.

Because of the potential for high variability of nutrient concentrations in the study streams, it is difficult to develop an expected range for concentrations in environmental samples. However, most NCPN water-quality samples have low concentrations of nutrients. Sixty-eight percent of Kjeldahl-nitrogen samples, and 55% of dissolved-nitrite-plus-nitrate samples, had at least one censored value.

2.1.3 Trace elements

Of 255 comparisons of dissolved trace element measurements, 252 (99%) were within the target range (i.e., RPD of less than 30% or within two times the reporting limit if one of the values was censored below the reporting limit). Almost all measurements fell below the reporting limits (Table 2-3). Data for arsenic, barium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc were more than 90% acceptable. Aluminum did not meet quality goals for variability, with only 15 of 17 pairs (88%) falling within the acceptable range. In both cases when aluminum concentrations had an RPD of more than 30%, a relatively high concentration of aluminum was reported for the environmental sample and the replicate sample fell near or below the reporting limit. One of the analysis dates corresponded to a date identified as an outlier for aluminum across several sites, as discussed below.

2.2 Bias

2.2.1 Blanks

Contamination bias is generally assessed in water-quality data by submitting field, trip, and/or equipment blanks to the laboratory to ensure that constituents (1) fall below the reporting limits for nutrients and trace elements and (2) have low concentrations of major ions. No blanks were submitted during WY2006–2013, so contamination bias cannot be assessed for this period. Field blanks were added to the sampling program in October 2013.

2.2.2 Proficiency testing

The U.S. Environmental Protection Agency (EPA) has certified the Utah Public Health Laboratory to analyze water samples. Every six months, the EPA provides reference samples with known concentrations of con-

Table 2-3. Number of replicate pairs meeting acceptance criteria for trace element analyses.

Analyte	Number of replicate pairs	Pairs with both values censored	Pairs with one value censored	Percent one or more censored	Number of pairs acceptable	Percent acceptable
Aluminum	17	15	1	94.1	15	88.2
Arsenic	17	17	0	100	17	100.0
Barium	17	11	0	64.7	17	100.0
Boron	17	15	2	100	17	100.0
Cadmium	17	17	0	100	17	100.0
Chromium	17	8	4	70.6	17	100.0
Copper	17	17	0	100	17	100.0
Iron	17	15	1	94.1	17	100.0
Lead	17	15	2	100	16	94.1
Manganese	17	11	0	64.7	17	100.0
Mercury	17	17	0	100	17	100.0
Nickel	17	17	0	100	17	100.0
Selenium	17	17	0	100	17	100.0
Silver	17	17	0	100	17	100.0
Zinc	17	15	2	100	17	100.0

stituents to the laboratory. An estimate of laboratory bias can be made using proficiency-testing (PT) data that compare the laboratory results to the known reference concentration. To maintain certification, the PT results for these reference samples must fall within an acceptable range for each constituent at least once per year. The Utah Public Health laboratory maintained its EPA certification throughout the period analyzed in this report.

NCPN obtained PT data for the Utah Public Health Laboratory from June 2011 to September 2013, for a total of six comparisons. Data prior to June 2011 were not available. For major constituents, reported concentrations of alkalinity, calcium, chloride, magnesium, potassium, sodium, and TSS were acceptable for all samples and did not show bias over time (Table 2-4). Sulfate bias appeared to be low from 2011 to 2013 (Figure 2-5), and TDS appeared to be biased high from 2011 to 2013 (Figure 2-6). All nutrients met acceptability criteria, including ammonia, Kjeldahl nitrogen, nitrite + nitrate (fraction unspecified), dissolved phosphorus, and total phosphorus (Table 2-5). Because trace elements generally fall below reporting limits in our water-quality samples, we did not investigate PT data for trace elements.

Table 2-4. Proficiency-testing data for the Utah Public Health laboratory, major constituents, 2011–2013.

Analyte	# of reference samples	# of acceptable samples	% acceptable	Average bias (%)
Alkalinity	6	6	100	-1.8
Calcium	6	6	100	-0.2
Chloride	5	5	100	6.9
Magnesium	6	6	100	0.6
Potassium	6	6	100	0.0
Sodium	6	6	100	-0.3
Sulfate	5	4	80	-19.9
Total dissolved solids	6	4	67	12.3
Total suspended solids	6	6	100	-10.1

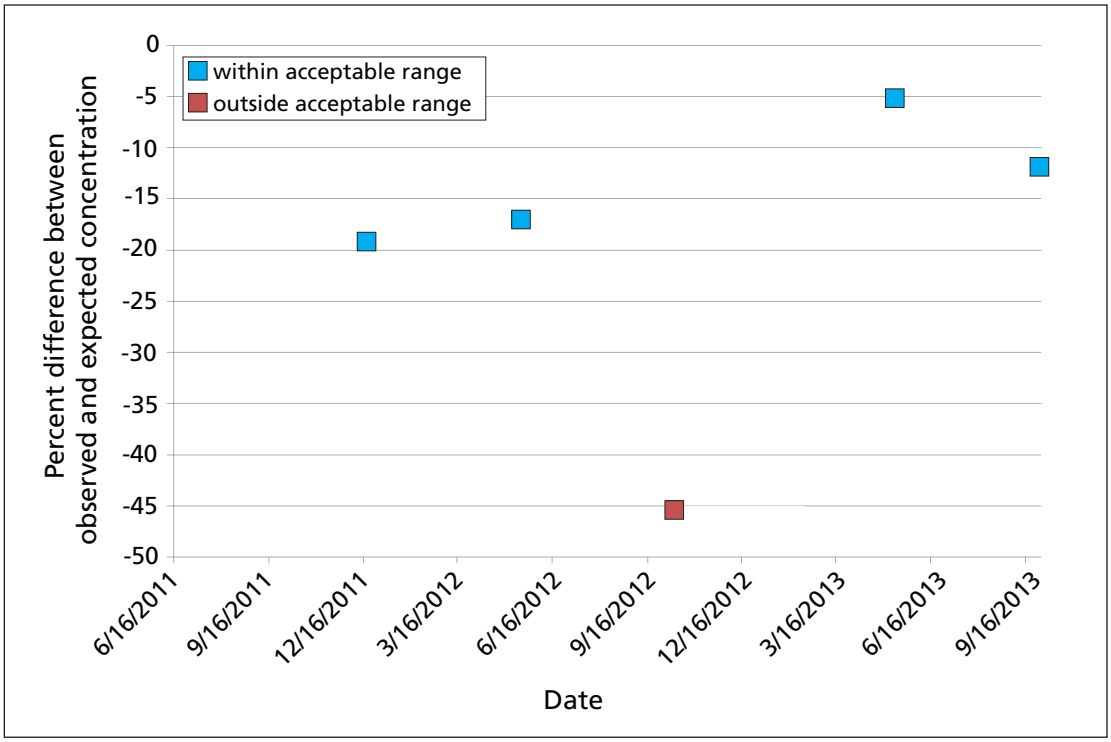


Figure 2-5. Proficiency-testing data for sulfate. The difference between observed and expected concentrations should approach zero, at the top of the y-axis in this figure. Labeled sample dates fell out of the acceptable range for EPA certification. Sulfate concentrations were consistently lower than expected. Because the acceptable range depends on the expected concentration, concentrations closer to the reporting limit have a higher percentage of allowable variation than concentrations further from the reporting limit.

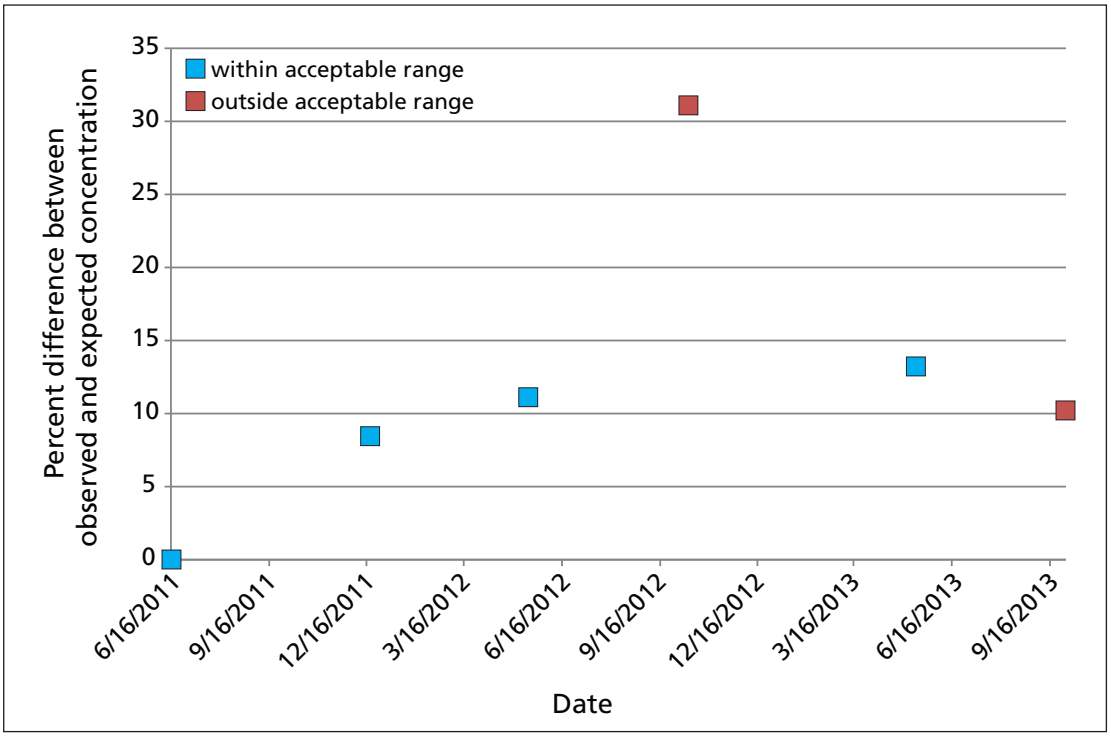


Figure 2-6. Proficiency-testing data for total dissolved solids. The difference between observed and expected concentrations should approach zero, at the bottom of the y-axis in this figure. Labeled sample dates fell out of the acceptable range for EPA certification. Because the acceptable range depends on the expected concentration, concentrations closer to the reporting limit have a higher percentage of allowable variation than concentrations further from the reporting limit. TDS concentrations were consistently higher than expected.

Table 2-5. Proficiency-testing data for the Utah Public Health laboratory, nutrients, 2011–2013.

Analyte	# of reference samples	# of acceptable samples	% acceptable	Average bias (%)
Ammonia	6	6	100	0.6
Kjeldahl nitrogen	6	6	100	-0.6
Nitrite + nitrate (fraction unspecified)	6	6	100	-7.4
Dissolved phosphorus	5	5	100	1.2
Total phosphorus	6	6	100	-2.6

3 Quality Assurance

3.1 Major-ion balances

Major-ion data were quality-assured by calculating a cation-anion balance, which included the major cations, calcium, magnesium, potassium, and sodium; and the major anions, bicarbonate, carbonate, chloride, and sulfate. The sum of concentrations of major dissolved cations in milliequivalents per liter should roughly equal the sum of concentrations of major dissolved anions in milliequivalents per liter. In our results, bicarbonate and carbonate were from an unfiltered sample aliquot, so concentrations could potentially be higher than if the measurement was made on a filtered aliquot. Trace-element ions were evaluated for inclusion in the charge-balance equation but were not present in concentrations high enough to affect the calculations.

The percent difference, or charge balance, between the sum of concentrations of cations and anions in milliequivalents per liter was calculated using the following formula:

$$\%\ \text{charge balance} = \left(\frac{\text{sum of cations - sum of anions}}{\text{sum of cations + sum of anions}}\right) \times 100$$

If an ion concentration fell below its reporting limit for a sample, then half of the reporting limit was substituted to complete the calculation for that sample. Samples with charge balances of +/- 15% or less were assumed to have major-ion analyses of good quality. Departures in the charge balance of greater than 15% were further evaluated by looking at temporal patterns in charge balance and sum of cations and anions. Positive charge balances indicate high cation concentrations or low anion concentrations, while negative charge balances indicate the reverse.

Out of 625 samples with a complete ion suite, 18 samples (3%) fell outside the desired ion balance range. Of these, the majority of suspect ion-balance samples had unusual values for sulfate (13 of 18), compared to the rest of the site's record. Two samples had unusual chloride values and for one sample, the unusual ion concentration(s) could not be determined. Two samples had cation sums that did not match the site history. Further investigation of the cation records indicated that all cations were also outliers for their sites, as discussed below, indicating possible mislabeling of sample bottles.

A systematic increase in the percent charge balance was apparent at all NCPN sites where samples were collected from April 2012 through September 2013. This increase was largely driven by a low bias in one of the anion determinations (see Figures 3-1 and 3-2 for examples). The Utah Public Health Laboratory replaced its alkalinity titrator, used to calculate bicarbonate and carbonate, in March 2012. However, the laboratory PT data did not show a corresponding negative bias in alkalinity during this time period. The unfiltered sample used to calculate bicarbonate and carbonate would potentially result in a high bias, if any. The low bias in sulfate shown by the PT data is consistent with the charge-balance trends, and appears to provide a reasonable explanation for the negative charge balance during this time. Over time, a longer dataset may provide greater context for evaluating the departures shown in 2012 and 2013.

3.2 Outlier analysis

For each site and constituent, individual results were compared to the range of concentrations over time, and outlier concentrations that fell outside of three standard deviations of the mean were further evaluated for potential errors. We compared outliers to flow and turbidity records, site history, replicates, and other QA checks. We retained all records that were associated with a flood or high-turbidity event. We rejected values for major constituents that were visually far from the normal range but occurred under normal flow and turbidity conditions, or when multiple outliers were found for an analyte at multiple sites for a single analysis date. Trace-element and nutrient outliers were not rejected unless multiple outliers occurred for a single analysis date. Dates with clusters of trace-element and nutrient outliers included October 2006 (arsenic, barium, manganese), July 2008 (aluminum, boron, dissolved nitrite + nitrate, Kjeldahl nitrogen), and August 2008 (dissolved nitrite + nitrate, Kjeldahl nitrogen). Of more than 12,900 records, 190 (approximately 1.5%) were flagged as potential outliers, and 58 records (0.4%) were rejected after inspection.

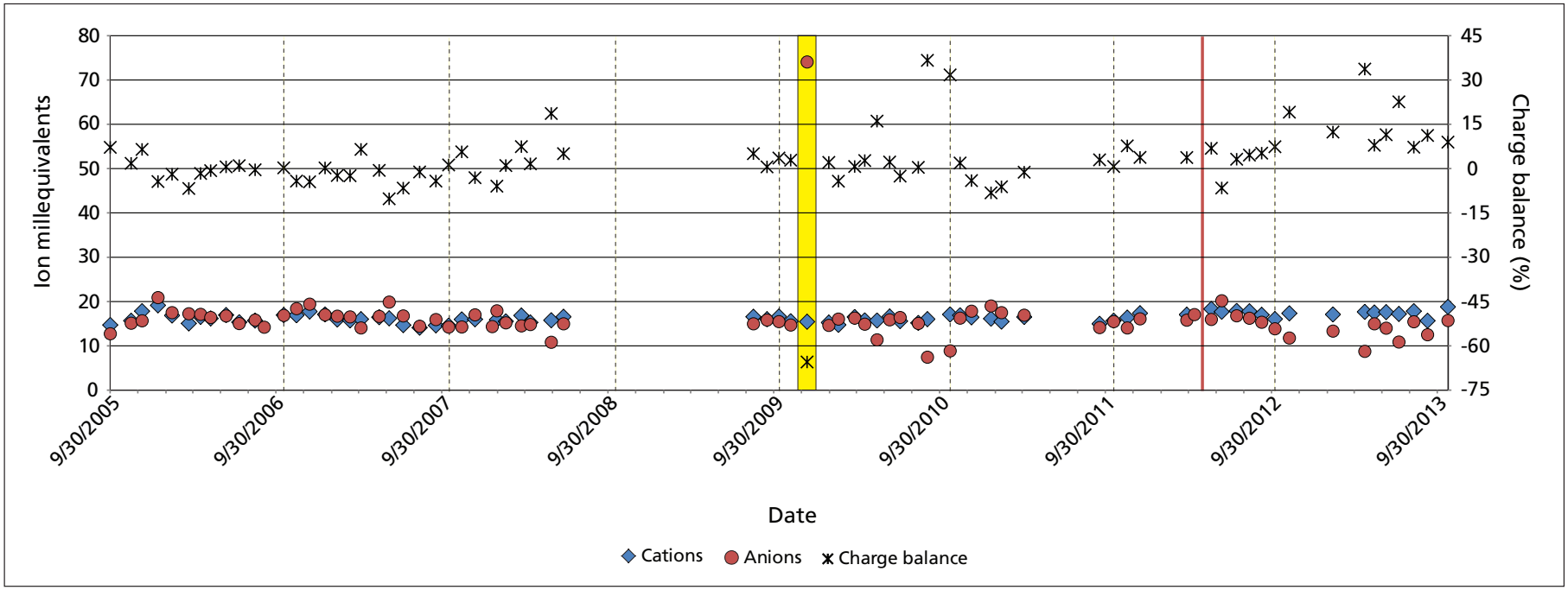


Figure 3-1. Charge balance over time at Sheep Creek, Bryce Canyon National Park. Dotted lines show the correspondence of three different elements of a single sample: a sum of cations (blue diamond), a sum of anions (red circle), and a calculated charge balance (black star). In the highlighted sample, an anomalously high anion sum leads to a negative charge balance well out of the acceptable range of +/- 15%. Note the decrease in anion concentrations beginning in April 2012 (red line), and the concurrent rise in charge balance.

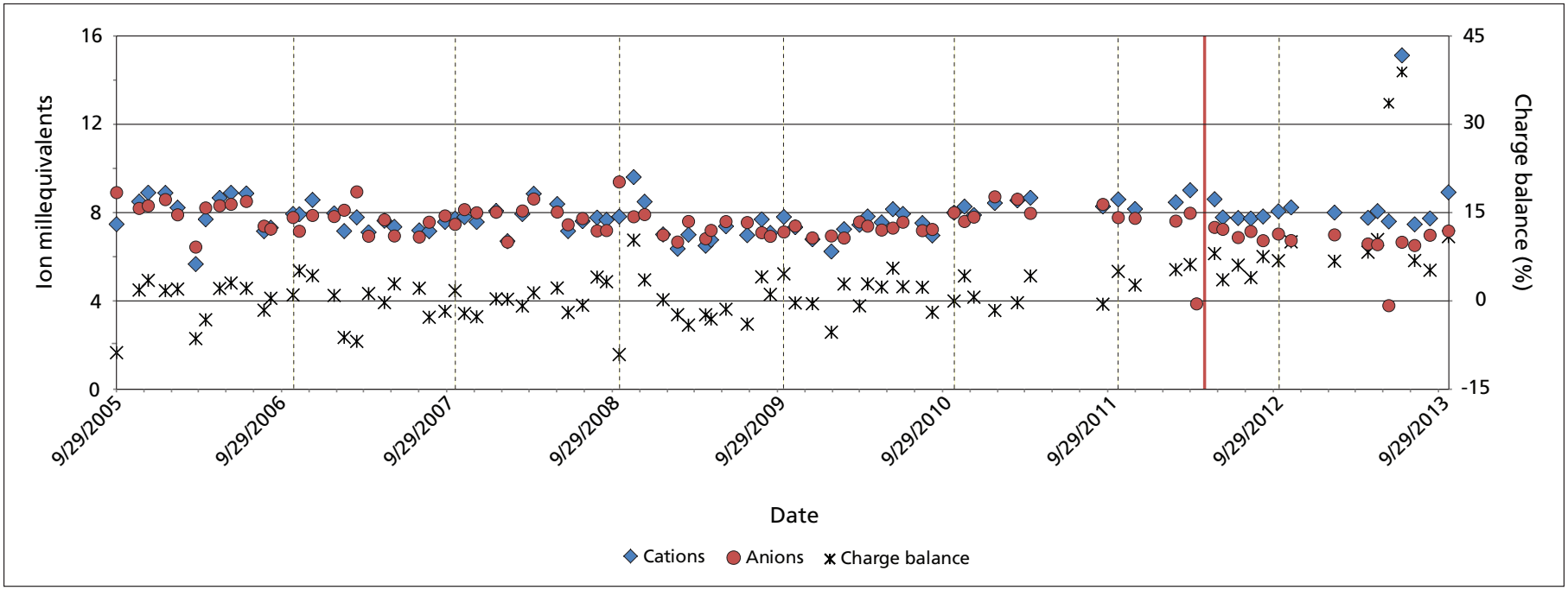


Figure 3-2. Charge balance over time at LaVerkin Creek, Zion National Park. Note the decrease in anion concentrations beginning in April 2012 (red line), and the concurrent rise in charge balance. Dotted lines show the correspondence of three different elements of a single sample: a sum of cations (blue diamond), a sum of anions (red circle), and a calculated charge balance (black star).

3.3 Dissolved and total phosphorus fractions

Dissolved-phosphorus concentrations are recovered from a filtered sample that removes sediment larger than 0.45 μm. Total phosphorus concentrations include both the dissolved fraction and phosphorus that is present in suspended sediment in the water column. As such, total concentrations should always be equal or greater than dissolved concentrations for the same sample. Dissolved phosphorus was not collected prior to July 2008.

From July 2008 to September 2013, out of a total of 427 comparisons of dissolved and total phosphorus fractions, 56 samples (13%) had lower concentrations of total phosphorus than dissolved phosphorus. We confirmed with the state laboratory that a flag is triggered when dissolved phosphorus is greater than total phosphorus, and the dissolved fraction is reanalyzed (T. Johnson, pers. comm.).

We compared differences to the relevant reporting limits (0.02 mg/L from July 2008 to April 2011, and 0.003 mg/L from September 2011 to September 2013). Eighteen samples had a discrepancy of greater than 0.02 mg/L, and 12 samples had a discrepancy of greater than 0.003 mg/L for the applicable time periods. In three cases, replicate samples were available. Dissolved phosphorus results were anomalous for one visit, while total phosphorus results were anomalous for two visits. Turbidity and flow conditions were normal for most of the flagged samples but were considered moderately elevated for three of the samples in which concentrations of dissolved phosphorus were greater than those of total phosphorus.

The Utah Division of Water Quality has noticed a similar issue with their data and is investigating possible reasons for these discrepancies (T. Johnson, pers. comm.). In the cases where no replicates exist, both dissolved phosphorus and total phosphorus results were rejected when dissolved phosphorus was more than total phosphorus plus the reporting limit.

4 Conclusions

4.1 Implications for trend analysis

The goal of NCPN water-quality monitoring is to track long-term trends in water-quality constituents at National Park Service sites on the northern Colorado Plateau. The majority of water-quality data reported from WY2006 to WY2013 met data-quality objectives for long-term trend monitoring. Quality-control variability was higher than expected in sulfate, total suspended solids, Kjeldahl nitrogen, and dissolved nitrite + nitrate, which may affect our ability to detect trends in these constituents over time.

In portions of our record, a low bias for sulfate and sum of anions and a high bias for total dissolved solids could cause spurious short-term trends in the data. Decreasing trends in sulfate and anions, and increasing trends in total dissolved solids, should be viewed with caution. These trends should disappear over time as issues of bias are corrected over the long-term record.

Under current conditions, sample-handling variability is inherent for total suspended solids. These data should not be used for trend analysis until a full sample bottle is used for preparing samples. Field-measured turbidity should provide a more accurate representation of suspended sediment loads during sampling. Concentrations of dissolved phosphorus were often higher than those for total phosphorus. Investigations into the source of this discrepancy must be continued.

4.2 Improvements to the protocol

This review of data quality has resulted in improvements to QA and QC practices for NCPN's water-quality monitoring program. NCPN published several reports comparing water-quality data to state water-quality standards prior to thoroughly reviewing the laboratory data (Thoma et al. 2008; Van Grinsven et al. 2010; Hackbarth and Weissinger 2013). The State of Utah does not have water-quality standards for the constituents of greatest concern in this report; therefore, the analyses in these previous reports remain valid. However, future reporting will only occur after the quality of data has been reviewed and documented.

In 2013, the NCPN began submitting field blanks and rotating replicate samples across several sites with a wider range of constituent concentrations. The network has suggested that the Utah Public Health Laboratory incorporate graphing of PT data into their next database upgrade.

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Natural Resource Stewardship and Science
1201 Oak Ridge Drive, Suite 150
Fort Collins, Colorado 80525

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