Nutrient dynamics in a headwater stream: use of continuous water quality sensors to examine seasonal, event, and diurnal processes in the East Fork Jemez River, NM

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Lauren Sherson
Candidate
Earth and Planetary Sciences
Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Laura Crossey, Chairperson
Cliff Dahm
Yemane Asmerom
NUTRIENT DYNAMICS IN A HEADWATER STREAM: USE OF CONTINUOUS WATER QUALITY SENSORS TO EXAMINE SEASONAL, EVENT, AND DIURNAL PROCESSES IN THE EAST FORK JEMEZ RIVER, NM

by

LAUREN SHERSON

B.S. GEOLOGY
B.S. BIOLOGY
UNIVERSITY OF OREGON

THESIS
Submitted in Partial Fulfillment of the Requirements for the Degree of

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Nutrient Dynamics in a Headwater Stream: Use of Continuous Water Quality Sensors to Examine Seasonal, Event, and Diurnal Processes in the East Fork Jemez River, NM

by

Lauren Sherson
B.S. Geology, B.S. Biology, University of Oregon, 2006
M.S. Earth and Planetary Sciences, University of New Mexico, 2012

PREFACE
Stream water quality can change substantively over seasonal, event, and diurnal scales. Multiple biogeochemical processes operate on a 24-hour timescale, and also may be influenced by local weather and precipitation events. Increased sampling frequency, made possible by recent developments in continuous water quality monitors, allows us to better understand biogeochemical responses to these events. Continuous water quality sensors were deployed in the East Fork Jemez River (located in northern New Mexico) from 2010 – 2011 to investigate the temporal variability of nutrient concentrations and biogeochemical parameters and the controls on this variation.

This thesis is split into two chapters representing two separate manuscripts intended for publication with L. Sherson as the first author. Chapter 1 reports on seasonal and diurnal variation observed in nutrient concentrations and biogeochemical parameters, and the biological and hydrological controls on these processes. Additional co-authors will be Van Horn, D.J., Gomez, J.D., Shafer, B.M., Bixby, R.J., Crossey, L.J., and Dahm, C.N. Chapter 2 summarizes nutrient and biogeochemical responses observed during event periods in the East Fork Jemez watershed. These events include spring snowmelt and precipitation, fall precipitation, and summer monsoons occurring after wildfire.
Additional co-authors will be Van Horn, D.J., Gomez, J.D., Crossey, L.J., and Dahm, C.N.

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CHAPTER 1

Nutrient Dynamics in a Headwater Stream: Use of Continuous Water Quality Sensors to Examine Controls on Seasonal and Diurnal Processes

ABSTRACT

Stream water quality can change substantively over diurnal, event, and seasonal scales. Seasonal and diurnal patterns in surface water nutrient concentrations (nitrate and phosphate) and biogeochemical parameters (temperature, specific conductance, dissolved oxygen, pH, and turbidity) were discovered through deployment of several continuous water quality sensors from March to October 2011 in the East Fork Jemez River, located in northern New Mexico, USA. Seven weeks (approximately one each month) representing baseflow conditions were identified for in-depth analysis. Surface water nitrate (NO₃⁻) concentrations increased during summer months when biological production rates were at maximum levels, while phosphate (PO₄³⁻) showed minimal seasonal variability. Substantive diurnal variability was observed in both NO₃⁻ and PO₄³⁻ concentrations during all week-long intervals with increased diurnal variability of NO₃⁻ up to (Δ 3µM day⁻¹) during the months of July and August. Data also showed periods of substantial diurnal variability in dissolved oxygen (DO) (up to Δ 9 mg l⁻¹day⁻¹) and pH (up to Δ 2 pH unit day⁻¹). Maximum diurnal variability in NO₃⁻, DO, and pH was found to be greater than 50% total seasonal variability. Although daily amplitude of nutrients and biogeochemical parameters (DO, pH, specific conductance) was highly variable between intervals, NO₃⁻ and PO₄³⁻ consistently reached maximum values in the late afternoon (between 15:00 h and 19:00 h). Results indicate that diurnal variability of
nutrients is controlled by both biological and hydrological processes, and highlight the importance of continuous water quality monitoring to better understand biogeochemical cycling in headwater streams.

**INTRODUCTION**

In freshwater ecosystems, nitrogen and phosphorus are important limiting nutrients for aquatic plant and animal communities. Factors influencing the processing and retention of these nutrients in headwater streams are important, as many streams and rivers are affected by anthropogenic nutrient loading (Peterson et al. 2001, Mulholland et al. 2008) and transport nutrients to downstream aquatic systems (Rabalais 2002). Nutrient concentrations in streams vary as a result of complex biological and hydrological processes, which are highly variable in space (Dent and Grimm 1999) and time (Walling and Webb 1986, Mulholland and Hill 1997). The complex nature of these processes requires examination of data on a variety of timescales to truly understand the controls on nutrient cycling in any ecosystem.

Metabolism and dissolved oxygen concentrations are closely linked to nutrient uptake in streams. Diurnal and day-to-day variations in NO$_3^-$ uptake and primary production have been observed by using solute injections to investigate daily changes in retention processes (Hall Jr and Tank 2003, Fellows et al. 2006, Mulholland et al. 2006). Results from these studies consistently indicate a strong relationship between nutrient uptake and increasing rates of metabolism. Diurnal variability in NO$_3^-$ concentrations has also been examined, with minimum concentrations typically corresponding with maximum rates of primary production (Manny and Wetzel 1973, Grimm 1987, Mulholland 1992, Heffernan and Cohen 2010). Diurnal variability in phosphate (PO$_4^{3-}$) concentrations is not as widely
reported in the literature, but correlations between NO$_3^-$ uptake and primary production have been also shown to hold for PO$_4^{3-}$ (Hoellein et al. 2007).

Nutrient concentrations are additionally influenced by processes besides assimilatory demand. The redox environment and adsorption-desorption capacity of sediments can also alter nutrient concentrations (Findlay 1995, Duff and Triska 2000). Diurnal variability in NO$_3^-$ concentrations has been attributed to denitrification rates, resulting in higher concentrations during periods of daylight (Laursen and Seitzinger 2004, Harrison et al. 2005). Hydrological processes such as groundwater input or groundwater/surface water exchange (Dahm et al. 1998, Winter 1999) can also influence PO$_4^{3-}$ and NO$_3^-$ levels.

Numerous biogeochemical processes operate on a 24-hour timescale, and may go unnoticed with traditional water quality grab sampling techniques. Stream water quality can also change over event (McDiffett et al. 1989, Triska et al. 1990, Wondzell and Swanson 1996) and seasonal (Wondzell and Swanson 1996, Mulholland and Hill 1997, Dahm et al. 1998, Pionke et al. 1999) scales. Increased sampling frequency, made possible by recent developments in continuous water quality monitors (Kirchner et al. 2004) allows the examination of nutrient concentration patterns on a wide range of temporal scales. Continuous measurements of NO$_3^-$ (Pellerin et al. 2009, 2012, Heffernan and Cohen 2010) and PO$_4^{3-}$ can ultimately be linked to those of other biogeochemical parameters to better understand the controls on nutrient cycling in streams.

In this study we collected high frequency data from March-October, 2011 from a headwater stream located in north central New Mexico. Seven weeks (approximately one each month) found to represent baseflow or stable hydrologic conditions were identified
for in-depth analysis. The objectives of this study were to: (1) determine if nutrient (NO$_3^-$ and PO$_4^{3-}$) concentrations exhibit seasonal or diurnal patterns in this system and (2) elucidate the hydrological and biological controls on these patterns. Measurements of water temperature, dissolved oxygen, pH, and specific conductance were used to evaluate the biogeochemical cycling that occurs in this system throughout the year. In addition, in-stream production and respiration rates were calculated from high frequency dissolved oxygen measurements and compared to seasonal and diurnal variation in nutrient concentrations. Our results indicate that nutrient concentrations are highly variable in this ecosystem, varying substantially on diurnal and seasonal scales and highlight the importance of continuous water quality monitoring to better understand biogeochemical cycling in headwater streams.

**METHODS**

*Site Description*

The Jemez watershed is a snowmelt and monsoon-driven system in northern New Mexico (NM), USA that feeds into the Middle Rio Grande Basin. Our study site (35.8411, -106.5013) was located on the East Fork Jemez River near the southern boundary of the Valles Caldera National Preserve (Figure 1), a federally operated preserve that encompasses ~350 square kilometers (VCNP 2012). The site was located in a high elevation (2,590 meters) broad meadow valley with minimal overstory vegetation throughout the contributing basin. The 200 meter long study reach was located within an elk exclosure consisting of a 160 by 160 meter plot with a 2.5-meter high fence and includes 42 shallow monitoring wells. Discharge for the study reach typically averaged between 50-150 l s$^{-1}$, but increased substantively during precipitation events. Historically,
the largest flows occur between March and May, and are attributed to snowmelt (Rodriguez and Moser 2010). Monsoon precipitation occurring between July and September accounts for approximately 50% of the annual precipitation in this area (Bowen 1996) and commonly varies in strength depending on snowpack extent during the previous winter (Gutzler 2000).

**Continuous Measurements**

In situ measurements of nitrate (NO$_3^-$) and phosphate (PO$_4^{3-}$) were made using state-of-the-art real time nutrient analyzers. A Satlantic SUNA (Submersible Ultraviolet Nitrate Analyzer) provided readings of dissolved NO$_3^-$ using an ultra-violet adsorption method (Satlantic 2011). Measurements were made at 15-min or 30-min intervals from 15 March - 13 October 2011. Calibration and fouling checks on the SUNA were performed approximately monthly during the deployment, according to manufacturer specifications (Satlantic 2011). Measurements of PO$_4^{3-}$ were made at 1-hr intervals from 16 May to 9 September 2011 using a WETLabs Cycle-PO$_4$ dissolved phosphate analyzer. The Cycle-PO$_4$ analyzer uses micro-fluidics and state-of-the-art optics to measure the transmittance of a filtered water sample and calculate PO$_4^{3-}$ concentration (WETLabs 2011) using standard EPA analytical wet chemistry method 365.5. Instrument servicing needs and battery failure resulted in several gaps in NO$_3^-$ and PO$_4^{3-}$ data.

In situ measurements of temperature, specific conductance (SC), dissolved oxygen (DO), pH, and turbidity were made using Yellow Springs Instruments (YSI) model 6920 V2 (surface water) and 600XLM (groundwater) sondes. Sondes collected temperature corrected (25°C) SC readings. Measurements were made at 15-min intervals from 15 March to 02 November 2011. Groundwater measurements were obtained in well
S2, located on the stream bank just east of the study site (Figure 1), and were switched to 1 hour intervals after 22 September. Fouling checks and calibrations of YSI sondes were performed every 3-4 week using known standards (SC and pH sensors) and 100% water-saturated air (optical DO sensors).

Continuous river stage data from March to October 2011 was obtained from a pressure transducer co-located with the nutrient instruments. Groundwater level measurements were obtained from pressure transducers located throughout the well network. All pressure transducer data was corrected with local barometric pressure. High frequency air temperature, photosynthetically active radiation (PAR), and barometric pressure were obtained from flux towers located in the Valles Caldera National Preserve. Data from the Valles Caldera Mixed Conifer (35.8884, -106.5321) flux tower was primarily used, but data from the Valles Caldera Ponderosa Pine flux tower (35.8624, -106.5974) was used to supplement a data gap from 1 June 2011 to 18 July 2011. Precipitation data was obtained from the Valles Caldera National Preserve Headquarters (#11) meteorological station (35.8582, -106.5211). Daily snowpack data was acquired from the National Resources Conservation Services (NRCS) Senorita Divide #2 SNOTEL site (36.0000, -106.8333). East Fork Jemez streamflow data was obtained from the Valles Caldera National Preserve at the Hidden Valley Gage, approximately 0.5 km downstream from our study site. Jemez River streamflow was obtained from the U.S. Geological Survey (USGS) at Jemez River near Jemez, NM (08324000) (35.6620, -106.7434).

**Discrete Measurements**
Discrete surface water nutrient samples were collected in duplicate or triplicate approximately every 7-10 days throughout the study period to confirm sensor readings. Samples were filtered through 0.45 µm filters in the field and immediately frozen upon return to the laboratory. Groundwater and surface water field parameters were also collected on 10 June 2011 (pH, DO, and SC) and 29-30 March 2011 (pH, DO, SC, and \( \text{NO}_3^- \)) in selected wells using a YSI sonde (June) and a YSI Professional Plus (Pro Plus) field meter (March).

Discrete surface water samples were also collected every hour over a 24-hour period on 16 August 2011 using an ISCO automated sampler. Each sample was pumped from the stream into a container preserved with 0.25 ppm phenyl mercuric acetate (PMA). Samples were collected at the end of the 24 hour period, filtered in the laboratory, and immediately frozen before analysis. Samples were analyzed using ion chromatography (Dionex 500) in the Department of Earth and Planetary Sciences analytical laboratory in Albuquerque, New Mexico. A low-detection method was employed for analysis, consisting of low concentration standards (0.05 - 1 mg l\(^{-1}\)) and long sample loops (250 or 1000 µm). The low-detection method was not utilized for analysis of the samples collected 29-30 March 2012. If \( \text{NO}_3^- \) or \( \text{PO}_4^{3-} \) in one sample was more than 100% different an average of the other two, that single grab sample was removed from the dataset and considered to be invalid.

**Data Processing and Analysis**

Nitrate measurements made with the SUNA were logged to an external STOREX data logger and post-processed using Satlantic software (SatCon and SUNACom, Satlantic 2011). Data were collected in 1 Hz intervals and those collected after 20
seconds were averaged to create a single NO$_3^-$ concentration for that sampling interval. Data were corrected using AQUARIUS software (Aquatic Informatics 2011) to address outliers, fouling shifts, and data gaps. Fouling shifts were applied on 9 April 2011 (-0.714 μm) and 7 July 2011 (+0.714 μm), and low quality data was deleted between 30 May – 22 June 2011.

PO$_4^{3-}$ data were logged internally on the Cycle-PO$_4$ analyzer. Outliers were addressed using quality control algorithms developed and applied by WETLabs. Low quality data were removed primarily during the weeks following the installation of new reagent cartridges, which were exchanged on 16 May and 11 June 2011. Temperature, SC, DO, and pH data were examined to remove erroneous values during calibration visits. In addition, Aquarius was used to apply shifts in SC, DO, and pH when necessary due to fouling or calibration drift. Shifts were applied based on calibration data and field parameter measurements made during calibrations. A detailed description of sondes and data corrections is included in Appendix A.

Seven one-week intervals were chosen at approximately monthly intervals from March-September for diurnal analysis and seasonal comparison. Exact dates were shifted to coincide with baseflow or stable hydrologic conditions and data availability. All data were reduced to measurements taken at 30-minute frequencies when possible, with PO$_4^{3-}$ remaining at 1-hr intervals. Intervals from 2011 chosen for analysis were 25-31 March, 16-22 April, 23-29 May, 15-21 June, 19-25 July, 13-19 August, and 26 September-2 October. Production (P) and community respiration (CR) were calculated for each one week interval using diel oxygen concentration, air temperature, photosynthetically active radiation (PAR), and barometric pressure in ModelMaker (Grace 2011). A lowess smooth
was used to remove the non-linear trend evident in SC (August), $\text{PO}_4^{3-}$ (August), and $\text{NO}_3^-$ (July and August) due to the obvious fire effects on these parameters (Appendix C) before hysteresis curves were generated. In addition, $\text{PO}_4^{3-}$ data from May were excluded from statistical analyses due to patchiness of results after quality control. In addition, Welch two sample t-tests were performed to evaluate statistical significance of several parameters.

**RESULTS**

*Physical Conditions*

Discharge in the East Fork Jemez averaged approximately 80 l s$^{-1}$ for most of 2011 (VCNP 2012) (Figure 2b). This corresponds to an average local stage level of approximately 0.30 m, which increased slightly during select precipitation events and substantially during August monsoons (Figures 2a and 2b). A relatively small snowpack developed in 2011, with spring snowmelt flows downstream in the Jemez River peaking at 2237 l s$^{-1}$ on 19 April. Historically, snowmelt results in a peak above 9000 l s$^{-1}$ at this location (USGS 2012) (Figure 2c). Another key event during the study period was the Las Conchas fire, which began on 26 June and burned 156,593 acres primarily east of the study site, but included drainage areas feeding into the East Fork Jemez (InciWeb 2011).

*Seasonal Variability*

Surface water nutrient concentrations, temperature, DO, and pH exhibited substantial seasonal variation throughout the primary study period (15 March to 15 October 2011) (Figure 3; Table 1). Surface water nutrient concentrations were on average very low (<10 μM nitrate ($\text{NO}_3^-$) and < 2 μM phosphate ($\text{PO}_4^{3-}$), but increased substantially beginning in August (>20 μM $\text{NO}_3^-$ and > 12 μM $\text{PO}_4^{3-}$) during monsoon
pulses. Surface water NO$_3^-$ concentrations also exhibited a gradual increase beginning in July prior to the initiation of post-fire monsoons, with maximum instantaneous values of approximately 9 µM. Instantaneous surface water temperatures ranged from minimum values of 0.15 °C to maximum values of 25.49 °C (Figure 3) and daily mean temperature values increased from approximately 4°C in March to 18°C in July and August (Figure 4). Instantaneous DO values ranged from minimum values of 2.21 mg l$^{-1}$ to 13.81 mg l$^{-1}$ (Figure 3), while daily mean DO concentrations exhibited little variability throughout the study period, with a slight decrease observed between spring (8.5 mg l$^{-1}$) and summer (6.5 mg l$^{-1}$) and a subsequent increase into fall (10 mg l$^{-1}$) (Figure 4). Instantaneous pH reached minimum values of 7.07 and peaked at 9.57 (Figure 3), with relatively stable daily mean pH values observed during the study period, with a slight increase observed between March (pH 7) and late June (pH 9) (Figure 4).

Groundwater temperature also showed seasonal variation during the primary study period. Temperatures in well S2 increased from < 4°C in May to > 12°C in August. DO (0-0.5 mg l$^{-1}$) and pH (6.3-6.5) were relatively constant from May to October 2011, with no obvious seasonal pattern (Figure 4). Rapid increases in DO and decreases in pH were observed beginning in August 2011, and were associated with local monsoon events. Several of these events likely resulted in overland flow inundating well casings, thus these parameters may not accurately depict the biochemical conditions present in the groundwater.

Maximum production (P) rates varied between months, steadily increasing from < 10 mg O$_2$ l$^{-1}$ s$^{-1}$ in March to > 40 mg O$_2$ l$^{-1}$ s$^{-1}$ in June, July, and August (Table 1). Production rates observed in September were similar to those observed in May (21.2 and
27.1 mg O₂ l⁻¹ s⁻¹, respectively). Maximum respiration (R) rates also varied seasonally, with significantly (p < 0.0001) higher rates occurring in June, July, and August (0.00072 mg O₂ l⁻¹ s⁻¹ on average) than March, April, May, and September (0.00027 mg O₂ l⁻¹ s⁻¹ on average) (Table 1). Cloud cover occurring in July, August, and September resulted in decreased PAR and dampened P rates during these intervals.

**Diurnal Variability**

River stage exhibited regular diurnal variation, with maximum flow occurring at night throughout the seven intervals. Average diurnal variability increased from Δ 0.02 m in March and April to Δ > 0.04 m during the summer months. Unlike the patterns observed in biochemical constituents, a sinusoidal pattern was not observed in river stage variability. For all intervals, river stage increased immediately in the late afternoon when PAR was reduced to 0, and then remained relatively constant before decreasing in the early morning hours (Figure 5a).

Substantial and regular diurnal variability was observed in nutrient concentrations (up to Δ 3 µm day⁻¹ NO₃⁻ and Δ 1 µm day⁻¹ PO₄³⁻) for all weekly intervals examined (Figure 5d). Average diurnal variability for PO₄³⁻ was relatively constant throughout the study period, but daily changes in NO₃⁻ concentrations were significantly (p <0.0001) higher in July and August (Δ 2.17 µm day⁻¹ on average) than March, April, May, and September (Δ 0.96 µm day⁻¹ on average). Temperature, specific conductance (SC), DO, and pH also exhibited diurnal variability during all intervals (Figures 5b and 5c). Temperature showed maximum diurnal variability (Δ > 10°C day⁻¹) during April, May, and June intervals. Diurnal variability observed in SC was similar for all intervals, with average daily amplitudes of 0.01 mS cm⁻¹.
DO and pH exhibited similar patterns in diurnal variability throughout the study period. Average diurnal variability in pH increased from $\Delta < 0.5$ pH unit day$^{-1}$ in March to approximately $\Delta 2$ pH unit day$^{-1}$ in July and August. Average diurnal variability in DO concentrations ranged from $\Delta < 6$ mg l$^{-1}$ day$^{-1}$ in March, April, May, and September to $\Delta > 8$ mg l$^{-1}$ day$^{-1}$ in June, July, and August. Daily amplitude of $P$ and $R$ rates showed similar seasonal variations, with maximum values occurring in June, July, and August (Figure 5e). The daily amplitude of $\text{NO}_3^-$ concentrations were found to be positively correlated with daily amplitude of DO ($r^2 = 0.858$, $p < 0.0001$), pH ($r^2 = 0.644$, $p < 0.0001$), $P$ ($r^2 = 0.844$, $p < 0.0001$), and $R$ ($r^2 = 0.488$, $p < 0.0001$), all parameters whose diel variations are biological in origin (Figure 6a). Significant correlations were not observed between $\text{PO}_4^{3-}$ and DO ($r^2 = 0.048$), pH ($r^2 = 0.095$), $P$ ($r^2 = 0.022$), and $R$ ($r^2 = 0.020$) (Figure 6b). A significant positive correlation was not observed in daily amplitude of $\text{NO}_3^-$ or $\text{PO}_4^{3-}$ with that of temperature ($r^2 = -0.253$ and 0.030, respectively).

Timing of daily minimum and maximum values was consistent for all parameters over all intervals and all above-mentioned parameters showed peaks over 24 hour periods. River stage, temperature, $\text{NO}_3^-$, $\text{PO}_4^{3-}$, DO, pH, $P$, and $R$ reached maximum levels in the afternoon while SC exhibited maximum values at night (Figure 7). The first parameters to peak each day for all intervals were DO and $P$, consistently reaching maximum levels between 11:00 and 14:00 h. Temperature and $R$ were found to peak shortly after that, between 13:00 and 16:00 h. Maximum diurnal values of pH consistently occurred between 16:00 and 18:00 h, while $\text{NO}_3^-$ and $\text{PO}_4^{3-}$ concentrations typically peaked between 15:00 and 19:00 h. Minimum values reliably occurred 12 h from maximum values during all intervals (early morning minimums observed) for all
parameters except SC. Groundwater in well S2 exhibited minimal diurnal variability in temperature, DO, and pH (Figure 4). Temperature and pH showed no signs of diel variation, and only a slight discernible diurnal response ($\Delta < 0.01$ mg l$^{-1}$ day$^{-1}$) was observed in DO.

**Discrete Measurements**

Field parameter data collected on 10 June 2011 and 29-30 March 2012 groundwater sampling events exhibited significantly ($p < 0.0001$) higher levels of DO in the surface water (3.26 mg l$^{-1}$ on average) than groundwater (9.13 mg l$^{-1}$ on average) (Table 2). Although pH and temperature both exhibited lower levels in the groundwater relative to surface water (Table 2), variation in the time of sampling on both dates and high levels of diurnal variability in surface water makes statistical analysis of these differences assumptive. Field parameter results also revealed significant differences between groundwater and surface water SC and NO$_3^-$ levels. Groundwater was found to be on average higher in SC (115 mS cm$^{-1}$ compared to 67 mS cm$^{-1}$; $p < 0.0001$) and lower in NO$_3^-$-N (171.5 µM compared to 372.7 µM; $p < 0.0001$) than surface water (Table 2). Results from major ion analysis are further discussed in the following chapter and can be found in Appendix D.

Discrete measurements collected in duplicate and triplicate throughout the study period were highly variable among replicate samples and did not match well with in-situ NO$_3^-$ and PO$_4^{3-}$ data (Appendix B: Table 1 and Figure 1). It is suspected that our sample preservation (immediate freezing instead of immediate analysis) and the extremely low nutrient concentrations presented a problem for analysis. Discrete samples collected by the ISCO automated sampler beginning on 16 August, 2011 also deviated from
measurements obtained by in-situ instruments (Appendix B: Table 2 and Figure 2). Discrete NO$_3^-$ samples reflect much lower concentrations that in-situ results, possibly indicating another problem with sample preservation. Discrete PO$_4^{3-}$ samples, on the other hand, match fairly well with in-situ data. Despite the presence of a few outliers during early morning hours of 17 August 2011, discrete PO$_4^{3-}$ results are generally within 20% of in-situ results and show a similar diurnal trend (highest concentrations during the day and lowest concentrations during the night).

Although methods to obtain low detection limits were employed during IC analysis, grab sample results do not show the accuracy or precision necessary for data validation of our in-situ instruments. Accuracy of SUNA NO$_3^-$ readings were also investigated using calibration checks and laboratory standards. SUNA calibration was periodically checked using DI water and was out of range ($0.0 \pm 2 \mu$M) only twice during the deployment period (Appendix B: Table 3). In addition, on 20 June 2011 SUNA readings were checked on a series of laboratory prepared standards. SUNA readings during this test were highly accurate, reporting standard concentrations within an average of 6% of known value for standards $> 1.43 \mu$M and up to $14.28 \mu$M (Appendix B: Table 4).

**DISCUSSION**

*Seasonal Variability*

Continuous water quality monitors revealed seasonal variation in biogeochemical parameters and nutrient concentrations in the East Fork Jemez River. This variation appears to be a result of a combination of complex hydrological and biological processes, but is also strongly influenced by the Las Conchas fire of 2011. Large increases in SC,
NO$_3^-$, and PO$_4^{3-}$ between July and August intervals reflect an increase in nutrient and ion-rich monsoon floodwaters post-fire. Other parameters (temperature, DO, pH, P, and R) do not appear to be strongly affected by the fire pulses when comparing those two intervals pre- and post-flood event. During flood events, however, significant sags are observed in DO and pH (Sherson et al. unpublished). Although daily mean DO and pH values did not fluctuate greatly between seasons (Figure 4), increased daily variability was observed in these parameters during the summer months (Figure 5c). This can be attributed to higher levels of production and respiration in the summer than the spring and fall (Christensen et al. 1990) as a result of increased daytime sunlight and air temperature.

Nitrate (NO$_3^-$) concentrations also increased in the summer months (by approximately 5 µM), while PO$_4^{3-}$ concentrations were relatively constant for all measured intervals except August (post fire pulses). Seasonal changes in nutrient concentrations are typically attributed to alterations in hydrologic pathways (Grimm and Fisher 1986, Mulholland and Hill 1997, Holloway and Dahlgren 2001, Liu et al. 2008) and/or biological processes (Roberts and Mulholland 2007). Mulholland and Hill (1997) and Roberts and Mulholland (2007) reported maximum nitrate and phosphate concentrations during summer months in Tennessee streams, attributing this variation to increased in-stream nutrient uptake during spring and fall when shading from vegetation is at lower levels. Maximum levels of NO$_3^-$ were observed when P and R exhibited highest rates (summer), which suggests that biological uptake does not drive seasonal variability in nutrient concentrations. A strong correlation, however, existed between NO$_3^-$ variability and that of other biologically controlled parameters (DO and pH) on a
daily scale (Figure 6a), indicating that the drivers of this seasonal variability are, in fact, biological in origin. Although our results do not clearly elucidate what these biological mechanisms may be that lead to increased NO$_3^-$ concentrations in the summer, one hypothesis is that increased activity of primary producers and photo-degradation may result in organic nitrogen leakage and ammonification that stimulates nitrification during daylight periods.

Snowmelt and other seasonal precipitation events can also have substantial impacts on groundwater and surface water NO$_3^-$ concentrations and DO values (Dahm et al. 1998, Pellerin et al. 2012), but a minimal snowpack and subsequent snowmelt occurred in this watershed in 2011. In addition, river stage and downstream flows (Figure 2b) were relatively constant through the spring and summer, suggesting that hydrologic pathways do not control increased NO$_3^-$ during summer months. Alternatively, seasonal variation in nutrient concentrations during this period appears related to biological processes (NO$_3^-$) and catchment wildfire and subsequent hydrologic events (NO$_3^-$ and PO$_4^{3-}$).

**Diurnal Variability**

**Biological Control**

Nutrient uptake has been shown to increase with increased metabolism, due to stoichiometric demands (Hall Jr and Tank 2003, Webster et al. 2003, Hoellein et al. 2007). Hall and Tank (2003) found that gross primary production (GPP) explained 75% of the variation in NO$_3^-$ uptake velocity in 11 streams in Wyoming with low background nutrient concentrations. Nitrate uptake rates have also been investigated on a diurnal timescale in several studies. Uptake rates were reported as greater during midday hours
and cloud-free days by Mulholland et al. (2006), with variations attributed to primary productivity and light level. Fellows et al. (2006) and Roberts and Mulholland (2007) also reported an increase in uptake during daylight due to metabolic activity.

Although the above-mentioned body of literature details a common link between diurnal changes in metabolism and nutrient uptake rates, only a few of the studies also report nutrient concentrations. When examined, however, minimum concentrations of NO$_3^-$ were often found to occur during the day when GPP is at maximum levels (Roberts et al. 2007, Johnson and Tank 2009). Surface water NO$_3^-$ concentrations examined with near-real time or continuous measurements have exhibited minimum concentrations during the day (Heffernan and Cohen 2010, Heffernan et al. 2010, Pellerin et al. 2012), no discernible diurnal pattern (Pellerin et al. 2009), and two maxima and two minima per 24 hour period (Scholefield et al. 2005). Results from our study show an obvious diurnal pattern in NO$_3^-$ and PO$_4^{3-}$, with highest concentrations occurring consistently in the afternoon, only a few hours after P peaks (Figure 7). This suggests that assimilatory demand for NO$_3^-$ and PO$_4^{3-}$ is not the primary factor influencing temporal variability of nutrient concentrations in the water column.

The strong correlations observed between daily amplitudes of NO$_3^-$ and those of DO, pH, P, and R (Figure 6a), however, support the conclusion that biological processes likely play a secondary role in controlling NO$_3^-$ concentrations. Diurnal variation in nutrient concentrations can also be strongly influenced by the redox environment through biologically-mediated reactions (Duff and Triska 2000). With daily changes in pH between 0.5 and 2 pH unit day$^{-1}$ and DO concentrations ranging between 3-12 mg l$^{-1}$ during summer months and $> 2$ mg l$^{-1}$ even in early spring, it is possible that redox
reactions play a role in the variability observed in NO$_3^-$ concentrations. Additionally, nearby groundwater DO concentrations are consistently < 0.5 mg l$^-1$ (Figure 4), indicating that a strong gradient from oxic to anoxic conditions exists in the hyporheic sediments and benthic biofilms. Harrison et al. (2005) also observed a decrease in NO$_3^-$ concentration in the evening after photosynthesis stopped, and attributed this occurrence to the use of NO$_3^-$ as the most favorable electron acceptor under anoxic conditions when oxygen levels are sufficiently diminished.

The observed afternoon peak in NO$_3^-$ could also result from changing nitrification and denitrification processes in the stream and sediments. Nitrification, the microbially mediated oxidation of NH$_4^+$ to NO$_3^-$, only occurs in the presence of oxygen. This reaction is not only limited by NH$_4^+$ and oxygen availability, but can also be influenced by pH (Warwick 1986, Strauss et al. 2002), temperature (White et al. 1977), and ambient NO$_3^-$ concentrations (Bernhardt et al. 2002, Dodds et al. 2002, Hoellein et al. 2007). Bernhardt et al. (2002) attributed increased nitrification rates to higher background NO$_3^-$ concentrations, which functioned to reduce competition for NH$_4^+$ between nitrifiers and heterotrophs. Although previous work (Van Horn et al. unpublished) has found surface water NH$_4^+$ levels to be very low in this system, it is possible that nitrification pathways may be influencing changing NO$_3^-$, potentially supported by a significant correlation between NO$_3^-$ and pH (Figure 6b).

Denitrification, the reduction of NO$_3^-$ to N$_2$, tends to occur under anoxic conditions (< 0.5 mg l$^-1$) and can also impact surface water nutrient concentrations. Increased nighttime denitrification rates can result in higher NO$_3^-$ concentrations during the day (Harrison et al. 2005). Denitrification is also related to ecosystem respiration (Jones et al. 1995,
Mulholland et al. 2008) and can be influenced by NO$_3^-$ and O$_2$ concentrations (Christensen et al. 1990). During nighttime hours, for all intervals, we observe a diurnal hysteresis pattern in which NO$_3^-$ decreases while DO concentrations remain relatively constant (Figure 8a). This could be indicative of the occurrence of denitrification, or the consumption of NO$_3^-$ as an electron acceptor, both biological processes resulting from decreased DO levels during nighttime hours. Figure 8 also depicts the seasonal change in diurnal variability of NO$_3^-$ related to DO, with hysteresis loops expanding during the growing season (summer) and contracting into the fall during senescence.

In contrast to conclusions about the controls on NO$_3^-$, our results indicate that daily variation in PO$_4^{3-}$ concentrations is not strongly controlled by biological processes. PO$_4^{3-}$ is observed to peak at similar times to NO$_3^-$ and R (Figure 7), but the daily amplitudes of PO$_4^{3-}$ are not correlated with those of DO, pH, P, and R (Figure 6b). Phosphorus uptake can be influenced by ecosystem respiration (Mulholland et al. 1997, 2001), but that does not appear to be the primary driving factor on diurnal variation in this system. Previous research at this study site (Van Horn et al. unpublished) has found these systems to be nitrogen-limited with relatively long PO$_4^{3-}$ uptake rates. This also supports the conclusion that biological processes are more critical to NO$_3^-$ cycling than to that of PO$_4^{3-}$.

**Hydrological Control**

Hydrological processes may also have a strong influence on nutrient concentrations in streams. Increased discharge as a result of snowmelt or precipitation can function to affect chemistry through dilution, causing ion concentrations to decrease. Dilution processes may occur on a seasonal timescale, but also may be a result of individual precipitation events (Nagorski et al. 2003) or daily changes (Bales et al. 1993,
Diel fluctuations of snowmelt in mountain systems can cause increased discharge late in the day as a result of daytime melt patterns. Diurnal variations of stream discharge also exist due to variation in solar radiation and temperature. In evapotranspiration dominated systems, discharge is typically at maximum levels in the morning hours (Lundquist and Cayan 2002). Our observations indicate that SC is at minimum levels during late afternoon hours, when river stage is low but beginning to increase and reaches maximum levels in the early morning hours before river stage levels go down (Figure 7). In addition, NO$_3^-$ and PO$_4^{3-}$ concentrations are consistently highest when river stage begins to increase (Figure 7), indicating that dilution processes are not the primary control on diurnal variability in this ecosystem.

Diurnal fluctuations in river stage are observed that appear dominated by evapotranspiration in this system, and have also been observed in other studies (Burt 1979, Constantz 1998). In these systems, river stage levels are strongly responsive to PAR and air temperature. Mid-afternoon reductions in surface water flow can be attributed to increased evapotranspiration, but change in water temperature can also change hydraulic conductivity (Zellweger 1994, Holmes 2000). These processes may result in increased groundwater contribution to the surface water concentration, affecting diel shifts in water chemistry. Diurnal variation observed in SC with maximum values occurring at night) indicates that a hydrologic process is influencing surface water solute concentrations. Burt (1979) also observed a decrease in specific conductance during the day, attributing this pattern to relative contributions of groundwater and soil water sources that vary in chemical concentrations. Field parameter measurements (Table 2)
suggest that specific conductance is generally higher and that NO$_3^-$ concentrations are generally lower in the groundwater than the surface water, but nutrients are likely present in significant amounts in reduced forms (e.g. NH$_4^+$) in the shallow aquifer and can be rapidly transformed to NO$_3^-$ when in contact with oxygenated surface water (Findlay 1995, Jones and Holmes 1996, Dahm et al. 1998, Duff and Triska 2000). Higher stage levels during nighttime hours do not correspond precisely with highest surface water NO$_3^-$ concentrations, but it is possible that groundwater is delivering nitrogen-enriched water during nighttime that is later converted to NO$_3^-$ when redox conditions are optimal in the late afternoon hours. Increased stage levels during nighttime hours do coincide with higher SC values, possibly representing increased groundwater contribution during this time. Although increased groundwater contribution during late afternoon and evening hours cannot entirely explain diel variation in SC, NO$_3^-$, and PO$_4^{3-}$ due to the relative timing and magnitude of each process, it appears that evapotranspiration-dominated stage changes have some influences on solute concentrations in this system.

Adsorption to clays and iron oxides can also impact dissolved NO$_3^-$ and PO$_4^{3-}$ concentrations (Wetzel 2001). Dissolved oxygen and pH can strongly influence the adsorption (and desorption) of ions out of (and into) the water column. Reactions with soil minerals can function to remove PO$_4^{3-}$ from the water column (Schlesinger and others 1997, Hendricks and White 2000), and oxygen concentrations have been found to directly affect PO$_4^{3-}$ concentrations in lake sediments (Carlton and Wetzel 1988). Hendricks and White (2000) describe how the redox environment (controlled by DO and pH) can influence PO$_4^{3-}$ concentrations, finding that most studies have reported high pH and oxidizing conditions promote the removal of phosphate from solution through the
combination of \( \text{PO}_4^{3-} \) with iron hydroxides. Nitrate concentrations also can be dependent on adsorption and desorption processes. \( \text{NH}_4^+ \) can be adsorbed onto clays and organic material due to its positive charge. This can directly influence \( \text{NO}_3^- \) concentrations by limiting the \( \text{NH}_4^+ \) available for nitrification.

Although adsorption and desorption processes may play a role in the biogeochemical cycling in this system, lack of other high-frequency measurements (total phosphorus, total nitrogen, \( \text{NH}_4^+ \), etc.) makes these processes hard to tease apart from other biological and hydrological controls. In addition, preliminary analysis of the timing of nutrient peaks in relationship to those of DO and pH indicate that adsorption and desorption processes are not controlling the diurnal cycling observed here. Results suggest that a combination of biological and hydrological processes play integral roles in the diurnal cycling of nutrients and solutes in this stream, and that the hydrological processes involved are related to groundwater input, not abiotic retention.

**CONCLUSION**

Our study contributes to the growing body of literature investigating changes in nutrient concentrations and biogeochemical parameters on high-resolution timescales, with the seasonal and diurnal variability reported here highlighting the importance of continuous water quality monitoring to better understand biogeochemical cycling in headwater streams. We found maximum diurnal variability in \( \text{NO}_3^- \) concentrations to be greater than 50% of total seasonal variability observed (2.9 \( \mu \text{M} \) compared to ~5 \( \mu \text{M} \), respectively, excluding post-fire monsoon increases). In addition, maximum diurnal variability in DO and pH was greater than 80% of total seasonal variability observed (10.5 mg l\(^{-1}\) compared to 11.6 mg l\(^{-1}\) DO and 2.1 compared to 2.5 pH units). If diurnal
variability of water quality parameters, including nutrients, is as significant as suggested here, aquatic investigations based on traditional water quality grab sampling may be inadequate to describe and understand complete nutrient cycling on a diurnal basis.

Our results also demonstrate the complexity of hydrological and biological processes contributing to variability in surface water nutrient concentrations and the necessity of high-frequency data to accurately identify the drivers of this variability. Not only do nutrient concentrations vary naturally on a day-to-day basis due to biogeochemical and hydrologic processes, but variability in climatic and hydrologic conditions can also significantly affect measured concentrations. Climate change is expected to result in the alteration of precipitation and stream flow distributions throughout the year. Higher temperatures mean that a greater proportion of the winter precipitation falls as rain rather than snow (Knowles et al. 2006), and the snowmelt season begins earlier (Stewart 2009, Clow 2010, Pederson et al. 2011). Understanding the effects of changing precipitation regimes on nutrient concentrations is important from a management of water quality perspective.

Although we observe NO$_3^-$ and PO$_4^{3-}$ to fluctuate in phase (with peaks in the late afternoon), our results indicate a secondary biological control on diurnal variability in NO$_3^-$ but not PO$_4^{3-}$. Diurnal variability in other parameters, such as river stage and specific conductance, indicates that hydrological processes are also affecting surface water nutrient concentrations on a day-to-day basis. Uncertainty remains about the extent that each process plays on diurnal variability observed in this system, which should be investigated in the future using additional monitoring techniques. Quantification of nutrient consumption from metabolism calculations (Heffernan and Cohen 2010) and
application of stoichiometric models (Johnson et al. 2006) can be applied to this dataset for a better understanding on biological controls. Nutrient uptake rates and denitrification can also be measured, which will provide more insight on these processes and their influence on nutrient cycling. Ultimately, the combination of these established techniques to examine nutrient cycling needs to be used in conjunction with real-time water quality monitors to truly tease apart the controls on nutrient cycling in streams.
Figure 1. (a) Regional location map showing study site on the East Fork Jemez River and located within the Valles Caldera National Preserve (VCNP) (yellow line) and Jemez Watershed (light blue line) boundaries, (b) site map of shallow monitoring wells installed at the study site and surface water monitoring location (green circle), (c) photo of study site taken in summer 2010, and (d) photo of YSI sonde deployed in stream.
Figure 2. (a) Daily precipitation (mm) at the Valles Caldera flux towers and snow water equivalent (SWE) (cm) at Senorita Divide #2 (NRCS 2011), (b) streamflow (l s\(^{-1}\)) and river stage (m) in the East Fork Jemez River, and (c) Jemez River daily mean streamflow (l s\(^{-1}\)) and average daily mean streamflow (l s\(^{-1}\)) from 1954-2011 at Jemez River near Jemez, NM (08324000) (USGS 2011).
Figure 3. Continuous measurements of river stage (m), temperature (°C), DO (mg l⁻¹), pH, NO₃⁻ (µM), and PO₄³⁻ (µM) in the East Fork Jemez River between 15 March and 15 October 2011. Gaps in nutrient data are a result of battery connection problems (NO₃⁻; 27 August – 9 September 2011 and 12 September – 22 September 2011) and empty reagent cartridges (PO₄³⁻; 26 June to 11 July 2011). Gray bars represent weekly intervals selected for diurnal analysis (shown in Figure 5).
Figure 4. Continuous measurements of groundwater temperature (°C), pH, and DO (mg l⁻¹) in well S2 (blue) and daily mean surface water values (gray) in the East Fork Jemez River between 15 March and 15 October 2011. Battery failure resulted in a gap in groundwater data between 03 September and 22 September 2011.
Figure 5. Weekly intervals of continuous river stage (m), PAR (mumol m$^{-2}$ s$^{-1}$), specific conductance (mS cm$^{-1}$), temperature (°C), DO (mg l$^{-1}$), pH, NO$_3^-$ (µM), and PO$_4^{3-}$ (µM) in the East Fork Jemez River for selected week-long intervals between 15 March and 15 October 2011. Vertical lines represent a gap in time.
Table 1. Interval Averages and Standard Deviations

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SW = surface water (shaded gray), GW = groundwater.
Figure 6. Relationships between daily amplitude of (a) NO$_3$ (µM), (b) PO$_4^{3-}$ (µM), and DO (mg l$^{-1}$), pH, Temperature (°C), production (P) (mg O$_2$ l$^{-1}$ s$^{-1}$), and respiration (R) (mg O$_2$ l$^{-1}$ s$^{-1}$) for all weekly intervals. PO$_4^{3-}$ data from 23-29 May 2011 is excluded from these calculations and plots.
Figure 7. Box plots for all weekly intervals showing average time of occurrence for maximum (white box) and minimum (gray box) daily values. The boundaries of each box represent the 25th and 75th percentile of the data and the line through the center of each box represents the median value. PO$_4^{3-}$ data from 23-29 May 2011 is excluded from these calculations and plots.

Figure 8. Relationship between (a) NO$_3^-$ (µM) and DO (mg l$^{-1}$) and (b) NO$_3^-$ (µM) and pH during 2011 for each weekly interval in the East Fork Jemez River. Individual days are averaged into one representative day for the interval. All hysteresis patterns are counter-clockwise and 12:00 PM is represented by a red square.
REFERENCES


Sherson et al. Unpublished. Nutrient dynamics in a headwater stream: use of continuous water quality sensors to examine responses to wildfire and precipitation events.


CHAPTER 2

Nutrient Dynamics in a Headwater Stream: Use of Continuous Water Quality Sensors to Examine Responses to Wildfire and Precipitation Events

ABSTRACT

Stream water quality can change substantively over diurnal, event, and seasonal scales. In this study, event responses in surface water nutrient concentrations and biogeochemical parameters were assessed through deployment of continuous water quality sensors from March to October 2011 in the East Fork Jemez River, located in northern New Mexico (NM), USA. Events included four monsoon storms common in late summer in central NM and four non-monsoonal events (two in April and two in October). Two of the non-monsoonal and all four of the monsoon related events occurred after an extensive wildfire burned a significant portion of the contributing watershed. Surface water nitrate (NO$_3^-$) concentrations increased by an average of 50% after non-monsoonal precipitation events and were associated with small increases in turbidity (up to 15 NTU). Beginning one month after the start of a large regional wildfire, monsoonal precipitation events resulted in large multi-day pulses in NO$_3^-$ (>20 μM), phosphate (PO$_4^{3-}$) (>10 μM), specific conductance (SC) (>0.30 mS cm$^{-1}$ @ 25°C), and turbidity (>1200 NTU). These periods also correspond with substantial sags in dissolved oxygen (DO) (< 6 mg l$^{-1}$) and pH (< 6.5). Some studies report on increases in nutrient concentrations or sediment levels during and after precipitation and fire events, but few utilize the high-frequency data presented here. The short duration of and rapid rates of change during these events highlight the importance of continuous water quality monitoring to correctly quantify the timing and magnitude of event responses in streams.
INTRODUCTION

Nitrogen and phosphorus are important limiting nutrients in freshwater ecosystems that can be significantly impacted by precipitation and fire events. Snowmelt, rainfall, and regional fires substantially impact surface water nutrient concentrations and biogeochemical processes, with numerous solutes exhibiting a wide variety of responses during event periods (Walling and Webb 1986, Ranalli 2004). Surface water nutrient concentrations often increase dramatically during and immediately after snowmelt (Pellerin et al. 2012), precipitation events (McDiffett et al. 1989, Triska et al. 1990, Wondzell and Swanson 1996, Schlesinger and others 1997), and wildfires (Bayley et al. 1992, Earl and Blinn 2003, Burke et al. 2005, Lane et al. 2008, Mast and Clow 2008, Betts and Jones 2009, Blake et al. 2010, Rhoades et al. 2011). These events can also lead to increased sediment loads that may subsequently affect other biogeochemical parameters, such as dissolved oxygen and pH, due to impacts on primary production and respiration.

Climate change is expected to result in the alteration of precipitation and stream flow distributions throughout the year. Higher temperatures mean that a greater proportion of the winter precipitation falls as rain rather than snow (Knowles et al. 2006), and the snowmelt season begins earlier (Stewart 2009, Clow 2010, Pederson et al. 2011). In the southwestern United States, patterns of wildfire occurrence are also expected to undergo changes (Westerling et al. 2006, Allen et al. 2010). Understanding the impacts that snowmelt, precipitation events, and wildfires have on streams is important to assessing overall impacts of climate change on water quality. Large quantities of sediment delivered to streams after wildfires can be detrimental to the local and
downstream aquatic ecosystems through degraded water quality in addition to negatively affecting water supply (Meixner and Wohlgemuth 2004, Ranalli 2004, Goode et al. 2011, Smith et al. 2011).

Single events can cause significant changes in stream nutrient and biogeochemical dynamics (Dahm et al. 1998), but may go unnoticed using traditional grab-sampling techniques. Dramatically increased sampling frequency, made possible by recent developments in continuous water quality monitors (Kirchner et al. 2004), permit an increased understanding and quantification of biogeochemical responses to these events.

The purpose of this paper is to describe nutrient and biogeochemical responses to precipitation events throughout 2011 in a headwater stream located in north central New Mexico, USA. We used continuous water quality monitors to evaluate these responses at high resolution, and compare nutrient responses under typical precipitation events to those during post-wildfire precipitation events.

METHODS

Site Description

The Jemez mountain watershed is a snowmelt and monsoon-driven system in northern New Mexico (NM), USA that feeds into the Middle Rio Grande Basin of NM. Our study site (35.8411, -106.5013) was located on the East Fork Jemez River near the southern boundary of the Valles Caldera National Preserve (Figure 1), a federally operated preserve that encompasses ~350 square kilometers (VCNP 2012). The site was located in a high elevation (2,590 meters) expansive meadow valley with minimal overstory vegetation throughout the contributing basin. The 200 meter study reach was located within an elk exclosure consisting of a 160 by 160 m plot with a 2.5-m high fence
and includes 42 shallow monitoring wells. Discharge for the study reach typically averages between 50 - 150 l s$^{-1}$ (VCNP 2012), but increased substantively during precipitation events. Historically, the largest flows occur between March and May, and are attributed to snowmelt (VCNP 2010). Afternoon thunderstorms associated with North American Monsoon precipitation occurring between July and September account for approximately 50% of the annual precipitation in this area (Bowen 1996) and inversely varies in strength depending on snowpack extent during the previous winter (Gutzler 2000). Timing and magnitude of snowmelt and monsoons in this area are highly variable on an interannual scale, as represented by the high variability in Jemez River discharge (Figure 2).

**Continuous Measurements**

In situ measurements of nitrate (NO$_3^-$) and phosphate (PO$_4^{3-}$) were made using state-of-the-art real time nutrient analyzers. A Satlantic SUNA (Submersible Ultraviolet Nitrate Analyzer) provided readings of dissolved NO$_3^-$ using an ultra-violet adsorption method (Satlantic 2011). Measurements were made at 15-min or 30-min intervals from 15 March - 02 November 2011. Calibration and fouling checks on the SUNA were performed approximately monthly during the deployment, according to manufacturer specifications (Satlantic 2011). Measurements of PO$_4^{3-}$ were made at 1-hr intervals from 16 May to 9 September 2011 using a WETLabs Cycle-PO$_4$ dissolved phosphate analyzer. The Cycle-PO$_4$ analyzer uses micro-fluidics and state-of-the-art optics to measure the transmittance of a filtered water sample and calculate dissolved PO$_4^{3-}$ concentration (WETLabs 2011) using standard analytical wet chemistry method 365.5. Instrument servicing difficulties and battery failure resulted in several gaps in NO$_3^-$ and PO$_4^{3-}$ data.
In situ measurements of temperature, temperature corrected (25°C) specific conductivity (SC), dissolved oxygen (DO), pH, and turbidity were made using Yellow Springs Instruments (YSI) model 6920 V2 sondes. Measurements were made at 15-min intervals from 15 March to 02 November 2011. Fouling checks and calibrations of the YSI sonde were performed every 3-4 week using known standards (SC and pH sensors) and 100% water-saturated air (optical DO sensors).

River stage data from March to October 2011 was obtained from a pressure transducer co-located with the nutrient instruments and corrected with local barometric pressure. Precipitation data was obtained from the Valles Caldera National Preserve Headquarters (11) meteorological station (35.8582, -106.5211). Snowpack data was acquired from the National Resources Conservation Services (NRCS) Senorita Divide #2 SNOTEL site (36.0000, -106.8333). East Fork Jemez streamflow data was obtained from the Valles Caldera National Preserve at the Hidden Valley Gage, approximately 0.5 km downstream from our study site. Jemez River streamflow was obtained from the U.S. Geological Survey (USGS) at Jemez River near Jemez, NM (08324000)(35.6620, -106.7434).

**Discrete Measurements**

Discrete surface water nutrient samples were collected in duplicate or triplicate approximately every 7-10 days throughout the study period to check sensor readings. Samples were filtered through 0.45 µM filters in the field and immediately frozen upon return to the laboratory. Discrete surface water samples were also collected every hour over a 24-hour period on 16 August 2011 using an ISCO automated sampler. Each sample was pumped from the stream into a container preserved with 0.25 ppm phenyl
mercuric acetate (PMA). Samples were collected at the end of the 24 hour period, filtered in the laboratory, and immediately frozen before analysis. Groundwater and surface water samples were also collected on 10 June 2011 (nine groundwater samples), 13 October 2011 (9 groundwater samples), and 29-30 March 2011 (27 groundwater samples) in selected wells following standard USGS protocols (USGS 2006). On each date two samples were collected from each location (using a pump or bailer for groundwater wells), an unfiltered raw sample for alkalinity and anion analysis and a filtered (0.45 µM) and acidified (nitric acid (HNO₃)) sample for cation analysis. Field parameters were also collected on 10 June 2011 (pH, DO, and SC) and 29-30 March 2011 (pH, DO, SC, and NO₃⁻) sampling events using a YSI sonde (June) and a YSI Professional Plus (Pro Plus) field meter (March).

Alkalinity was determined using acid titration (0.020N sulfuric acid (H₂SO₄)) and then samples were filtered prior to anion analysis. Anion samples were analyzed using ion chromatography (IC) and cation samples were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) in the Department of Earth and Planetary Sciences analytical laboratory at the University of New Mexico in Albuquerque, New Mexico. A low-detection method was employed for IC analysis, consisting of low concentration standards (0.05 - 1 mg l⁻¹) and long sample loops (250 or 1000 µM). For discrete nutrient samples collected in triplicate, if NO₃⁻ or PO₄³⁻ in one sample was > 100% greater than the other two, that single grab sample was removed from the dataset and considered to be invalid.

**Data Processing and Analysis**
Nitrate measurements made with the SUNA were logged to an external STOREX data logger and post-processed using Satlantic software (SatCon and SUNACom, Satlantic 2011). Data were collected in 1 Hz intervals and those collected after 20 seconds (allowing for a warm-up period) were averaged to create a single NO$_3^-$ concentration for that sampling interval. Data were corrected using AQUARIUS software (Aquatic Informatics 2011) to address outliers, fouling shifts, and data gaps. Fouling shifts were applied on 9 April 2011 (-0.71 μM) and 7 July 2011 (+0.71 μM), and low quality data was deleted between 30 May – 22 June 2011.

Data for PO$_4^{3-}$ were logged internally on the Cycle-PO$_4$ analyzer. Outliers were addressed using quality control algorithms developed and applied by WETLabs. Low quality data were removed primarily during the weeks following the installation of new reagent cartridges, exchanged on 16 May and 11 June 2011. Temperature, SC, DO, pH, and turbidity data were closely examined to remove erroneous values during calibration visits. In addition, Aquarius was used to apply shifts in SC, DO, and pH when necessary due to fouling or calibration drift. Shifts were applied based on calibration data and field parameter measurements made during calibrations. A detailed description of sondes and data corrections is included in Appendix A. Eight event periods were identified in 2011, two in April (precipitation after snowmelt), four throughout August and early September (post-wildfire monsoons), and two in October (precipitation after monsoon season). A Butterworth filter with five poles was used to remove the diurnal signal present during the events before hysteresis analysis (Appendix C).

RESULTS
Winter precipitation in 2010-2011 yielded a below-average snowpack in this region (NRCS 2011), and discharge in the East Fork Jemez averaged approximately 85 l s\(^{-1}\) for most of the year (VCNP 2012). This corresponded to an average local stage level of approximately 0.3 m, which increased slightly during selected non-monsoonal precipitation events in April and October (Figure 3b) and substantially during August monsoons (Figure 4b). Beginning on 26 June 2011, the Las Conchas fire burned 156,593 acres primarily south and east of the study site, but included drainage areas feeding into the East Fork Jemez (InciWeb 2011).

Continuous data exhibited variability on seasonal, event, and diurnal scales (Figures 3 and 4). Seasonal and diurnal variability are examined in detail in Chapter 1 of this thesis. Sondes and nutrient sensors captured biogeochemical and nutrient responses to precipitation events throughout the study period (15 March to 02 November 2011); but substantial event-related increases in nutrient concentrations were only observed in the months of April, August, September, and October (Table 1). These responses were related to snowmelt and rainfall (April and October) and monsoon events that occurred after the Las Conchas fire (August to mid-September).

**Precipitation Responses**

Continuous data revealed four strong non-monsoonal precipitation events with biochemical responses in the East Fork Jemez River (beginning on 07 April, 24 April, 04 October, and 26 October) (Figure 3). Other minor events were observed during the study period, but none as significant as the four identified here. For April events, river stage increased from approximately 0.30 m to 0.33 m for periods of 6-7 days in duration following local precipitation events. During events initiated on 04 October and 26
October, river stage increased from approximately 0.27 m to 0.36 m and was sustained for durations of 11 and 7 days, respectively (Figures 3a and 3b). Diurnal variability observed in temperature (Figure 3b), DO and pH (Figure 3c) was reduced substantively during the October events, but only minimally during the April events. Specific conductance exhibited minimal response during the April events, with only a slight decrease in diurnal variability observed. October precipitation events, on the other hand, resulted in an increase of approximately 0.02 mS cm\(^{-1}\) for SC. Turbidity levels were found to increase rapidly over the initial 24-48 hours of each precipitation event by approximately 5-10 NTU and subsequently decline to previous levels over the next 4-6 days (Figure 3d). Nitrate concentrations during all four precipitation event periods increased from ambient levels of approximately 4 µM to > 7 µM in similar fashion to turbidity (rapid increase and gradual descending limb) (Figure 3e).

**Monsoon/Fire Responses**

Approximately one month after the beginning of the Las Conchas fire, monsoonal precipitation events resulted in large pulses in NO\(_3^-\) (> 20 µM), PO\(_4^{3-}\) (> 10 µM), specific conductance (> 0.30 mS cm\(^{-1}\)), and turbidity (> 1200 NTU). These periods corresponded with multi-day sags in DO and pH (Figure 4). Precipitation events resulted in river stage increases of between 0.1 and 0.4 m; with the three largest pulses occurring over several days between 21 August and 09 September (Figure 4b). Overbank flow could have occurred during these events, due to the magnitude of stage change, possibly impacting the intensity of these observations. Diurnal variability of temperature exhibited minimal change during the event periods (Figure 4b), but was almost completely removed for DO and pH. For the four primary event periods (beginning 04 August, 21
August, 28 August, and 05 September), DO (< 4 mg l\(^{-1}\)) and pH (to ~6) sags were observed for periods of 2-3 days (Figure 4c).

Specific conductance, turbidity, and nutrient concentrations increased simultaneously with all monsoon events during the study period (Figures 4d and 4e). The initial pulse (04 August) resulted in greater increases in specific conductance (0.10 to 0.33 mS cm\(^{-1}\)) than turbidity (0 to 300 NTU). The three latter pulses (21 August, 28 August, and 05 September) showed the opposite pattern of response in the same parameters. During these events, increases in turbidity (0 to > 1200 NTU) were more substantial than those of specific conductance (0.11 to ~ 0.20 mS cm\(^{-1}\)) (Figure 4d). Nutrient concentrations also increased during event periods (Figure 4e), with NO\(_3^-\) increasing from ~9 to > 20 µM and PO\(_4^{3-}\) increasing from ~1 to > 12 µM. Data gaps resulting from battery failure (NO\(_3^-\), 27 August to 09 September) and instrument difficulties from high turbidity (NO\(_3^-\) and PO\(_4^{3-}\) during all pulses prior to 27 August) indicate that nutrient concentrations recorded during these pulses most likely underestimate true maximum concentrations.

**Event Comparison**

Changes in streamflow were compared to variation in solute levels in order to compare events and better understand flowpaths. Although exact streamflow values are not available at the study site (downstream flows may be inaccurate due to flow escaping the channel banks), high resolution river stage data can be utilized as an approximation for changes in flow during precipitation events. Hysteresis loops were generated to investigate and compare the relationship between discharge (river stage) and turbidity, SC, and NO\(_3^-\) during non-monsoonal precipitation event periods (Figure 5). A counter-
clockwise pattern was observed in NO\textsubscript{3} during April and October precipitation events with increased river stage and NO\textsubscript{3} concentrations during the October events. A similar relationship (counter-clockwise) was observed for turbidity during April events, with October events varying in direction but exhibiting more of a linear trend with river stage. Specific conductance exhibited little variation during April precipitation event periods, but showed clear counter-clockwise hysteresis during October precipitation events. Turbidity and NO\textsubscript{3} data were not collected at the study site prior to 2011, but sondes installed during 2010 captured precipitation events during the fall representative of pre-fire conditions. A precipitation event in the East Fork Jemez River in October of 2010 resulted in increased river stage and SC, also with a counter-clockwise pattern, but with a much different shape than post-fire events during October of 2011 (post-fire) (Figure 5).

**Discrete Measurements – Nutrient Validation Samples**

Discrete measurements collected in duplicate and triplicate throughout the study period were highly variable among replicate samples and did not match well with in-situ NO\textsubscript{3} and PO\textsubscript{4}\textsuperscript{3-} data (Appendix B: Table 1 and Figure 1). It is suspected that our sample preservation (immediate freezing instead of immediate analysis) and the extremely low nutrient concentrations presented a problem for accurate laboratory analysis. Discrete samples collected by the ISCO automated sampler beginning on 16 August, 2011 also deviated from measurements obtained by in-situ instruments (Appendix B: Table 2 and Figure 2). Discrete NO\textsubscript{3} samples reflect much lower concentrations that in-situ results, indicating another problem with sample preservation. Discrete PO\textsubscript{4}\textsuperscript{3-} samples, on the other hand, match fairly well with in-situ data. Despite the presence of a few outliers during early morning hours of 17 August 2011, discrete PO\textsubscript{4}\textsuperscript{3-} results are generally within
20% of in-situ results and show a similar diurnal trend (highest concentrations during the day and lowest concentrations during the night).

Although methods to obtain low detection limits were employed during IC analysis, grab sample results do not show the accuracy or precision necessary for data validation of our in-situ instruments. Accuracy of SUNA NO$_3^-$ readings were also investigated using calibration checks and laboratory standards. SUNA calibration was periodically checked using DI water and was out of range (0.0 ± 2 µM) only twice during the deployment period (Appendix B: Table 3). In addition, SUNA readings were checked on a series of laboratory prepared standards on 20 June 2011. SUNA readings during this test were highly accurate, reporting standard concentrations within an average of 6% of known value for standards > 1.43 µM and up to 14.28 µM (Appendix B: Table 4).

**Discrete Measurements – Major Ion Results**

Field parameter data collected on 10 June 2011 and 29-30 March 2012 during groundwater sampling exhibited significantly (p < 0.001) higher levels of DO in the surface water (9.13 mg l$^{-1}$ on average) than groundwater (3.26 mg l$^{-1}$ on average) (Table 2). Although pH and temperature both exhibited lower levels in the groundwater relative to surface water (Table 2), variation in the time of sampling on both dates and high levels of diurnal variability in surface water makes statistical analysis of these differences problematic. Field parameter results also revealed significant differences between groundwater and surface water SC and NO$_3^-$ levels. Groundwater was found to be on average higher in SC (115 mS cm$^{-1}$ compared to 67 mS cm$^{-1}$; p < 0.001) and lower in NO$_3^-$ (171.5 µM compared to 372.7 µM) than surface water (Table 2). Although the difference between groundwater and surface water NO$_3^-$ was statistically significant (p
<0.001), the accuracy and precision of the data recorded with the YSI Professional Plus (Pro Plus) field meter is assumed to be poor. Nitrate is measured with an ion-selective probe on this meter and is questionable due to poor performance during laboratory testing of low NO₃⁻ concentrations and problems with calibration.

Major ion data collected from surface water and groundwater on 10 June 2011, 13 October 2011, and 29-30 March 2012 are detailed in Appendix D and indicate that general water chemistry is similar between locations for all sample dates, but that the Las Conchas fire altered chemistries in both surface water and groundwater. Bicarbonate is the dominant anion in all samples, with calcium and sodium dominating the cation chemistry (Figure 6). Substantial changes were not observed in relative cation composition before and after the fire, but an increase in sulfate (surface water and groundwater samples in October 2011 and groundwater samples in March 2012) and chloride (surface water and selected groundwater samples in March 2012) was observed (Figure 6). Nutrient results (NO₃⁻ and PO₄³⁻) from this dataset were not analyzed due to exceedance of hold times and sample preservation issues.

DISCUSSION

Analysis of four non-monsoonal precipitation events and associated stage changes revealed an increase in turbidity and NO₃⁻ concentrations that is of similar pattern and magnitude for all events. Precipitation events can function to flush groundwater with higher nutrient concentrations (Triska et al. 1990, Wondzell and Swanson 1996, Pellerin et al. 2012), turbidity, and organic matter (Saraceno et al. 2009) into surface water, and rainfall/runoff can directly contribute to increased nutrient and sediment levels in streams (Schlesinger and others 1997.) Field parameter data and previous work in this area has
revealed that groundwater NO$_3^-$ concentrations are, in fact, lower than those found in surface water (Valett et al. 1996), likely due to the reducing nature of the groundwater compared to the surface water at this site (Table 2), but has also found shallow soils to contain significant amounts of nitrogen (Van Horn et al. unpublished). Biogeochemical reactions are enhanced within groundwater as is kept in contact with subsurface minerals and microbial communities during subsurface exchange (Findlay 1995, Jones and Holmes 1996), and contribute to increased nitrogen and phosphorus levels in these areas. Increases in groundwater levels following precipitation events were first observed in wells furthest away from the stream (Appendix C), supporting the hypothesis that pulses of groundwater were moving through the shallow aquifer into the stream during these periods (i.e., the stream was gaining).

The counterclockwise pattern observed in the relationship between river stage and SC, turbidity, and NO$_3^-$ (Figure 5) during these periods also indicate slow diffusion of groundwater into surface water during non-monsoonal precipitation events. Many studies have examined the relationship between streamflow and solute or sediment concentrations during precipitation events to investigate sources contributing to increased runoff (McDiffett et al. 1989, Williams 1989, House and Warwick 1998, Evans and Davies 1998, Bowes et al. 2005, Butturini et al. 2005). Often a pattern of hysteresis is discovered, in which greater values of certain chemical constituents are different on the rising limb of the hydrograph compared to similar discharge on the falling limb (Walling and Webb 1986). Commonly these patterns can be related to an initial flushing of the system at the beginning of an event (Walling and Webb 1986, Evans and Davies 1998) and vary depending on distance downstream (Bowes et al. 2005). Pellerin et al. (2012)
observed a counterclockwise relationship between streamflow and dissolved organic matter (FDOM) using continuous instrumentation, characterized by different patterns during snowmelt and rainfall events.

Snowmelt events are expected to result in different biogeochemical responses than those associated with monsoon or other precipitation events. This can be due to the source of the water itself, or the alteration of hydrologic pathways expected during such events (Mulholland and Hill 1997, Dahm et al. 1998, Liu et al. 2008). Pellerin et al. (2012) observed that NO$_3^-$ concentrations peaked during maximum snowmelt and in a Vermont watershed. Nitrate concentration also increased during precipitation events after snowmelt had subsided, but these responses were relatively muted. The similarity we observed in nutrient and biogeochemical responses to precipitation events occurring in April and October (Figure 3) indicate that snowmelt had minimal influence on the precipitation events in April, likely attributable to much reduced snowpack and subsequent muted snowmelt experienced in 2011 in this region (Figure 2).

Storm events were also found to affect specific conductance in our study, with an increase during the October events and a slight reduction during the April precipitation events (Figure 3). We hypothesize that this difference can be attributed to post-fire effects in the watershed. Increased levels of discharge as a result of precipitation can affect water chemistry through dilution, causing ion concentrations to decrease (Nagorski et al. 2003, Saraceno et al. 2009); but that does not appear to be the case in this system. Temperature, DO, and pH also exhibit a response during these precipitation events, with a slight reduction in diurnal patterns (Figure 3). A dampening of the diurnal signal in these parameters can be attributed to reduced sunlight and in-stream photosynthesis and has
been reported in other studies using continuous water-quality monitors (Roberts et al. 2007, Saraceno et al. 2009).

Sediment transport processes and nutrient biogeochemistry during the study period were also greatly affected by the Las Conchas fire of 2011 and subsequent precipitation events. Rapid increases in turbidity and nutrient concentrations were observed during four distinct monsoon rainfall events between 01 August and 10 September (Figure 4). Increases in nutrients post-fire have also been observed in other fire-affected watersheds (Bayley et al. 1992, Earl and Blinn 2003, Burke et al. 2005, Lane et al. 2008, Mast and Clow 2008, Betts and Jones 2009, Blake et al. 2010, Rhoades et al. 2011) as a result of nutrient-rich ash and debris reaching the stream channel. Post-fire increases in nutrient concentrations are ultimately controlled by the proximity and severity of the fire, the magnitude of precipitation events post-fire, and the slope steepness and vegetation type and distribution within the catchment (Ranalli 2004). The large increases we observed in surface water nutrient concentrations (> 10-fold increase for dissolved $\text{PO}_4^{3-}$ and > twofold increase for dissolved $\text{NO}_3^-$) occur after monsoon rainfall events and coincide precisely with large increases in river stage (Figure 4), indicating that post-fire precipitation is the primary control on timing of nutrient increases during August and September.

Although instrument difficulties in handling very high turbidities during the peaks of these monsoon flow events did not allow the capture of the entirety of nutrient responses, dissolved nutrient data indicate that $\text{PO}_4^{3-}$ concentrations increased at higher rates than $\text{NO}_3^-$ concentrations during the initial pulse beginning on 04 August. This monsoon pulse also had higher SC but lower turbidity values (Figure 4d) than the three
subsequent pulses (21 August, 28 August, and 05 September). Stage changes were much
greater (Figure 4a) during the three latter pulses, suggesting that sediment loading from
the burned areas during these events was substantial. We hypothesize that increased
levels of PO$_4^{3-}$ and specific conductance during the initial pulse may be related to more
ash entering the stream, while the latter pulses were dominated by sediment and debris
flow.

Wildfires, when coupled with precipitation events, can lead to substantial
sediment loading in streams (Moody and Martin 2009) and can have detrimental impacts
on downstream water management and aquatic habitat (Goode et al. 2011). Increased
sediment loads (turbidity values > maximum instrument range of 1000 NTU) (Figure 4d)
resulted in DO and pH sags (Figure 4c) during the post-fire monsoon pulses that were
sustained over several days and could be followed downstream through the Jemez River
and Rio Grande (unpublished data). Low levels of DO and pH can be severely
detrimental to the aquatic community, particularly when sustained for several days. The
sags we documented during these events were likely linked to the high sediment load
present in the stream and the inhibition of in-stream photosynthesis. Other studies
examining DO and pH responses during post-fire flow events and over subsequent years
after forest fires have reported various responses. For example, Raison et al. (1990) found
surface water pH to increase during ash flow events in an Australian stream while Hall
and Lombardozzi (2008) examined wildfire effects on Colorado streams and found lower
DO but no change in pH two years post-burn.

Our results showed minimal non-precipitation related fire effects on surface water
nutrient concentrations and biogeochemical properties during the fire but prior to
initiation of the monsoon season. Despite high levels of smoke in the atmosphere for a majority of July, DO and pH data show little impact on photosynthetic processes during this time (Figure 4c). NO$_3^-$ and PO$_4^{3-}$ concentrations exhibited minimal increases until monsoon flow events in August (Figure 4e). Spencer and Hauer (1991) observed a strong increase in phosphorus and nitrogen species during a wildfire in northwest Montana, attributing ash deposition and smoke diffusion as the sources of nutrients. Several sites in the Spencer and Hauer (1991) study were located within the burn area of the wildfire, likely leading to a more significant effect on water chemistry during the initial stages of fire.

Wildfires have also have been shown to affect stream biota (Earl and Blinn 2003, Minshall 2003, Spencer et al. 2003) and metabolism rates (Betts and Jones 2009). The close link between nutrient biochemistry and stream metabolism (Hall Jr and Tank 2003, Fellows et al. 2006, Mulholland et al. 2006) and the widespread damage possible to drainage areas suggests that wildfires can affect nutrient cycling in indirect and direct ways for periods long after the initial disturbance. Surface water nutrient concentrations post-wildfire have been shown to remain elevated for time frames ranging from one to three years (Hall and Lombardozzi 2008), four to five years (Spencer et al. 2003, Mast and Clow 2008, Rhoades et al. 2011), and up to nine years (Bayley et al. 1992). In a summary of fire influences on surface water nutrient concentrations, Ranalli (2004) found that, on average, most studies report elevated NO$_3^-$ concentrations for three to five years and elevated PO$_4^{3-}$ concentrations for one to two years after fire occurrence. This continuous dataset has documented biogeochemical response in the months immediately following wildfire and preliminary grab samples taken in March 2012 (Figure 5, Table 2,
Appendix D) indicate increased NO$_3^-$ concentrations and altered major ion makeup during post-fire snowmelt in 2012.

Non-monsoonal precipitation events pre-fire and post-fire also exhibited different hysteretic patterns. Non-monsoonal precipitation events just after snowmelt in April exhibited little change in SC, but showed sharp increases followed by gradual decreases in NO$_3^-$ and turbidity (Figure 5) that were likely related to the flushing of these parameters into surface water from soil and groundwater stores. During post-fire monsoons in August and September, SC and turbidity exhibited rapid and substantial increases that were sustained throughout the event for SC but not turbidity. This suggests that turbidity increases were caused by fire-related debris and sediment, while dissolved ion concentrations remained high after these particulate pulses. Non-monsoonal precipitation events in October showed increased NO$_3^-$ and turbidity compared to those in April and increased SC compared to events in April and October of 2010. Because seasonal changes in SC can be excluded from causing this difference due to the interannual comparison and similarity in stage increases, these hysteresis loops indicate that fire effects remain in the system during October of 2011. In summary, these relationships between biogeochemical constituents and river stage highlight the different hydrologic processes that contribute to changes in stream water quality during precipitation event periods and the variability in responses revealed by continuous monitoring.

CONCLUSION

Our results show the importance of continuous water quality monitors to accurately quantify the timing and magnitude of nutrient and biogeochemical responses
to storms and wildfire. High resolution data collected during these events allows for a much more precise understanding of the timing and magnitude of event responses, often occurring over periods of hours or days. Increases in surface water NO$_3^-$ and turbidity during non-monsoonal precipitation events post-snowmelt reflect a flushing of nutrient-rich groundwater that increased in magnitude between April and October events. Increases in SC were observed in October, but not April, indicating that effects of summer wildfire remain in the system for months after the fire. In addition, multi-day pulses of NO$_3^-$PO$_4^{3-}$, SC, and turbidity corresponding with sags in DO and pH were measured in late summer. These large pulses occurred after the fire was 100% contained (InciWeb 2011) during high intensity monsoonal precipitation. The and timing and magnitude of these results show substantial impacts of forest fire on water quality, but also that high intensity precipitation events are critical for the delivery of fire-related nutrients and sediment loads to streams within and well outside of the burned area.

Climate change and human activities have contributed to shifts in snowmelt runoff and precipitation regimes (Knowles et al. 2006, Stewart 2009, Clow 2010, Pederson et al. 2011) and an alteration of wildfire patterns in recent history. Westerling et al. (2006) reviewed forest fire occurrence in the western United States in recent decades and found an increase in wildfire frequency, duration, and season length. The Las Conchas fire was the largest recorded forest fire in New Mexico history at the time, and we expect that surface water in the Jemez Watershed and Rio Grande Basin will show effects from this event for several years to come. Currently, forest management practices are underway to reduce the risk of large fires in other parts of the Jemez watershed. All of
the precipitation events examined here, although of different magnitude and duration, result in an increase in surface water nutrient concentrations and turbidity levels.

Biogeochemical responses to storm events can occur over hours, days, or weeks, and cannot be accurately measured without high resolution data. Significant increases in nutrient concentrations and turbidity levels observed in this study occur rapidly during precipitation events and can have detrimental impacts to downstream water quality and ecosystem health. Specifically, substantial suspended sediment and nutrient pulses can lead to downstream eutrophication, increased sediment and nutrient loading, and dangerously low levels of DO (Ranalli 2004). Continuous water quality monitors deployed during storm events provide valuable insight concerning how streams and rivers respond to disturbance to inform management and mitigation of climate change and wildfire impacts on water quality.
Figure 1. (a) Regional location map showing the study site on the East Fork Jemez River and located within the Valles Caldera National Preserve (VCNP) (yellow line) and Jemez Watershed (light blue line) boundaries, (b) site map of shallow monitoring wells installed at the study site and surface water monitoring location (green circle), (c) photo of study site taken in summer 2010, and (d) photo of YSI sonde deployed in stream.
Figure 2. Jemez River near Jemez discharge from USGS gage 08324000 (USGS, 2011). High interannual variability in timing and magnitude of snowmelt is observed. Extreme values of high snowmelt in 2010 (orange) and low snowmelt in 2011 (pink) are highlighted.

Table 1. Precipitation events and Biogeochemical Responses

<table>
<thead>
<tr>
<th>Storm Initiation Date</th>
<th>Duration of Stage Increase (days)</th>
<th>Event precipitation (mm)</th>
<th>Stage Increase (m)</th>
<th>Maximum SC (ms cm^-1)</th>
<th>Maximum Turbidity (NTU)</th>
<th>Comment</th>
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<td>07 April 2011</td>
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<td>0.10</td>
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<tr>
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<td>6</td>
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<td>0.33</td>
<td>330.1</td>
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<tr>
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<td>965.6</td>
<td>Post-fire monsoon</td>
</tr>
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<td>0.31</td>
<td>1179.3*</td>
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<tr>
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<td>0.20</td>
<td>1174.4*</td>
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</tr>
<tr>
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<td>0.12</td>
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</tr>
<tr>
<td>26 October 2011</td>
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Turbidity measured beginning 28 August and 05 September (*) are outside of the manufacturer’s specified range (0-1000 NTU). Event precipitation (mm) includes precipitation before and during event periods and is from the Valles Caldera National Preserve Headquarters Site (VCNP, 2012).
Figure 3. Continuous measurements during event periods of (a) precipitation (mm) from the VCNP Headquarters meteorological station, (b) river stage (m) and temperature (°C) (c) DO (mg l\(^{-1}\)) and pH, (d) SC (mS cm\(^{-1}\)) and turbidity (NTU), and (e) NO\(_3\) (µM) in the East Fork Jemez River between 02 April and 02 May 2011 (left) and 02 October and 02 November 2011 (right).
Figure 4. Continuous measurements during post-fire monsoons of (a) precipitation (mm) from the VCNP Headquarters meteorological station, (b) river stage (m) and temperature (°C) (c) DO (mg l\(^{-1}\)) and pH, (d) SC (mS cm\(^{-1}\)) and turbidity (NTU), and (e) NO\(_3^-\) (µM) and PO\(_4^{3-}\) (µM) in the East Fork Jemez River between 26 July and 14 September 2011.
Table 2. Field Parameter Data from Groundwater Sampling Events

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<th>Sample ID</th>
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<th>Sample Date</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>DO (mg l⁻¹)</th>
<th>SC (µS cm⁻¹)</th>
<th>NO₃-N (mg l⁻¹)</th>
<th>NO₃ (µM)</th>
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</table>

SW = surface water (shaded gray), GW = groundwater.
Figure 5. Relationship between river stage (m) and specific conductance (SC) (ms cm$^{-1}$), turbidity (NTU), and NO$_3^-$ (µM) during non-monsoonal precipitation event periods of 2011 and 2010. April 2011 (teal and blue) and October 2011 (orange and red) events show counter-clockwise hysteresis for SC (October), turbidity (April), and NO$_3^-$ (April and October). Arrows represent the direction of hysteresis.
Figure 6. Piper diagram showing major ion results in mole fraction percent from groundwater (circles) and surface water (squares) samples collected on 10 June 2011 (black), 13 October 2011 (teal), and 29-30 March 2012 (red). October and March sampling events occurred after the Las Conchas wildfire of 2011.
REFERENCES


68


STATION ANALYSIS

STATION NAME: East Fork Jemez River – Lower (EFSWL)

STATION LOCATION: East Fork Jemez River (364405, 3967339)

PERIOD OF RECORD: 5/17/10-1/10/12

DESCRIPTION OF EQUIPMENT:

YSI 6920V2 Sonde

PARAMETERS MEASURED:

Temperature, pH, Specific Conductance, ROX Optical Dissolved Oxygen, Turbidity

MEASUREMENT METHOD:

The sonde was positioned horizontally in the stream channel facing downstream. A protective stainless steel casing was used to cover the sonde beginning in November 2010. Measurements were recorded at 15 minute intervals.

CALIBRATION DATES:


MAJOR DATA GAPS/REMARKS:

- Turbidity probe bad 5/17/10 - 11/18/10
- Turbidity periodically reading out of range 11/18/10 – 6/22/11; data deleted 5/1/11 – 6/22/11
- Turbidity reading negative, various dates
- Specific Conductance suspected fouling 8/3/10 - 8/20/10
Figure 1. Raw (red) and corrected (orange) sonde data from the East Fork Jemez River, 17 May 2010 to 10 January 2012. Data were corrected for fouling and calibration shifts using Aquarius software.
STATION ANALYSIS

STATION NAME: East Fork Jemez River – S2 (EFS2)

STATION LOCATION: East Fork Jemez River Meander (364416, 3967341)

PERIOD OF RECORD: 8/20/10 – 1/10/12

DESCRIPTION OF EQUIPMENT:

YSI 600XLM Sonde

PARAMETERS MEASURED:

Temperature, pH, Specific Conductance, ROX Optical Dissolved Oxygen, Depth

MEASUREMENT METHOD:

The sonde was hung vertically from the top of well casing. Measurements were recorded at 15 minute intervals from 8/20/10 – 9/3/11 and 1 hour intervals 9/3/11 – 1/10/12

WELL CHARACTERISTICS:

Installed 6/15/2010 using 2-inch PVC composed of a solid upper casing and a screened intake that intersects the watertable.

Total Well Length = 201.5 cm

Casing Height = 90.0 cm

Total Screen Length = 93.0 cm

Effective Screen Length = 81.5 cm

Elevation = 2583.28 m

CALIBRATION DATES:


MAJOR DATA GAPS/REMARKS:

- Sonde frozen in, batteries dead 1/23/11 - 5/4/11
- Specific Conductance questionable 8/20/10– 7/27/11 due to questionable calibration data
- Depth data for entire period has not been corrected with barometric pressure changes
- Overland flow likely occurred in August of 2011 during monsoon pulses, possibly affecting some of the parameters
Figure 2. Raw (red) and corrected (orange) sonde data from Well S2, 21 August 2010 to 10 January 2012. Sonde was frozen in well during spring 2011. Data were corrected for fouling and calibration shifts using Aquarius software.
### SUMMARY OF DISCRETE MEASUREMENTS

*Discrete Grab Samples*

Table 1. Analytical results from surface water grab sample collection throughout the study period to confirm sensor readings. If NO$_3^-$ or PO$_4^{3-}$ in one sample was > 100% greater than the other two, that single grab sample was removed from the dataset and considered to be invalid. ND = non-detect.

<table>
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<tr>
<th>Sample Date</th>
<th>Sample Time</th>
<th>NO$_3^-$ (μM)</th>
<th>PO$_4^{3-}$ (μM)</th>
<th>Comment</th>
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<tr>
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<td>4.25</td>
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</tr>
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<td>7.77</td>
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<td>1.25</td>
<td>1.93</td>
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</tr>
</tbody>
</table>
Appendix B

Figure 1. Analytical results from surface water grab sample collection (white circles) compared with in-situ NO$_3^-$ (a) and PO$_4^{3-}$ (b) data (black lines) from 15 March to 15 October, 2011.

ISCO Grab Samples

Table 2. Analytical results from surface water grab sample collected with an Isco automated sampler over a 24-hour period beginning on 16 August, 2011. ND = non-detect.
**Appendix B**

**Figure 2.** Analytical results from surface water grab sample collection (white triangles) compared with in-situ NO$_3^-$ (a) and PO$_4^{3-}$ (b) data (black circles) over a 24-hour period beginning on 16 August, 2011.

**SUNA Standard Checks and Calibrations**

<table>
<thead>
<tr>
<th>Sample Date</th>
<th>NO$_3^-$ (µM)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
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<td>3/8/2011</td>
<td>1.1</td>
<td>In lab: prior to deployment</td>
</tr>
<tr>
<td>5/16/2011</td>
<td>-2.0</td>
<td>In lab: temperature test</td>
</tr>
<tr>
<td>6/13/2011</td>
<td>3.0</td>
<td>In lab. *Re-calibrated</td>
</tr>
<tr>
<td>8/3/2011</td>
<td>0.8</td>
<td>*Re-calibrated</td>
</tr>
<tr>
<td>9/9/2011</td>
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<td></td>
</tr>
<tr>
<td>11/11/2011</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>2/9/2011</td>
<td>3.0</td>
<td>*Re-calibrated</td>
</tr>
</tbody>
</table>

**Table 3.** SUNA NO$_3^-$ readings of DI water. According to manufacturer specifications, the instrument is within range if reading 0.0 ± 0.2 µM. Instrument was recalibrated on 6/13/11, 8/3/11, and 2/9/11.

**Standard Test 6/20/2011**

<table>
<thead>
<tr>
<th>Standard NO$_3^-$ (µM)</th>
<th>SUNA NO$_3^-$ (µM)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.04</td>
<td>200%</td>
</tr>
<tr>
<td>0.71</td>
<td>0.25</td>
<td>96%</td>
</tr>
<tr>
<td>1.43</td>
<td>1.25</td>
<td>13%</td>
</tr>
<tr>
<td>3.57</td>
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</tr>
<tr>
<td>7.14</td>
<td>7.2</td>
<td>1%</td>
</tr>
<tr>
<td>14.28</td>
<td>15.45</td>
<td>8%</td>
</tr>
</tbody>
</table>

**Table 4.** SUNA NO$_3^-$ readings of laboratory-prepared standards, and associated % differences. For standards > 1.0 µM the average % difference is 6%.
Lowess smoothing applied to interval data in order to reduce fire effects prior to hysteresis analysis for (a) NO$_3^-$ (mg l$^{-1}$ NO$_3^-$-N) 19 - 25 July, (b) SC (mS cm$^{-1}$) 13 - 19 August, (c) NO$_3^-$ (mg l$^{-1}$ NO$_3^-$-N) 13 - 19 August, and (d) PO$_4^{3-}$ (mg l$^{-1}$ PO$_4^{3-}$-P) 13 – 19 August.
Butterworth Filter applied to parameters (pH, DO (mg l$^{-1}$), NO$_3$ (µM), SC (mS cm$^{-1}$), turbidity (NTU), PPT (m), soil water content (%), stage (m), soil temperature (°C), water table (m), and stream temperature (°C)) during events 1-2: 02 April - 02 May 2011. Soil water content and temperature unavailable during these intervals.
Appendix C

Butterworth filter applied to parameters (pH, DO (mg l\(^{-1}\)), NO\(_3\) (µM), SC (mS cm\(^{-1}\)), turbidity (NTU), PPT (m), soil water content (%), stage (m), soil temperature (°C), water table (m), and stream temperature (°C)) during events 3-6: 01 August – 15 September 2011.
Butterworth filter applied to parameters (pH, DO (mg l\(^{-1}\)), NO\(_3\) (µM), SC (mS cm\(^{-1}\)), turbidity (NTU), PPT (m), soil water content (%), stage (m), soil temperature (°C), water table (m), and stream temperature (°C)) during events 7-8: 02 October – 02 November 2011.
### Table 1. Major cation and anion results from laboratory analysis for surface water (shaded gray) in mg L⁻¹ and mg/L groundwater samples

| Sample ID | Sample Date | pH | Ca | Mg | Na | K | Cl | Br | SO₄ | Cl⁻ | NO₃ | PO₄ | HCO₃ | Cl⁻ | Br | NO₃ | PO₄ | HCO₃ | Charge Balance |
|-----------|-------------|----|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|----|----|-----|-----|-----|----------------|
| EFSWL     | 6/10/2011   | 52.11 | 854.24 | 12.25 | 532.84 | 9.25 | 260.86 | 5.93 | 290.61 | 0.68 | 65.79 | 2.62 | 32.23 | 1.34 | 30.23 | 0.13 | 7.74 | 17.64 |
| H3        | 6/10/2011   | 130.58 | 2140.60 | 27.38 | 1190.95 | 1.00 | 25.63 | 19.41 | 968.56 | 1.02 | 83.60 | 1.22 | 64.45 | 1.61 | 45.45 | 0.19 | 2.44 | 0.34 | 5.47 |
| S1        | 6/10/2011   | 37.83 | 620.17 | 8.99 | 369.99 | 3.28 | 18.97 | 0.51 | 25.55 | 0.26 | 36.79 | 0.25 | 13.11 | 1.70 | 47.07 | 0.00 | 0.06 | 0.04 | 5.39 |
| T1        | 6/10/2011   | 62.73 | 1028.29 | 17.53 | 762.51 | 0.39 | 10.05 | 6.56 | 327.60 | 0.06 | 4.94 | 1.47 | 77.42 | 1.42 | 40.08 | 0.19 | 2.40 | 0.35 | 5.72 |
| W10       | 6/10/2011   | 45.32 | 246.21 | 10.23 | 444.98 | 0.99 | 25.27 | 4.87 | 243.21 | 0.50 | 41.38 | 0.48 | 25.00 | 1.51 | 42.51 | 0.18 | 2.24 | 0.20 | 3.19 |
| W11       | 6/10/2011   | 77.49 | 1270.35 | 8.04 | 784.69 | 1.10 | 20.83 | 7.06 | 350.52 | 0.86 | 70.69 | 0.92 | 48.20 | 0.66 | 18.72 | 0.25 | 3.13 | 0.77 | 12.43 |
| W34       | 6/10/2011   | 81.76 | 1540.70 | 17.78 | 733.18 | 1.54 | 39.46 | 12.00 | 598.80 | 1.56 | 128.9 | 0.40 | 21.11 | 0.54 | 15.18 | 0.16 | 2.00 | 0.26 | 4.16 |
| W6        | 6/10/2011   | 113.49 | 1860.52 | 25.06 | 1090.04 | 1.88 | 48.14 | 12.01 | 599.30 | 1.28 | 105.00 | 0.41 | 21.58 | 0.94 | 26.51 | 0.24 | 2.97 | 0.65 | 10.50 |
| W8        | 6/10/2011   | 108.61 | 1870.30 | 50.42 | 1322.18 | 1.06 | 28.76 | 17.01 | 959.08 | 0.05 | 38.25 | 0.21 | 27.03 | 0.44 | 15.73 | 0.01 | 0.48 | 0.72 | 8.20 |
| W10       | 6/10/2011   | 31.33 | 824.22 | 11.64 | 586.31 | 1.32 | 37.57 | 8.61 | 454.17 | 0.56 | 11.32 | 0.12 | 6.44 | 0.10 | 5.40 | 0.00 | 0.14 | 0.28 | 2.18 |

**Note:** The table shows the concentration of various ions in mg/L for different samples collected on various dates. The charge balance is calculated to ensure that the total positive and negative charges are equal, which is important for maintaining electrical neutrality in aqueous systems.