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Nutrient dynamics in an alpine headwater stream: use of continuous water quality sensors to examine responses to wildfire and precipitation events

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Abstract:

Stream water quality can change substantively during diurnal cycles, discrete flow events, and seasonal time scales. In this study, we assessed event responses in surface water nutrient concentrations and biogeochemical parameters through the deployment of continuous water quality sensors from March to October 2011 in the East Fork Jemez River, located in northern New Mexico, USA. Events included two pre-fire non-monsoonal precipitation events in April, four post-fire precipitation events in August and September (associated with monsoonal thunderstorms), and two post-fire non-monsoonal precipitation events in October. The six post-fire events occurred after the Las Conchas wildfire burned a significant portion of the contributing watershed (36%) beginning in June 2011. Surface water nitrate (NO_3–N) concentrations increased by an average of 50% after pre-fire and post-fire non-monsoonal precipitation events and were associated with small increases in turbidity (up to 15 NTU). Beginning 1 month after the start of the large regional wildfire, monsoonal precipitation events resulted in large multi-day increases in dissolved NO_3–N (6 × background levels), dissolved phosphate (100 × background levels), specific conductance (5 × background levels), and turbidity (>100 × background levels). These periods also corresponded with substantial sags in dissolved oxygen ($<4\ \mathrm{mg\,l^{-1}}$) and pH (<6.5). The short duration and rapid rates of change during many of these flow events, particularly following wildfire, highlight the importance of continuous water quality monitoring to quantify the timing and magnitude of event responses in streams and to examine large water quality excursions linked to catchment disturbance.

KEY WORDS nutrient dynamics; continuous monitoring; wildfire; monsoonal storms; water quality; headwater streams

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INTRODUCTION

Nitrogen and phosphorus are important limiting nutrients in freshwater ecosystems that can be significantly impacted by routine as well as catastrophic and infrequent hydrologic events. Snowmelt, rainfall, and fires substantially impact surface water nutrient concentrations and biogeochemical processes, with numerous solutes exhibiting a wide variety of responses during events (Walling and Webb, 1986; Ranalli, 2004). Surface water nutrient concentrations often increase markedly during and immediately after snowmelt (Pellerin *et al.*, 2012), precipitation events (McDiffett *et al.*, 1989; Triska *et al.*, 1990; Wondzell and Swanson, 1996; Schlesinger, 1997), and wildfires (Bayley *et al.*, 1992; Riggan *et al.*, 1994; 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 also alter sediment loads with subsequent effects on other biogeochemical parameters, such as dissolved oxygen and pH, because of impacts on primary production and respiration (Smith *et al.*, 2011).

Climate change is expected to result in the alteration of precipitation and streamflow distributions throughout the year. Higher temperatures cause a greater proportion of the winter precipitation to fall as rain rather than snow (Knowles *et al.*, 2006) with earlier seasonal snowmelt (Stewart, 2009; Clow, 2010; Pederson *et al.*, 2011). In the southwestern United States, patterns of wildfire occurrence are also expected to undergo changes that include increased frequency and intensity (Westerling *et al.*, 2006; Allen *et al.*, 2010). Large quantities of sediment

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delivered to streams after wildfires are detrimental to 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.*, 2012; Smith *et al.*, 2011). Understanding the implications that snowmelt, precipitation events, and wildfires have on stream ecosystems is important to assessing overall impacts of climate change on water quality.

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; Johnson *et al.*, 2007, Kirchner and Neal, 2013; Neal *et al.*, 2013) permits an increased understanding and quantification of biogeochemical responses to these events. The purpose of this study was to describe nutrient and biogeochemical responses to precipitation events during spring through fall of 2011 in a headwater stream located in north-central New Mexico, USA. We used continuous water quality monitors to evaluate these responses at high temporal resolution and to compare nutrient responses during pre-fire precipitation events with those during post-fire precipitation events.

METHODS

Site description

The Jemez River watershed is a snowmelt and monsoon-driven system in northern New Mexico (NM), USA, that flows into the Middle Rio Grande Basin of NM. Our study site (35.8411, −106.5013) is located on the East Fork Jemez River near the southern boundary of the Valles Caldera National Preserve (Figure 1a), a federally operated preserve encompassing ~350 km^2 (VCNP, 2012). The site is situated at a high elevation (2590 m) in an expansive meadow valley with minimal overstory vegetation throughout much of the contributing basin. The 200-m study reach is 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 (Figure 1c). Discharge for the study reach typically averages between 50 and 150 l s^{-1} (Rodriguez and Moser, 2010) but increases substantively during snowmelt and precipitation events. Historically, the largest flows occur between March and May and are attributed to snowmelt (Rodriguez and Moser, 2010). Afternoon thunderstorms associated with the North American monsoon occurring between July and September account for approximately 50% of the annual precipitation in this area (Bowen, 1996). The strength of the summer monsoon is inversely correlated to the regional snowpack extent during the previous winter (Gutzler, 2000). The timing and magnitude of snowmelt and monsoons in this area are highly variable on an interannual scale, as seen in the Jemez River discharge (Supplementary Figure 1). Runoff is normally dominated by spring snowmelt except during winter drought years when summer monsoonal precipitation dominates.

Continuous measurements

In situ measurements of nitrate (NO_3–N) and phosphate (PO_4–P) were made using real-time nutrient analyzers. A Satlantic V1 submersible ultraviolet nitrate analyser (SUNA) provided readings of dissolved NO_3–N using an ultraviolet adsorption method (Satlantic, 2011). Wipers were not available for this instrument when it was purchased, so cleaning of the sensor window was performed manually during calibration/maintenance checks every 3–4 weeks. The detection range of SUNA is 0.007–28 mg l^{-1} NO_3–N with an overall accuracy of ±0.028 mg l^{-1} NO_3–N. Measurements were made at 15- or 30-min intervals from 15 March to 2 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–P were made at 1-h intervals from 16 May to 9 September 2011 using a WETLabs Cycle-PO_4 dissolved phosphate analyser. The Cycle-PO_4 analyser uses microfluidics and optics to measure the transmittance of a filtered water sample and calculate dissolved PO_4–P concentration with a lower detection limit of 0.002 mg l^{-1} PO_4–P (WETLabs, 2011) using the standard analytical wet chemistry EPA method 365.5. A total of 85% and 74% of the possible measurements for PO_4–P and NO_3–N, respectively, were available for analysis following removal of data assessed to be of poor quality by manufacturer and data gaps due to instrument servicing and power failures.

In situ measurements of temperature, temperature-corrected (25 °C) specific conductivity (SC), dissolved oxygen (DO), pH, and turbidity were made using Yellow Springs Instruments model 6920 V2 sondes. Measurements were made at 15-min intervals from 15 March to 2 November 2011. Fouling checks and calibrations of the Yellow Springs Instruments sondes were performed every 3–4 weeks using known standards (SC and pH sensors) and 100% water-saturated air (optical DO sensor).

River stage data from March to October 2011 were obtained from an Onset HOBO U20 pressure transducer colocated with the nutrient instruments and corrected with local barometric pressure. Precipitation data were acquired from the Valles Caldera National Preserve

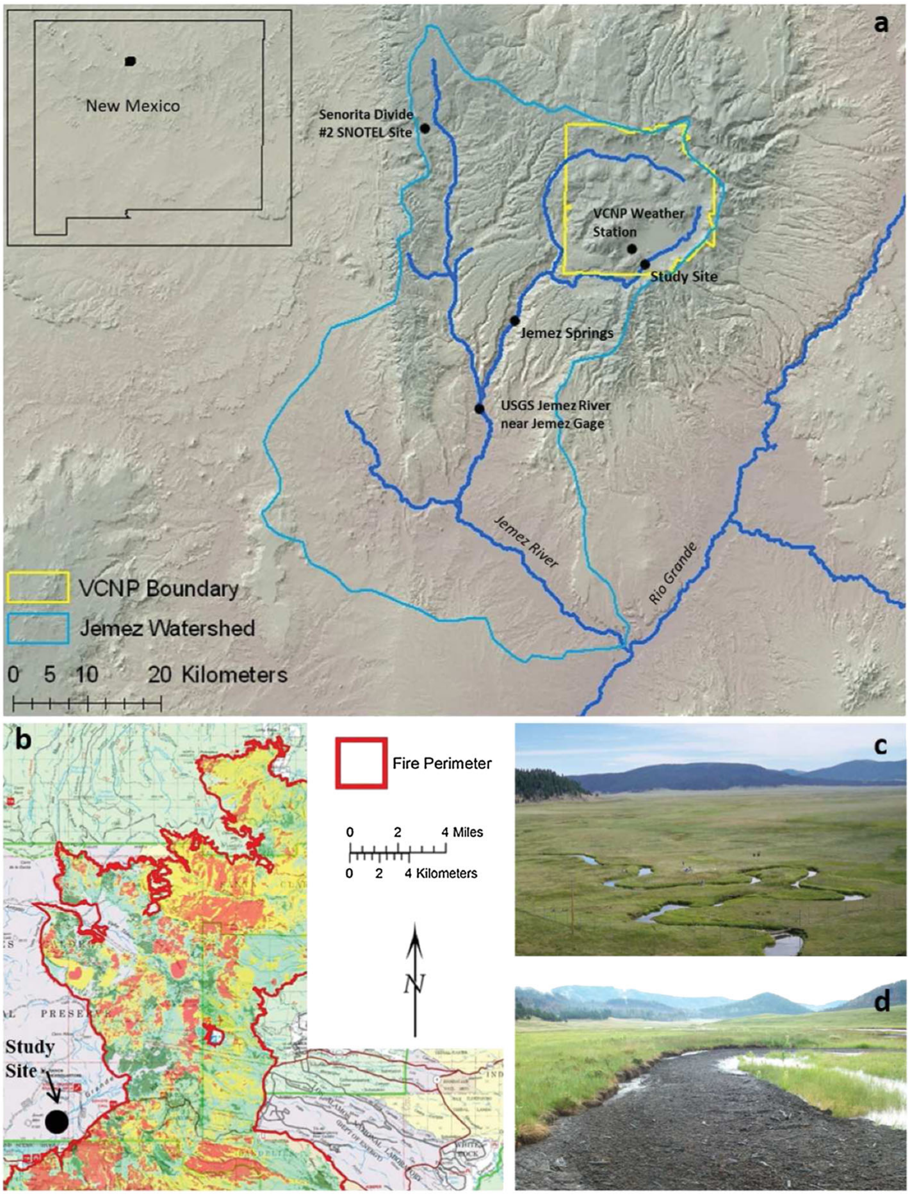

Figure 1. (a) Regional location map showing the study site on the East Fork Jemez River located within the Valles Caldera National Preserve (VCNP) (yellow line) and Jemez Watershed (light blue line) boundaries. (b) Perimeter of Las Conchas fire on 20 July 2011 (courtesy of John Swigart, VCNP). (c) Photo of study site taken in the summer of 2010. (d) Photo upstream of study site taken in the summer of 2011 after the Las Conchas Fire (courtesy of Bob Parmenter, VCNP)

headquarters (station 11) meteorological station (35.8582, −106.5211). Snowpack data were acquired from the National Resources Conservation Services Senorita Divide #2 SNOTEL site (36.0000, −106.8333). East Fork Jemez River streamflow data were obtained from the Valles Caldera National Preserve at the Hidden Valley Gage, approximately 0.5 km downstream from our study site. Jemez River streamflow data were obtained from the US Geological Survey at Jemez River near Jemez, NM (08324000) (35.6620, −106.7434) approximately 40 km downstream of the study site (USGS, 2011).

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 at a frequency of 1 Hz during the sampling interval (i.e. 15 or 30 min). A single NO_3–N concentration for the interval was obtained by averaging the high-frequency measurements after removing the data collected during the first 20 s, allowing for a warm-up period. AQUARIUS software (Aquatic Informatics, 2011) was used to address outliers, fouling shifts, and data gaps. Fouling shifts were applied on 9 April 2011 ($-0.01\,mg\,l^{-1}$ NO_3–N) and 7 July 2011 ($0.01\,mg\,l^{-1}$ NO_3–N), and data were deleted between 30 May and 22 June 2011 because of instrument malfunction. Data for PO_4–P were logged internally on the Cycle-PO_4 analyser. Outliers were identified and removed using quality control algorithms developed and applied by the instrument manufacturer. These included values significantly exceeding the instrument specified range (0–12.5 μM), analyses (runs) for which the 100% transmission values showed excessive noise (>5% coefficient of variation), and when bubble spikes, were detected during the mixing of reagents with sample. Runs were also removed that lacked a reaction curve indicative of correct sample and reagent mixing. 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 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. Eight event periods were identified in 2011: two in April (precipitation events after snowmelt), four throughout August and early September (post-wildfire monsoonal thunderstorms), and two in October (precipitation events after monsoon season). A Butterworth filter was used to remove the diurnal signal present during the events before hysteresis analysis (Butterworth, 1930). Complete data are available at the New Mexico EPSCoR Data Portal (http://nmepscor.org/dataportal).

Discrete measurements – nutrient validation samples

In order to validate continuous *in situ* nutrient measurements (NO_3–N and PO_4–P), discrete surface water samples were collected in duplicate or triplicate approximately every 7–10 days throughout the study period. Samples were filtered through 0.45 μm hydrophilic polyethersulfone filters in the field and immediately frozen upon return to the laboratory. Discrete surface water samples were also collected every hour over a 24-h period on 16 August 2011 using an ISCO automated sampler. Samples were pumped from the stream into a container preserved with 0.25 ppm phenyl mercuric acetate to stop microbial activity prior to freezing, collected at the end of the 24-h period, filtered in the laboratory, and immediately frozen before analysis. Samples were analysed for anions using ion chromatography (IC) in the Department of Earth and Planetary Sciences analytical laboratory at the University of New Mexico in Albuquerque, New Mexico. A low-detection method (~$0.01\,mg\,l^{-1}$) was employed for IC analysis, consisting of low concentration standards (0.05–$1\,mg\,l^{-1}$) and long sample loops (250 or 1000 μm).

Results from the IC for the aforementioned discrete measurements (weekly and ISCO samples) were frequently near or below detection (variable detection limit amongst runs) and variable, warranting further sampling for data validation. To address this validation issue, a 24-h sampling event was done on 16 June 2012. Discrete surface water nutrient samples were collected in triplicate every hour for 24 h to check sensor readings. Samples were filtered through pre-fired 0.7 μm pore-sized Whatman glass fiber filters and immediately placed on dry ice in the field, remaining frozen for approximately 1 month until analysis. Nitrate (NO_3–N) analysis was done on the IC using the low-detection method mentioned in the previous text. Phosphate (PO_4–P) analysis was completed on the IC with the use of the stannous chloride method (Standard Method 4500-P D; Clesceri *et al*., 1998).

RESULTS

Winter precipitation in 2010–2011 yielded a much below-average snowpack in this region (NRCS, 2011) and discharge in the East Fork Jemez River averaged approximately $85\,l\,s^{-1}$ for most of the year (Rodriguez and Moser, 2010). This corresponded to an average local stage level of approximately 0.3 m, which increased slightly (~0.1 m) during pre-fire and post-fire non-monsoonal precipitation events in April and October (Figure 2b) and more substantially increases (up to ~0.4 m) during post-fire monsoonal thunderstorms (Figure 3b). Beginning on 26 June 2011, the Las Conchas fire burned 63 370 ha primarily south and east of the study site (Figure 1b), including drainage areas feeding into the East Fork Jemez River (InciWeb, 2012). The fire burned for 36 days, reaching full containment on 1 August 2011, and resulted in higher-than-average and overbank monsoonal flood events in August and September (Supplementary Figure 2).

Continuous data exhibited variability on seasonal, event, and diurnal time scales (Figures 2 and 3). Event variations observed were responsible for the largest changes in the system during the period of continuous measurements. Seasonal and diurnal variability in nutrient concentrations as a part of this study are examined elsewhere (Sherson, 2012) but have been demonstrated in several other studies (Wondzell and Swanson, 1996; Mulholland and Hill, 1997; Dahm *et al*., 1998, Fellows *et al*., 2006, Cohen *et al*., 2013). Sondes and nutrient sensors captured biogeochemical and nutrient responses to precipitation events throughout the study period (15

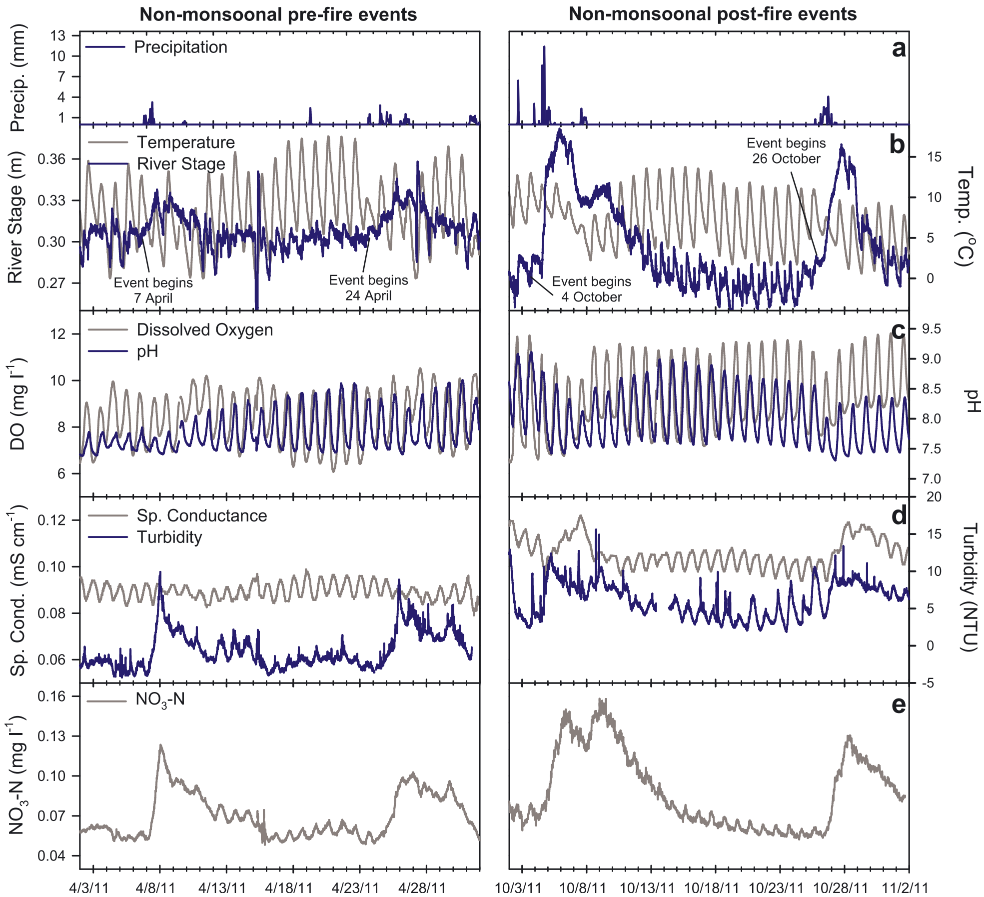

Figure 2. Continuous measurements during event periods of (a) precipitation (mm) from the Valles Caldera National Preserve (VCNP) headquarters meteorological station, (b) river stage (m) and temperature (°C), (c) dissolved oxygen (DO) (mg l^{-1}) and pH, (d) specific conductance (mS cm^{-1}) and turbidity (NTU), and (e) NO_3–N (mg l^{-1}) in the East Fork Jemez River between 2 April and 2 May 2011 (left) and 2 October and 2 November 2011 (right)

March to 02 November 2011); substantial event-related increases in nutrient concentrations, however, were only observed in the months of April, August, September, and October (Table I). These responses were related to pre-fire precipitation in April and post-fire precipitation in August, September, and October.

Pre-fire precipitation responses

Continuous data showed two distinct non-monsoonal precipitation events with biogeochemical responses in the East Fork Jemez River (beginning on 7 April and 24 April, Figure 2). For these events, river stage increased from approximately 0.30 to 0.33 m (0.03 m total increase) for periods of 6–7 days in duration following catchment-wide precipitation events (Figure 2a and b). The observed increases of 0.03 m are well above the sensor's resolution (0.002 m) and accuracy (0.005 m). DO, pH, and SC exhibited minimal change during the April precipitation events, with only a slight decrease in diurnal variability of SC observed (Figure 2c and d). Turbidity increased from ~0 to ~10 NTU during the April precipitation events (Figure 2d). Nitrate concentrations during the April precipitation events increased from ambient levels of approximately 0.06 to >0.10 mg l^{-1} in similar fashion to turbidity (rapid increase and gradual descending limb) (Figure 2e).

Post-fire monsoonal precipitation responses

Approximately 1 month after the beginning of the Las Conchas fire (Figure 1b), precipitation events resulted in river stage increases of between 0.1 and 0.4 m, with the three largest events occurring over several days between 21 August and 9 September (Figure 3b). These events coincided with large pulses in NO_3–N (>0.28 mg l^{-1}), PO_4–P (>0.31 mg l^{-1}), SC (>0.30 mS cm^{-1}), and turbidity (>1000 NTU) (Figure 1d) in addition to multi-day sags in DO and pH (Figure 3). Overbank flow occurred during these events because of the magnitude of stage change (Supplementary Figure 2). Diurnal variability of temperature exhibited minimal change during the event

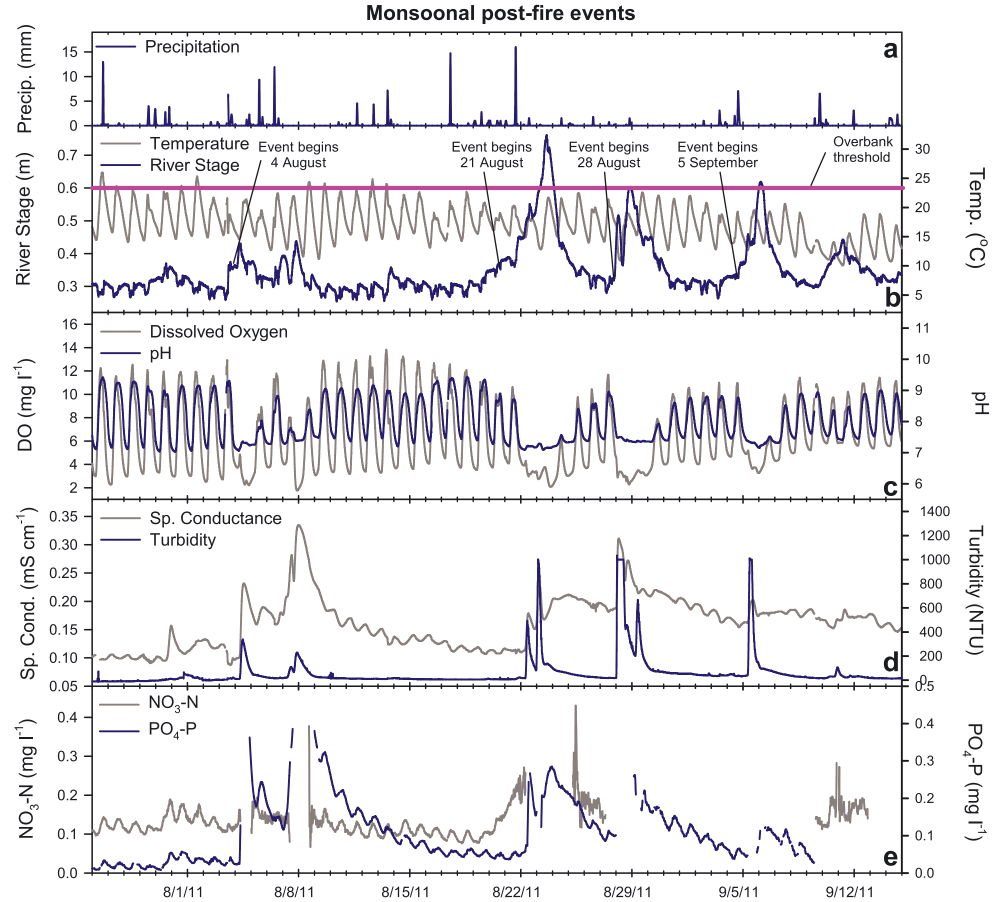

Figure 3. Continuous measurements during post-fire monsoons of (a) precipitation (mm) from the Valles Caldera National Preserve (VCNP) headquarters meteorological station, (b) river stage (m) and temperature (°C), (c) dissolved oxygen (DO) (mg l^{-1}) and pH, (d) specific conductance (mS cm^{-1}) and turbidity (NTU), and (e) NO_3–N (mg l^{-1}) and PO_4–P (mg l^{-1}) in the East Fork Jemez River between 26 July to 14 September 2011. The Las Conchas fire burned from 26 June to 1 August 2011

periods (Figure 3b), and diurnal variability was almost completely removed for DO and pH. For the four primary post-fire monsoonal event periods (beginning on 4 August, 21 August, 28 August, and 5 September), DO (<4 mg l^{-1}) and pH (to ~6) sags were observed for periods of 2–3 days (Figure 3c).

Specific conductivity, turbidity, and nutrient concentrations increased concurrently with all monsoonal events during the study period (Figure 3d and e). The initial stage increase after the fire (4 August) resulted in a threefold increase in SC (0.10 to 0.33 mS cm^{-1}) and a >50-fold increase in turbidity (<5 to 330 NTU). The three latter stage increases (21 August, 28 August, and 5 September) showed a different pattern of response for the same parameters with more substantial increases in turbidity (<5 to >1000 NTU; >100-fold) than those of SC (about twofold from 0.11 to ~ 0.20 mS cm^{-1}) (Figure 3d). Nutrient concentrations also increased during monsoonal event periods (Figure 3e), with NO_3–N increasing from ~0.13 to >0.28 mg l^{-1} and PO_4–P increasing from ~0.03 to >0.37 mg l^{-1}. Data gaps resulting from battery failure (NO_3–N, 27 August to 9 September) and instrument difficulties from high turbidity (NO_3–N and PO_4–P during all stage increases from 4 August to 27 August) indicate that dissolved nutrient concentrations recorded during these pulses most likely underestimate true maximum concentrations.

Post-fire non-monsoonal precipitation responses

Continuous data also revealed two post-fire non-monsoonal precipitation events resulting in biogeochemical responses in the East Fork Jemez River (beginning on 04 October and 26 October, Figure 2). For these events, river stage increased from approximately 0.27 to 0.36 m (0.09 m total increase), and elevated stage was sustained for durations of 11 and 7 days, respectively (Figure 2b). Diurnal variability observed in temperature (Figure 2b), DO, and pH (Figure 2c) was reduced substantively during these post-fire non-monsoonal events. Muting of diurnal variability lasted about 7 days for temperature and pH and 4 days for DO. October precipitation events resulted in an

Table I. Precipitation events and biogeochemical responses in 2011

Storm initiation date	Durationof stage increase (days)	Event precipitation (mm)	Stage increase (m)	Maximum specific conductance (mS cm^{-1})	Maximum turbidity (NTU)	Comment
07 April	6	14.2	0.03	0.10	9.4	
24 April	7	25.1	0.04	0.10	8.9	
04 August	6	43.2	0.12	0.33	330.1	Post-fire monsoon
22 August	5	39.9	0.45	0.23	965.6	Post-fire monsoon
28 August	4	3.3	0.30	0.31	1179.3*	Post-fire monsoon
05 September	4	22.1	0.28	0.20	1174.4*	Post-fire monsoon
04 October	11	58.7	0.08	0.12	15.6	
26 October	7	27.9	0.07	0.12	10.6	

Event precipitation (mm) includes precipitation before and during event periods and is from the Valles Caldera National Preserve headquarters site.
*Turbidity measured beginning 28 August and 5 September is outside of the manufacturer's specified range (0–1000 NTU).

increase of approximately 0.02 mS cm^{-1} for SC (Figure 2d). Turbidity levels increased most quickly over the initial 24–48 h of each precipitation event (~5–10 NTU) and subsequently declined to pre-event levels over the next 4–6 days, similar to the response observed during the April events (Figure 2d). Nitrate concentrations during the October precipitation events increased from ambient levels of approximately 0.06 to >0.12 mg l^{-1} (Figure 2e).

Event comparison

Changes in streamflow were compared with variations in solute levels in order to compare events and better understand hydrologic flow paths. High-resolution river stage data were utilized to approximate changes in flow during precipitation events that caused overbank flow. Hysteresis loops were generated to investigate and compare the relationship between discharge (river stage) and SC, turbidity, and NO_3–N during non-monsoonal pre-fire (April) and post-fire (October) precipitation event periods (Figure 4). SC exhibited little variation during April precipitation event periods but showed clear counterclockwise hysteresis during October precipitation events. A similar relationship (counterclockwise) was observed for turbidity during April events, with October events varying in direction but exhibiting more of a linear trend with river stage. Turbidity exhibited clockwise hysteresis patterns during August and early September whilst conductivity patterns were both clockwise and counterclockwise (data not shown). A counterclockwise pattern was observed in NO_3–N during April and October precipitation events with higher river stage and NO_3–N concentrations during the October events. Continuous turbidity and NO_3–N data were not collected at the study site prior to 2011, but sondes without turbidity probes captured precipitation events during the fall of 2010 representative of pre-fire conditions. For example, a precipitation event in the East Fork Jemez River in October 2010 resulted in increased river stage and SC, also with a counterclockwise pattern, but with a much different shape than post-fire events during October 2011 (Figure 4). Seasonal changes cannot explain these differences in SC because of little interannual differences in SC during 2010 even with similar increases in stage. Therefore, these shapes to the hysteretic loops indicate that fire effects were being sensed in the system during precipitation events in October 2011.

Discrete measurements – nutrient validation samples

Discrete measurements collected in duplicate and triplicate throughout the study period were variable amongst replicate samples and did not always match well with the *in situ* sensor NO_3–N and PO_4–P data (Figure 5). We suspect that our sample preservation and storage methodology (immediate freezing after filtration instead of immediate analysis) and the extremely low *in situ* nutrient concentrations created problems for obtaining accurate laboratory analysis in samples near the established (but not always actualized) detection limits of the analytical methods employed. Discrete samples collected by an ISCO automated sampler beginning on 16 August 2011 also showed deviations from NO_3–N measurements obtained by *in situ* instruments (Figure 5). Discrete NO_3–N samples measured in the lab (0.06 ± 0.06 mg l^{-1} NO_3–N) on average had lower concentrations and much higher variability than *in situ* sensor results (0.10 ± 0.01 mg l^{-1} NO_3–N).

Discrete PO_4–P samples collected by an ISCO automated sampler matched fairly well with *in situ* sensor data. Despite the presence of a few outliers during the early morning hours of 17 August 2011, discrete PO_4–P

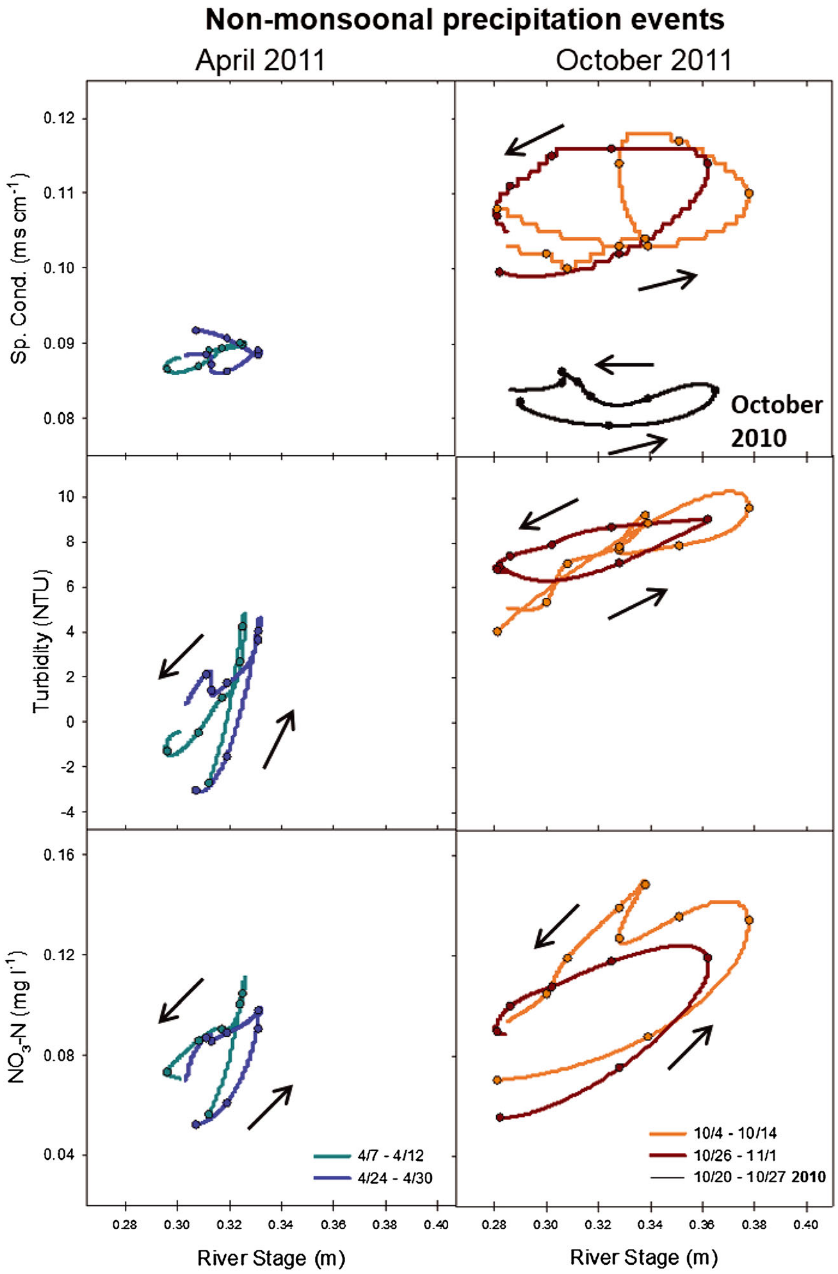

Figure 4. Relationship between river stage (m) and specific conductance (mS cm^{-1}), turbidity (NTU), and NO_3– (μM) during non-monsoonal precipitation event periods of 2011 and 2010. April 2011 (left panel) and October 2010 and 2011 (right panel) events show counterclockwise hysteresis for specific conductance (October), turbidity (April), and NO_3– (April and October). Arrows represent the direction of hysteresis

results were generally within 20% of *in situ* results and showed a similar diurnal trend (highest concentrations during the day and lowest concentrations during the night) (Supplementary Figure 3). Discrete NO_3–N (analysed on the IC) and PO_4–P [analysed spectrophotometrically using the stannous chloride method (Clesceri *et al.*, 1998)] results from the 24-h sampling event on 16 June 2012 also deviated from *in situ* measurements on a sample-by-sample basis but show similar results when all measurements are averaged (Supplementary Figure 4). The *in situ* sensors were measuring comparable values to the complete set of laboratory analyses, but the deviation around the mean of the NO_3–N values for laboratory analyses was much greater than for sensor values (Supplementary Figure 4).

The accuracy of SUNA NO_3–N readings were also investigated using calibration checks and laboratory standards. SUNA calibration was periodically checked using deionized water and was out of range (0.0 ± 0.028 mg l^{-1} or 2 μM) only twice during the entire deployment period.

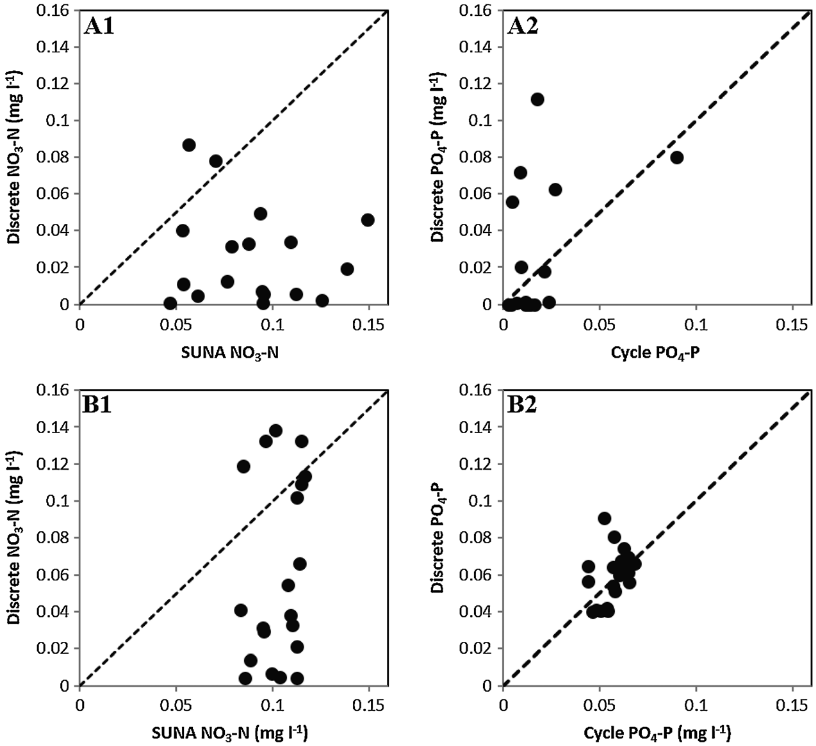

Figure 5. *In situ* NO_3–N [collected with the submersible ultraviolet nitrate analyser (SUNA)] (A1 and B1) and PO_4–P (collected with the Cycle-PO_4) (B1 and B2) compared with laboratory analytical results from surface water grab sample collection (A) throughout the study period in duplicate and triplicate and (B) during a 24-h sampling period on 16 August 2011

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 >0.02 and up to $0.20\,\mathrm{mg\,l^{-1}}$.

DISCUSSION

Results from this study describing nutrient and biogeochemical responses to monsoonal and non-monsoonal precipitation events during spring through fall of 2011, before and after a large fire, suggest variation is due to numerous hydrologic drivers. The hydrologic drivers for each time period are discussed below and synthesized in a simple conceptual model (Figure 6).

Pre-fire precipitation responses

Analysis of pre-fire non-monsoonal precipitation events and associated stage changes revealed an increase in turbidity and NO_3–N concentrations consistent with observations from other studies of precipitation-related flushing of groundwater with elevated nutrient (Triska *et al.*, 1990; Wondzell and Swanson, 1996; Pellerin *et al.* 2012) and organic matter concentrations (Saraceno *et al.*, 2009) into surface water (Figure 6). In the Valles Caldera, soils near stream channels contain large pools of available nutrients (Baker *et al.*, 2000; Van Horn *et al.*, 2012) that are flushed into surface water because of inundation by a rising water table and near-surface flow during storm and snowmelt events (Liu *et al.*, 2008b). Liu *et al.* (2008b) concluded that variations in source water flow paths are a major determinant of Valles Caldera National Preserve in-stream nutrient concentrations. Additionally, biogeochemical reactions are commonly enhanced within groundwater as the fluid is in long-term contact with subsurface minerals and microbial communities during subsurface exchange (Findlay, 1995; Jones and Holmes, 1996). Depending on the dominant microbial processes, these reactions can contribute to increases or decreases in nitrogen and phosphorus levels as compared with surface waters. Pre-fire storm events also affected SC with a slight short-lived decrease in diurnal variability likely due to precipitation-related dilution (Nagorski *et al.*, 2003; Saraceno *et al.*, 2009).

Hysteresis patterns are observed when flow event-related concentrations of a given solute differ on the rising and falling limbs of the hydrograph (Walling and Webb, 1986). This occurs when solutes enter stream systems at different times from various hydrologic compartments, typically thought to follow the temporal order of overland flow, soil water, and groundwater (McDiffett *et al.*, 1989; Williams, 1989; House and

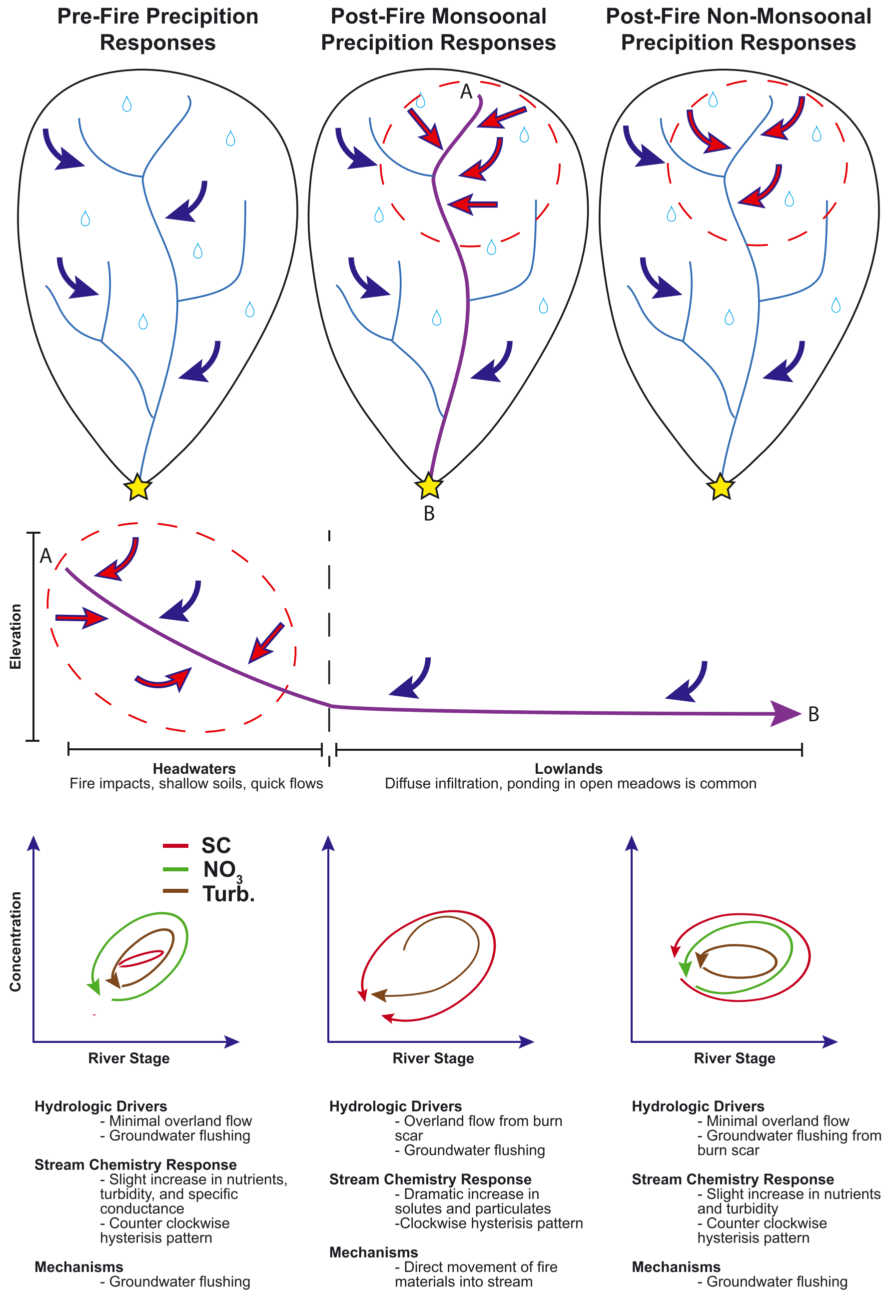

Figure 6. A conceptual figure showing the responses to precipitation events for (1) the movement of groundwater (curved arrows) and overland flow (straight arrows) from non-fire (blue arrows) and fire (red arrows, red dashed fire perimeter) impacted areas of a watershed, (2) an along-channel profile of the change in gradient and flow paths from headwaters (A) to lowland areas (B), and (3) the hysteresis curves produced by these events and potential mechanisms responsible for these patterns as observed at the monitoring site (yellow star)

Warwick, 1998; Evans and Davies, 1998; Bowes *et al.*, 2005; Butturini *et al.* 2005). Counterclockwise hysteresis patterns occur when the solute concentrations from the first part of the hydrologic response are lower than those found in slower flow paths. For example, if the timing order described in the previous text is accurate, then counterclockwise patterns are observed when solute concentrations in soil water and/or groundwater are higher than in overland flow (Evans and Davies, 1998).

The counterclockwise hysteresis pattern observed in the relationship between river stage and SC, turbidity, and NO_3–N (Figure 4) during these periods indicate the slow movement of groundwater from recently saturated near-stream soils into surface water during and immediately after non-monsoonal precipitation events. We interpret the counterclockwise hysteresis observed in these non-monsoonal precipitation events to be the result of limited overland flow with bank storage and groundwater flushing, driven by percolation in the low-gradient valley, being the primary mechanisms that generate gradual return flows enriched with solutes, nitrate, and fine suspended sediment (Figure 6, Supplementary Figure 2). Pellerin *et al*. (2012) also observed hysteresis relationships between streamflow and fluorescent dissolved organic matter. Continuous instrumentation documented counterclockwise patterns during snowmelt and rainfall events as surface and subsurface water with a high concentration of fluorescent dissolved organic matter was transported to the stream via slow moving subsurface flow paths.

Snowmelt events sometimes result in different biogeochemical responses than those associated with other precipitation events. This difference may be due to the source of the water itself or to the alteration of hydrologic pathways during such events (Mulholland and Hill, 1997; Dahm *et al*., 1998; Liu *et al*., 2008b). Using continuous sensors, Pellerin *et al*. (2012) observed that NO_3–N concentrations peaked during maximum snowmelt in a Vermont watershed. Nitrate concentration also increased during precipitation events after snowmelt had subsided, but these responses were relatively muted compared with the peak snowmelt signal. We observed similar nutrient and biogeochemical responses to precipitation events in April and October (Figure 2), suggesting that snowmelt had minimal influence on stream chemistry due to a highly reduced snowpack and subsequent strongly muted snowmelt experienced in 2011 throughout this region (Supplementary Figure 1).

Post-fire monsoonal precipitation responses

Sediment transport processes and nutrient biogeochemistry during the study period were greatly affected by the Las Conchas fire of 2011 and subsequent monsoonal precipitation events likely due to an increase in fast and erosive Hortonian flow due to the fire-induced removal of groundcover and litter. Rapid increases in turbidity and nutrient concentrations were observed during four distinct monsoonal rainfall events between 4 August and 5 September (Figure 3d and e). 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; Smith *et al*., 2011; Verkaik *et al*., 2013) as a result of nutrient-rich ash and erosional debris reaching the stream channel via overland flow. Post-fire increases in nutrient concentrations are ultimately controlled by the proximity and severity of the fire, the magnitude of precipitation events post-fire, the catchment gradient, and the types and distribution of vegetation within the catchment (Ranalli, 2004). The large increases we observed in surface water nutrient concentrations (>tenfold increase for dissolved PO_4–P and >twofold increase for dissolved NO_3–N) occurred after monsoonal rainfall events and coincided with large increases in river stage and turbidity (Figure 3), suggesting that post-fire precipitation on burn scars and the subsequent overland flow in the headwaters and groundwater flushing in the open meadows of the lowlands were the primary controls for nutrient increases during August and September (Figure 6). 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 for turbidity. Turbidity generally exhibited a clockwise hysteresis pattern (shown conceptually in Figure 6), but the hysteresis pattern for SC was not consistent between events. The observed clockwise hysteresis pattern for turbidity supports the importance of overland flow of fire-related debris and sediment directly from the burn scar into the stream as a hydrologic driver during post-fire monsoonal precipitation events (Figure 6). This pattern is typical of events in which overland flow produces higher concentrations of sediment than soil water and/or groundwater (Evans and Davies, 1998).

Although instrument limitations related to very high turbidity during the peaks of these monsoonal flow events prevented the capture of the entirety of nutrient responses, dissolved nutrient data indicate that PO_4–P concentrations increased at higher rates than NO_3–N concentrations during the initial pulse beginning on 4 August. This monsoon pulse also had higher SC but lower turbidity values (Figure 3d) than the three subsequent pulses (21 August, 28 August, and 5 September). Stage changes were much greater (Figure 3a) during the three latter pulses, suggesting that ash, charcoal, and sediment transport loading from the burned areas during these events was more substantial. We hypothesize that increased levels of PO_4–P and SC during the initial pulse are related to increased groundwater infiltration in this low-gradient alluvial valley from runoff emanating from the burn scars and enhanced dissolution of solutes from the first wetting of extensive ash deposits after the high-intensity forest fire. This behaviour is consistent with observations of groundwater levels in the well observation network (not shown) and previously published runoff mechanisms for this system (Liu *et al*., 2008a; Liu *et al*., 2008b).

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*., 2012). Increased sediment loads (turbidity values > maximum instrument range of 1000 NTU)

(Figure 3d) and DO and pH sags (Figure 3c) during the post-fire monsoonal pulses were sustained over several days and could be followed downstream through the Jemez River and Rio Grande (CN Dahm, RI RI Candelaria-Ley, CS Reale, JK Reale, DJ Van Horn, University of New Mexico, Albuquerque, NM, unpublished results). Low levels of DO and pH are detrimental to aquatic communities, 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 with high chemical and biological oxygen demand coupled with inhibition of in-stream photosynthesis. Other studies examining DO and pH responses during post-fire flow events over subsequent years after forest fires have reported a variety of responses. For example, Raison *et al*. (1990) found that surface water pH increased during ash flow events in an Australian stream, whilst Hall and Lombardozzi (2008) found lower DO but no change in pH 2 years post-burn in Colorado streams affected by wildfire. Significant sags in DO and pH associated with flow events immediately after wildfire are best captured using continuous real-time sensors as deployed for this study.

Our results showed minimal non-precipitation-related fire effects on surface water nutrient concentrations and biogeochemical properties during the time the fire was burning but prior to initiation of the monsoon season. Despite smoke in the atmosphere from late June through July, DO and pH data showed little inhibitory effect on photosynthetic processes during this time (Figure 3c). The NO_3–N and PO_4–P concentrations also exhibited minimal increases up until monsoonal flow events in August (Figure 3e). 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 than our study site that was not burned and downstream of major fire impacts.

Wildfires have also 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 biogeochemistry and stream metabolism (Hall and Tank, 2003; Fellows *et al*., 2006; Mulholland *et al*., 2006) and the widespread damage within catchments 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 remained elevated for time frames ranging from 1 to 3 years (Hall and Lombardozzi, 2008), 4 to 5 years (Spencer *et al*., 2003; Mast and Clow, 2008; Rhoades *et al*., 2011), and up to 9 years (Bayley *et al*., 1992; Meixner *et al*., 2006). In a summary of fire influences on surface water nutrient concentrations, Ranalli (2004) found that, on average, most studies report elevated NO_3–N concentrations for 3–5 years and elevated PO_4–P concentrations for 1–2 years after fire occurrence.

Post-fire non-monsoonal precipitation responses

Biogeochemical responses to non-monsoonal precipitation following the Las Conchas fire were similar to pre-fire responses with a few exceptions. The slight increase in precipitation-related nitrate responses as compared with pre-fire concentrations suggests that unlike other stream systems discussed in the previous text, the East Fork of the Jemez quickly returned to pre-fire nutrient concentrations. This is likely because most of the fire occurred in the headwaters, where steep terrain with shallow soils was burned and accumulated much ash. Events immediately following the fire efficiently flushed headwater solutes downstream, resulting in strong initial responses in concentration. Given the low gradient in this valley, solutes from spatially extensive dry deposition are expected to percolate into the aquifer as a diffuse source with relatively lower concentrations and not through a direct input as the early headwater and near-bank flushing. These diffuse inputs to alluvial aquifers result in lower concentrations and take longer to be detected in the stream.

The more severe dampening of DO and pH values as compared with pre-fire events can be attributed to reduced sunlight, increased turbidity, and decreased in-stream photosynthesis resulting from continued movement of fire-related materials into the stream and resuspension of materials deposited during monsoonal overland flow events (Figure 2b and c). Similar responses have been reported in other studies using continuous water quality monitors (Roberts *et al*., 2007; Saraceno *et al*., 2009). Counterclockwise hysteresis patterns observed in the relationship between river stage and SC, turbidity, and NO_3–N (Figure 4) were similar in direction to the pre-fire non-monsoonal precipitation responses, also supporting the dominance of groundwater flushing as the dominant hydrologic driver during post-fire non-monsoonal precipitation responses (Figure 6). Post-fire storm events exhibited increased SC as compared with pre-fire events (Figure 4). We hypothesize that this difference can be attributed to post-fire effects within the watershed as ions liberated from the large quantities of ash in the burned forests in the upper catchment were flushed into streams from shallow groundwater pathways (Figure 6).

Sensor validation

Results from the analysis of nutrient validation samples highlight the difficulty in obtaining discrete sample validation when nutrient concentrations are low. Although methods to obtain low detection limits were employed during IC analysis for NO_3–N and PO_4–P, grab sample results do not show the precision of our *in situ* instruments. We attribute this problem to sample collection, storage, and transport effects and to analysing samples that are near the detection limits of the laboratory methods. We conclude that the *in situ* sensors are better able to accurately and precisely measure low levels and small changes in nutrients on short time steps than our laboratory-based methods. Similar challenges have been identified by other researchers when comparing *in situ* data to results from laboratory analyses (Cohen *et al*., 2013), and we are more confident in the data produced by calibrated *in situ* sensors than laboratory analyses subjected to challenges from sampling, storage, transport, and laboratory analyses.

CONCLUSIONS

Our results showed the value of continuous water quality monitoring to accurately quantify the timing and magnitude of biogeochemical responses to storms and wildfire. This study also highlights the difficulties in obtaining discrete sample validation for *in situ* sensors when nutrient concentrations are very low. High-resolution data allowed for a more precise understanding of the timing and magnitude of event responses, often occurring over periods of hours to days. Increases in concentrations of surface water NO_3–N and turbidity during non-monsoonal precipitation events post-snowmelt reflected a flushing of nutrient-rich near-stream groundwater and localized overbank flooding that increased in magnitude between April and October events after a catastrophic forest fire in the upper catchment. Increases in SC were observed in October but not April, indicating that effects of a major summer wildfire remained in the system for months after the fire. In addition, multi-day pulses of NO_3–N, PO_4–P, SC, and turbidity corresponding with sags in DO and pH were measured in late summer. These large pulses occurred after the fire and were directly related to high-intensity monsoonal thunderstorm precipitation. The timing and magnitude of these results showed substantial impacts of forest fire on water quality, but also that high-intensity precipitation events were critical for the delivery of fire-related nutrients and sediment loads to streams draining the burned area. Continuous water quality monitors provided valuable insight concerning how streams and rivers respond to catastrophic disturbance and changing hydrology that could not be accurately obtained without the high-resolution data provided by these *in situ* sensors.

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