THESIS

NITRATE REMOVAL ALONG A COLORADO MONTANE HEADWATER STREAM: THE ROLE OF BIDIRECTIONAL HYDROLOGIC EXCHANGE AT REACH TO CATCHMENT SCALES

Submitted by

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ABSTRACT

NITRATE REMOVAL ALONG A COLORADO MONTANE HEADWATER STREAM: THE ROLE OF BIDIRECTIONAL HYDROLOGIC EXCHANGE AT REACH TO CATCHMENT SCALES

Bidirectional hydrologic exchanges between surface water and groundwater along a stream reach can act to dilute nutrient levels (physical processes), and/or can facilitate biogeochemical cycling (physical and biological processes). Such exchanges thus affect nitrogen transport within stream catchments, many of which have been altered in high-elevation locations along Colorado's Front Range due to elevated nitrogen levels from industrialization in recent decades. We applied a fully informed hydrologic mass balance model and nitrate mass balance model that include gross gains and gross losses along a 1000 m study reach, to better understand nitrate removal potential for a Colorado montane zone catchment, Lower Gordon Gulch. We collected data during four synoptic stream tracer and sampling campaigns along our study reach during the 2014-2015 water year, and also analyzed near-stream riparian lateral hydraulic gradients to assess groundwater and surface water interactions from a second perspective. Three distinct hydrologic regimes are captured in our results, including two experiments during baseflow, one experiment following snowmelt, and one experiment following late-spring rainfall. Results show a transition from hydrologic sources of nitrate following snowmelt, to biological sources during rainfall, and finally to hydrologic removal during baseflow. Higher hillslope water content appears to be directly correlated with nitrate sources, and lower in-stream discharge appears to be directly correlated with in-stream nitrate removal. This finding combined with lateral hydraulic gradient results point to groundwater-surface water interactions. Our findings corroborate earlier work in montane zone streams that show preferential flow on south-facing slopes and matrix flow with greater microbial activity on north-facing slopes following snowmelt. We provide a modeling framework that separates physical from biological processes to assess the potential of such catchments to cycle nitrate, which can help scientists and environmental planners in assessing ecosystem changes in Colorado due to anthropogenic influences.

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1.1 Introduction

Nutrient cycling and export within stream networks is a cornerstone of our understanding of ecosystem processing and the relation to hydrologic processes [*Tetzlaff et al.*, 2007; *Covino et al.*, 2010]. To understand where and when water composition changes along a stream reach, both the biology and the hydrology of the system must be understood [*Alexander et al.*, 2009]. Hydrologic exchanges along a reach can dilute or further enrich stream solute concentrations, and/or can facilitate biogeochemical cycling (physical and biological processes) through water's role in microbial and vegetative habitat and transport [*Hall et al.*, 2002]. Bidirectional hydrologic exchange, or the concurrent lateral inflows (gains) and lateral outflows (losses) between the stream and adjacent groundwater through space and time, provides both a means for hillslope water to reach the stream, and for stream water to reach the groundwater aquifer. Gains and losses to and from the stream can happen over spatial scales of tens of meters to kilometers, and over temporal scales of minutes to days [*Payn et al.*, 2009]. By simply assessing net changes in discharge and/or hydraulic gradients between the groundwater and surface water, we likely do not account for all space and time scale interactions [*Payn et al.*, 2009; *Covino et al.*, 2010, 2011; *Ward et al.*, 2013]. With the knowledge that bidirectional exchange along the riparian corridor captures the two-way hydrologic regime along a stream, these gains and losses can dictate the potential for flushing as well as hyporheic exchange and subsequent nutrient cycling.

Along Colorado's Front Range, nutrient cycling has been extensively studied in high-elevation, snowmelt-dominated alpine catchments. Elevated levels of biologically available nitrogen in the atmosphere, from industrialization and fertilizers, have impacted stream networks and ecosystems [*Hedin et al.*, 1995]. Through either wet deposition or dry deposition, atmospheric nitrogen can reach terrestrial and aquatic systems, which can shift such ecosystems from N limited to N saturated [*Baron et al.*, 1994; *Barnes et al.*, 2012]. N saturation is problematic as elevated nitrate export can disrupt water quality levels, and nutrient level shifts within ecosystems can result in eutrophication [*Campbell et al.*, 2000]. Lower elevation catchments within the montane zone of Colorado, although studied in far less detail at present, are also vulnerable to climate change and anthropogenic forcings in disrupting the current ecosystem balance.

Within the rain-snow transition zone, nutrient export can be a more complex process, as montane catchments can receive substantial spring and summer rain, and thus snowmelt is not the only dominant hydrologic event throughout the season [*Hinckley et al.*, 2014a]. Following rain or snowmelt, hillslope water and dissolved constitutes, such as nitrate, may move overland to the stream. Alternatively, the water and any dissolved solutes reach the channel through infiltration and subsequent groundwater discharge, or through subsurface through flow or preferential flowpaths [*Freeze*, 1974; *Larkin and Sharp*, 1992]. Once water enters the main channel, flowpaths may exit the reach to the adjacent groundwater interface, or the hyporheic zone, and may return to the stream at a downstream location at some future time [*Bencala and Walters*, 1983].

The importance of both biological processes and physical flushing has been studied with respect to nitrate export [*Hedin et al.*, 1995; *Covino et al.*, 2010], and both play a role in biogeochemical cycling patterns. Biogeochemical studies have typically focused on hyporheic exchange, as locations where surface water and groundwater mix provide hotspots for potential biogeochemical activity [*Mulholland et al.*, 1997]. Hyporheic exchange can occur due to a variety of hydrologic factors/connections, laterally, vertically, and longitudinally. In a lateral sense, or hillslope/riparian to stream interactions, inflows to the stream from adjacent groundwater can move organisms and nutrient-rich water to the surface, while outflows from the stream to groundwater pools can move oxygen-rich water into the subsurface [*Boulton et al.*, 1998]. This interaction (which is physically driven by bidirectional exchange) can distribute infiltrated hillslope water to the stream network, transfer solutes, and transform nutrients such as nitrate via biological transformations [*Alexander et al.*, 2009; *Mallard et al.*, 2014]. In the absence of precipitation, deeper, slower groundwater flowpaths act to flush older water from the hillslopes, continuing the potential for exchange long after a specific hydrologic event.

In a vertical sense, geomorphic elements along the channel such as pools and riffles move water into and out of the subsurface through downwelling and upwelling gradients, driving exchange [*Harvey and Bencala*, 1993]. Finally, in a longitudinal sense, flow along the stream corridor can also be influenced by the geomorphology, as features such as steps and pools can change the dominant flow processes affecting a water parcel and any dissolved solutes. Slow-moving backwater locations or eddies, for instance, can allow for significant "in-stream storage", or locations of delayed downstream transport. At such locations, there is significantly more potential for residence time and interactions between surface-water and groundwater, and thus a greater potential for biogeochemical cycling [*Zarnetske et al.*, 2008].

Thus, the water quality observed at the catchment outlet, both during times of rain and snowmelt and during baseflow conditions, is influenced by both hillslope processes and in-stream processes. The hillslope and in-stream elements can drive interaction between surface water and groundwater laterally, vertically, and longitudinally, which may either provide a location for biological transformation of nitrate and other solutes, or may provide a location where hydrologic flushing can move elements out of the stream or riparian zone. While a substantial body of literature describes the importance of these hydrologic processes in nitrate levels, there have been few studies that explicitly link the hydrologic and biological component. Moreover, very few studies include a detailed understanding of surface water-groundwater interactions following snowmelt, rain, and periods of baseflow. Hydrologic flushing is now known to be an important and often dominant process controlling nutrient export in stream networks yet there is a gap in our understanding pertaining to the dual processes affecting this exchange (hillslopes and stream characteristics), and the ways in which they interact with one another. By assessing bidirectional exchange from both the stream's perspective and the hillslope's perspective, we can begin to unravel the relative importance of each during different hydrologic regimes.

1.2 Goals

We seek to address gaps in the current eco-hydrologic literature regarding the role of bidirectional hydrologic exchange in nitrate export through field measurements and modeling of surface water and groundwater inputs along Lower Gordon Gulch (GGL), a tributary to Boulder Creek and a site within the Boulder Creek Critical Zone Observatory (BcCZO). We seek to understand export as a concurrent hydrologic and biological process, by applying a physical (hydrologic) mass balance model and a biological (nitrate) mass balance model in synchronization for snowmelt-dominated periods, rain-dominated periods, and baseflow conditions to capture seasonal changes in biogeochemical processing. We conceptualize the hydrologic mass balance to reflect the physical component of nutrient cycling. We conceptualize the chemical mass balance to reflect the influence of the physical component on the biological component, and as a combination of the lateral, vertical, and longitudinal components of exchange. These include hillslope to stream exchange from infiltrated groundwater that reaches the stream along the riparian corridor, and in-stream exchange vertically and longitudinally from geomorphic effects that may drive flowpaths into/out of the bed vertically or move water into or out of the stream along a hyporheic flowpath. Specifically, we wish to: 1) Determine the current biological removal rates of nitrate along GGL through resolving both the hydrologic and nitrate mass balances 2) Determine the role of groundwater inputs to the stream in regulating in-stream hydrologic processes and both hydrologic and biological nitrate removal 3) Apply our findings to help increase our understanding of nitrate transport during various hydrologic regimes within Colorado's montane zone.

1.3 Background on Nitrogen Cycle and Mass Balance Methodology

Within the nitrogen cycle, nitrate in the stream can be removed biologically through denitrification or assimilation, or physically, through a hydrologic flowpath leaving the main channel [*Campbell et al.*, 2000]. There are a variety of environmental factors that affect this process: namely, the geologic setting, the physical makeup of the streambed and near-stream areas, and the hydrology of the system. Vegetation type and density, soil type, precipitation patterns, snowpack cover, and bed topography all act to influence the potential for nitrogen removal, whether that be denitrification or another mechanism [*Laursen and Seitzinger*, 2002]. Vegetated hillslopes and microbial communities within soils act to perform these biological processes, and the interface of the local geology, vegetation, and climate can act to facilitate or disrupt them. Well-developed soils and vegetation can act to assimilate or denitrify. Snowpack cover can insulate soils and microbial communities, creating an environment more conducive to assimilation [*Brooks and Williams*, 1999]. Bedrock patterns and topography, can influence when and where the surface stream is gaining or losing to adjacent groundwater [*Hester and Doyle*, 2008].

Assessing the aforementioned characteristics can be a daunting task, and thus many studies attempt to use a simplified modeling framework to assess the current capacity of the system to remove nitrate either by physical (hydrologic) or biological processes. Once such a model is applied, the findings can be used along with knowledge of catchment characteristics to make inferences as to which factors are most important in nitrate removal. To model the physical (hydrologic) and biological component of nutrient export along a stream reach, a general approach for both is a mass balance. Mass balance models are simple tools that include upstream and downstream quantities and either measured or estimated inflow or outflow fluxes, which are combined to assess the change in discharge or the change in nutrient flux along a reach [*Boyer et al.*, 2006]. Generally, the models are used to solve for at least one unknown flux term, which can be determined through the resolved change in discharge or nutrient flux. The beauty of a mass balance model is that the unknown term allows us to infer the suite of physical or biogeochemical processes that are affecting the system and difficult to directly measure, such as hyporheic exchange, denitrification, assimilation, etc.

Before understanding how to model the hydrologic mass balance, which is used in this study, it is necessary to understand dilution gauging, one of the most widely used frameworks to measure discharge and to assess the physical quantities of stream water that may interact with groundwater [*Day*, 1977; *Bencala and Walters*, 1983; *Stream Solute Workshop*, 1990; *Harvey et al.*, 1996]. To measure discharge, dilution gauging can be used in one location, with a short mixing length. Under the assumption of complete mixing and full mass recovery following a known tracer injection mass, the measured rise in concentration through time can be converted to a discharge estimate. Over longer reaches, where we expect hydrologic gains and losses, exchange with groundwater can be quantified through tracer mass recovery following a conservative stream tracer injection. With a known quantity of injected tracer upstream, the amount that does not reach the downstream end over some recovery time interval can be modeled to explain transient storage [*Bencala and Walters*, 1983; *Runkel and Broshears*, 1991], indicative of hyporheic flowpaths, or lateral inflows or outflows that enter or leave the stream reach and may not re-enter until some distance farther downstream. While a tracer study and subsequent transport model provide a quick method to model stream processes governing exchange, the reliability of the stream tracer approach at higher discharge conditions is questionable, given reduced contact of surface water parcels with subsurface features [*Harvey et al.*, 1996].

Recovery times, moreover, are generally measured over short spatial and temporal scales, and thus do not capture longer length and/or duration hyporheic flowpaths. Thus, in order to inform a mass balance, appropriate recovery times over a greater number of longer sub-reaches should be included. Many studies that have shown the importance of bidirectional hydrologic exchange at various spatial and temporal scales employ more such robust field methods, independent of a transport model, to capture gross gains and losses of water [*Payn et al.*, 2009]. This allows for a better-informed hydrologic mass balance model along the stream reach, which includes two discharge measurements from dilution at an upstream and downstream location, as well as one upstream to downstream tracer mass recovery.

A nutrient mass balance model can be used to quantify nitrate export and retention [*Boyer et al.*, 2006; *von Schiller et al.*, 2011]. The general approach in such a study is to track changes in nitrate concentration across a set distance or to look at watershed scale budgets [*Likens et al.*, 1970]. The groundwater influence typically is accounted for via the increase or decrease in concentration from upstream to downstream. Such models are rarely linked to a well-informed hydrologic mass balance that includes appropriate recovery times, and thus do not include a detailed quantification of hydrologic gross gains and losses. A simplified view of surface water-groundwater interaction (i.e. a simplified view of physical retention and export) can alter our understanding of nutrient retention or export, as biogeochemical reactions are often driven by nutrient, oxygen, and temperature gradients, which are directly affected by hydrologic connections and the system's biology.

CHAPTER 2: METHODS

A combination of field instrumentation and long-term monitoring (including BcCZO datasets) with periodic experiments at Lower Gordon Gulch provided sufficient data to inform a hydrologic and nitrate mass balance for four separate experiment dates throughout the 2014-2015 water year. The experiments were conducted on 10/3/14, 11/8/14, 5/3/15, and 6/10/15 in order to capture different hydrologic regimes (i.e. baseflow, snowmelt-dominated, and rainfall-dominated). The October and November results together represent baseflow conditions, where discharge measurements were approximately 1 L/s throughout the 1000-meter study reach. May results represent snowmelt-dominated conditions, where discharge was exceptionally high relative to baseflow at approximately 100 L/s. June results represent rainfall-dominated conditions, where the experiment followed a record-breaking rainfall in May in Colorado. Due to low flow conditions in October and November, the mass balance experiments carried into the next calendar day (10/4/14 and 11/9/14, respectively). During these times, there was no precipitation or large increase in discharge throughout the catchment.

2.1 Site Description

GGL is a 2.7 km^2 headwater stream catchment located in the montane zone of Colorado's Front Range, within Arapahoe National Forest (Figures 1 and 2). Both rain and snow fall as precipitation each year. The catchment drains to a partially intermittent stream, Lower Gordon Gulch. The stream is intermittent in the upper portion, and perennial in the lower portion, and is generally no more than 1 m in width (Figure 3). The stream runs west to east, and has north-facing and south-facing hillslopes. The hillslopes have different aspects (Figure 4), and have different soil properties, vegetation types and patterns, snowpack properties, and bedrock patterns.

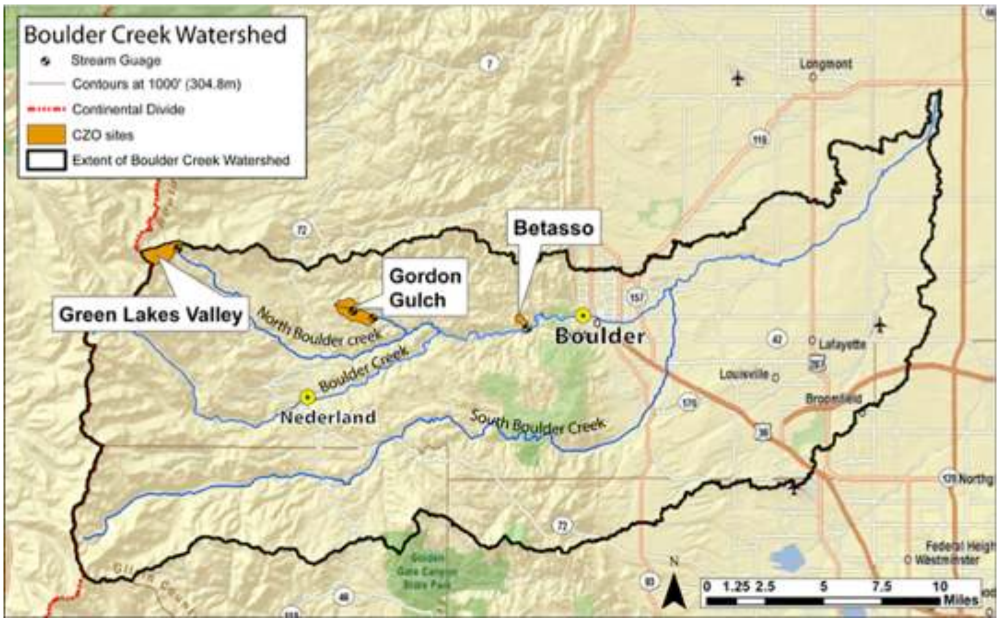

Figure 1: Location of Gordon Gulch within Boulder Creek Watershed (image courtesy of BcCZO).

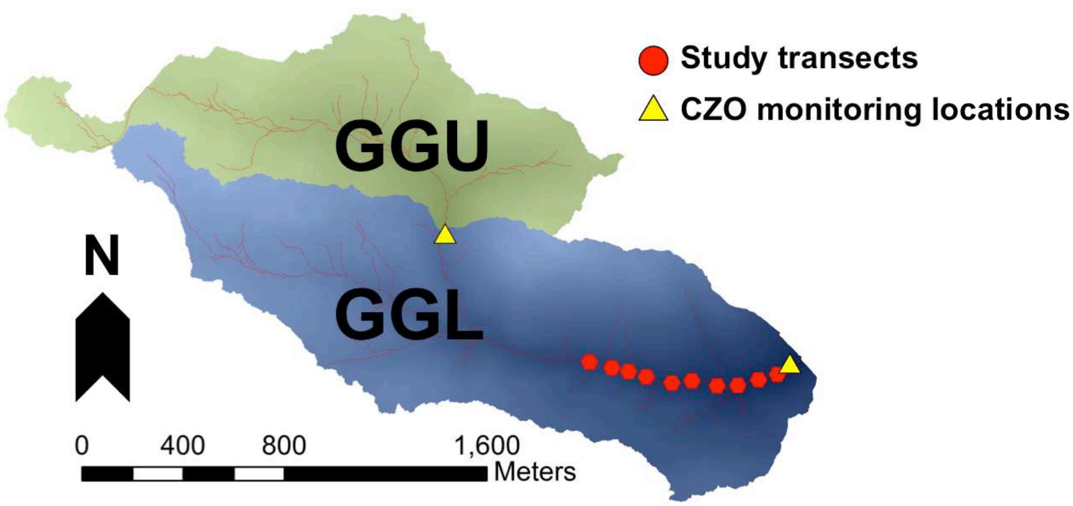

Figure 2: Delineated Watershed showing Upper Gordon Gulch (GGU) and Lower Gordon Gulch (GGL) derived via 1 m LiDAR data collected for the BcCZO.

Figure 3: Cross section view of Lower Gordon Gulch, photo taken Summer 2014 (width = ~1m and flow is from right to left).

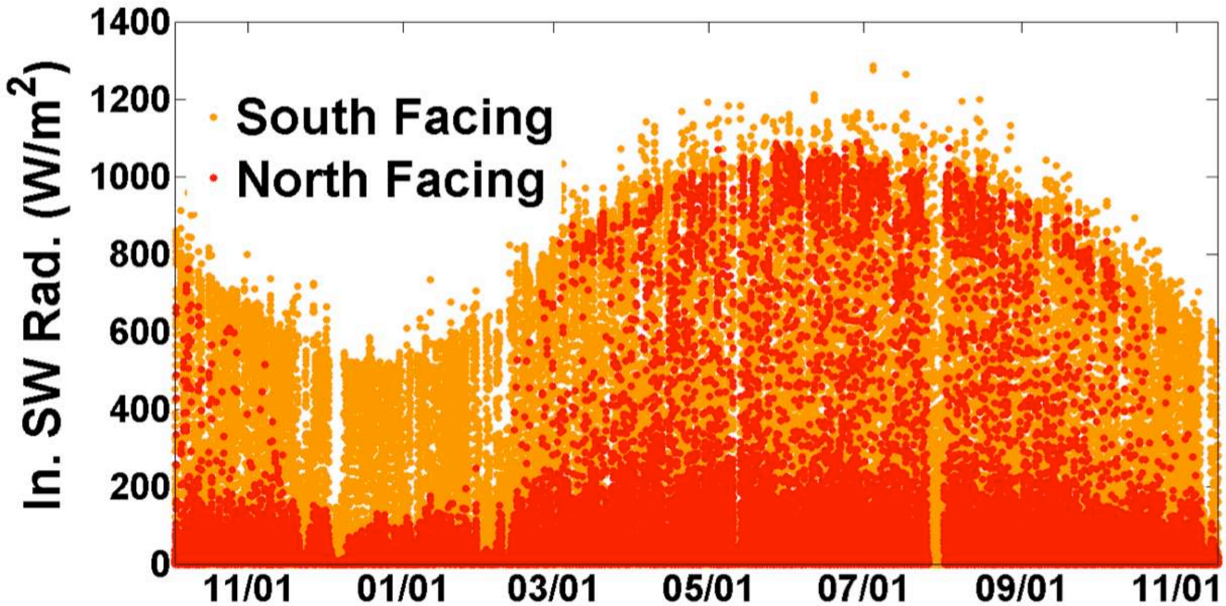

Figure 4: Incoming shortwave radiation measured at BcCZO north-facing and south-facing meteorological stations within Lower Gordon Gulch for a typical water year.

The catchment is underlain by Pre-Cambrian gneiss and granitic bedrock, with deeper bedrock weathering on the north-facing slopes compared to the south-facing slopes [*Anderson et al.*, 2014]. North-facing slopes are dominated by dense stands of lodgepole pine with more developed soils, whereas south-facing slopes are dominated by less dense stands of ponderosa pine. Aspen stands and other deciduous shrubs occupy much of the valley bottom [*Befus et al.*, 2011]. North-facing soils are primarily Alfisols, which typically have high nutrient cation content and high clay content. South-facing soils are primarily Mollisols [*Anderson et al.*, 2011]. Climatically, Lower Gordon Gulch lies within the rain-snow transition zone, with maximum precipitation during May and minimum during the winter months. North-facing hillslopes develop a seasonal snowpack, whereas south-facing hillslopes have a spatially and temporally variable snowpack dynamic [*Hinckley et al.*, 2014a, 2014b].

Lower Gordon Gulch is a tributary to Boulder Creek and a site within the Boulder Creek Critical Zone Observatory (BcCZO) (Figure 3), and the Boulder Creek Watershed is one of the many Front Range watersheds affected by industrial practices [*Barnes et al.*, 2012]. Within the Boulder watershed (Niwot Ridge), the alpine catchment has been studied intensely as a part of the Niwot Ridge LTER. This alpine catchment, also known as Green Lakes Valley, originates along the continental divide, and drains into North Boulder Creek. Gordon Gulch, within the montane zone, also drains to North Boulder Creek, which links with the main stem of Boulder Creek just upstream of Betasso, before reaching the City of Boulder, CO. Boulder Creek feeds the primary drinking water source for the city, and is a prime recreational attraction for the area. Studies have shown elevated N levels in stream water in Green Lakes Valley, and have attributed these changes to the Denver metropolitan area [*Williams et al.*, 1996]. Although N levels are not as high as eastern U.S. areas, many studies suggest that Front Range ecosystems are particularly vulnerable to small shifts in atmospheric levels due to poorly developed soils and greater exposure [*Baron et al.*, 1994]. There has been little work in quantifying the current state of N in lower elevation catchments within the Gordon Gulch watershed, however. Previous long-term records from past water years from CZO sampling and discharge measurements show a decrease in nitrate loading from along GGL from upstream to downstream (Figure 5), yet the mechanisms of removal are not widely understood. Moreover, generally, few studies in mountain catchments have incorporated a robust understanding of hydrologic connectivity and bidirectional water movement in nitrogen transport models [*Hinckley et al.*, 2014b].

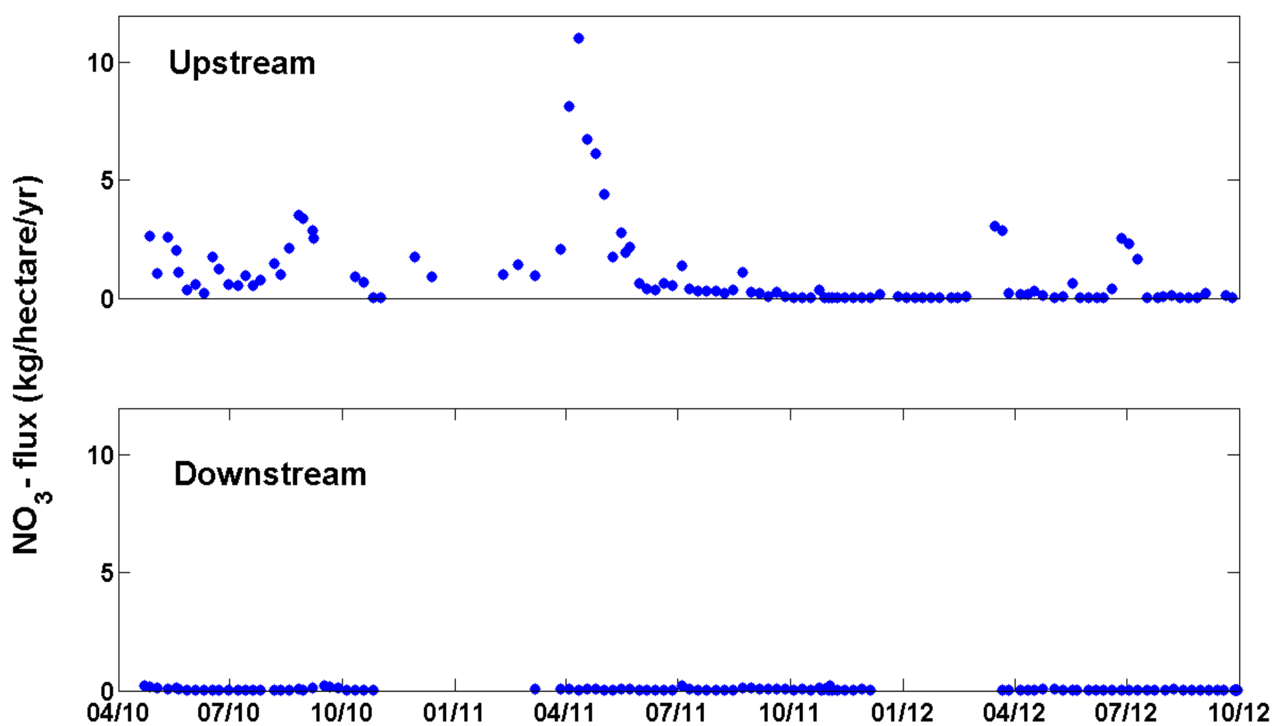

Figure 5: Upstream and downstream nitrate fluxes from data collected at BcCZO monitoring locations within Lower Gordon Gulch throughout 2010-2012.

2.2 Well Installation and Lateral Hydraulic Gradient Calculations

Reach-scale groundwater inputs to Lower Gordon Gulch were determined via riparian-stream water table gradients, and periodic hydrologic mass balance measurements. To determine the groundwater levels in the riparian zone and in the stream along the reach, 10 well transects were installed in ~100 meter increments along a 1000 meter perennial portion of the stream in the summer of 2014. Within each transect, we placed one HOBO U20 water level logger (absolute pressure accuracy = ±0.3%) in the approximate thalweg, and one logger in wells ~2-3 m from the stream on both the north- and south-facing riparian areas (Figure 6). Wells were drilled to consolidated bedrock through combined hand and gas-powered augering techniques, and were generally 0.5 to 1 m deep. The U20 water level loggers collected pressure heads at 15-minute intervals for nearly the majority of the 2014-2015 water year (10/1/14-06/20/15). Absolute pressures were converted to gauge pressures through use of barometric data from both the bottom and the top of the reach.

Figure 6: Well installation process in August 2014.

The stream reach was surveyed via traditional leveling techniques during baseflow conditions in the Fall of 2014. Uncertainty in surveying results is less of a concern for our purposes, as water gradients were used as a baseline estimate of groundwater-surface water dynamics during hydrologic mass balance experiments. In other words, the magnitude of the gradient is not as important as the dominant direction. From survey data, gauge pressure was corrected for barometric pressure and was converted to stage. Hydraulic heads at each transect are all analyzed with respect to the bed elevation at each transect. Specifically, the heads for the stream, south-facing well, and north-facing well are all relative to a zero datum, which is located where the in-stream logger is installed within the bed. This allows for an approximation of the direction of flow between the surface water and groundwater. Locations where the north-facing or south-facing groundwater heads are greater than the in-stream heads indicate locations where the stream is likely gaining from the north-facing or south-facing side, or where the groundwater table is higher than the stream water level. Locations where the north-facing or south-facing groundwater heads are less than the in-stream heads indicate locations where the stream is likely losing from the north-facing or south-facing side, or where the groundwater table is lower than the stream water level. Transects that show higher heads relative to the bed for one side of the stream and lower heads relative to the bed for the other side of the stream indicate cross-valley fluxes.

2.3 Hydrologic Mass Balance Experiments and Calculations

On four separate occasions throughout the 2014-2015 water year, a full mass balance was measured for the entire reach via slug dilution gauging, as this method works particularly well in mountainous headwater streams [*Day*, 1977a]. Potassium bromide

(KBr) which was used as the conservative salt for the low flow experiments, has low biological and chemical reactivity [*Germann et al.*, 1984; *Burns and Nguyen*, 2002], and sodium chloride (NaCl) was used for the high flow experiments. A known amount of tracer was injected at the bottom and top of 10 sub-reaches, each encompassing a well transect, totaling 11 injections per experiment. Appropriate mixing lengths were determined via visual analysis and trial runs, with careful avoidance of pools or slow eddies between injection and monitoring locations. Specific conductance was continuously tracked at 10-second intervals on HOBO U24 freshwater conductivity loggers (accuracy = ±3%) at each monitoring location via downstream tracer recovery. Specific conductance through time was integrated and converted to mg/L via a laboratory-established relationship for KBr and for NaCl. Discharge was subsequently calculated under the assumption of full mass recovery (equation 1).

$$\boldsymbol{Q_n} = \frac{\boldsymbol{m_{inj,n}}}{\int_0^t \boldsymbol{C_n(t)dt}} \tag{1}$$

where Q_n = discharge [L/s], $m_{inj,n}$ = mass injected of conservative salt [g], and $C_n(t)$ = back-ground corrected concentration through time of tracer at monitoring location [mg/L*s].

In addition to discharge calculations at 11 points along the stream reach, the full mass balance was determined for the 10 study transects (gross gains and gross losses) via methods described in [*Payn et al.*, 2009] (Figure 7). Studies have shown the sensitivity of tracer concentration in the stream to gross inflows [*McCallum et al.*, 2012]. It is important to have well defined end members (in this case, EC values) when performing a tracer experiment to ensure more reliable results. In this study, background conductivity of the stream was determined via in-situ monitoring of EC prior to and after a tracer experiment.

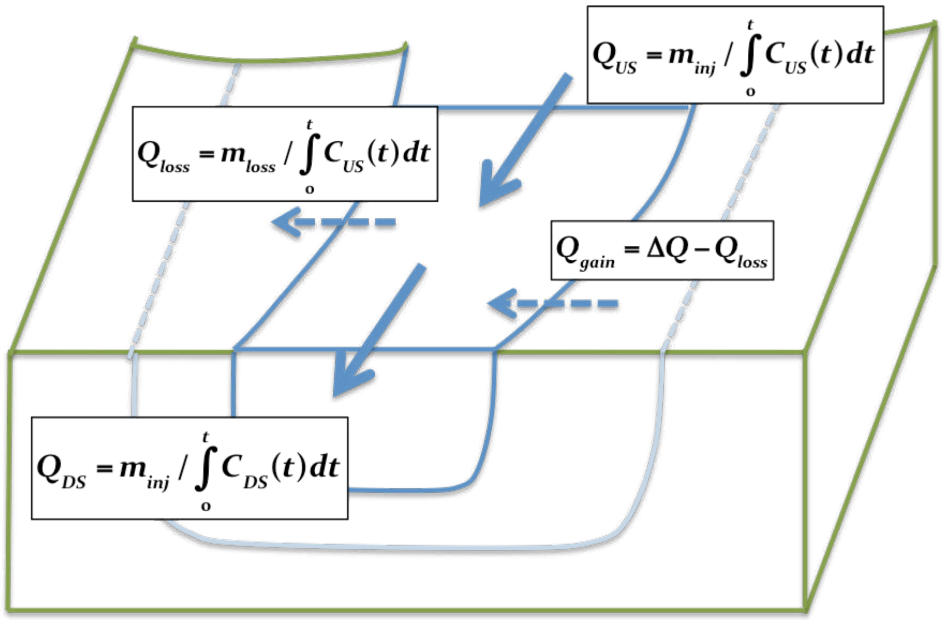

Figure 7: Conceptual hydrologic mass balance showing Q_{US}, Q_{DS}, Q_{gain} and Q_{loss}.

2.4 Nitrate Mass Balance Experiments and Calculations

Prior to each injection, water samples were taken within the stream, and also within the wells (when not dry). Water samples were filtered in the field when possible (i.e., low enough suspended sediments and organic content), or back in lab using 0.45 μm Nalgene syringe filters, and held in 125 ml narrow-mouth LDPE sample bottles. Samples were kept on ice until transported. The first three sets of samples were analyzed at the Niwot Ridge Long-term Ecological Research Station's Kiowa Environmental Chemistry lab at the University of Colorado Boulder. The last set of samples was in part analyzed at the Kiowa Lab and in part analyzed at the Soil, Water and Plant Testing Laboratory at Colorado State University. At the Kiowa lab, the first three sample sets were kept refrigerated in the lab before being run for nitrate+nitrite (NO_3^-+NO_2^-) and nitrite alone (NO_2^-). NO_3^-+NO_2^- and NO_2^- alone were run on a Lachat QuickChem 8500, which has a detection limit of 0.0012 mg N/L and run precision of 0.33%. NO_3^- was calculated by subtracting the NO_2^- value from the

NO_3^-+NO_2^- value. All four samples sets were also run for NH_4^+ and TDN at the Kiowa lab. These results were not directly used in this analysis, but are included in the sample data table seen in Appendix A and Appendix B. These components were not measured for the last sample set (June's) due to time constraints. At the Soil, Water, and Plant Testing lab, the last set of samples was run directly for nitrate with an OI Analytical Flow Solution 3000 Flow Injection Analyzer via EPA Method #353.2.

The nitrate mass balance was informed from the results of the hydrologic mass balance and in-stream and groundwater concentrations of nitrate. The physical and biological fluxes of nitrate were determined via equation 2.

$$C_{Ds}Q_{DS} = C_{US}Q_{US} + C_{gain}Q_{gain} - C_{loss}Q_{loss} + \lambda \qquad (2)$$

where $C_{DS}Q_{DS}$ is the downstream flux of nitrate, $C_{US}Q_{US}$ is the upstream flux of nitrate, $C_{gain}Q_{gain}$ is the physical inflow flux of nitrate, $C_{loss}Q_{loss}$ is the physical outflow flux of nitrate, and λ is the biological flux of nitrate (allowed to be positive or negative). All units are [mg NO_3-N/s].

For the four experiments, most transects had enough water in one or both of the riparian wells to take a sample for analysis. We calculated the physical inflow fluxes of nitrate along each transect as the product of the groundwater concentration and the hydrologic gross gain. Groundwater concentration (C_{gain}) is considered to be the average of the north-facing and south-facing concentrations if both wells were sampled. If only one was sampled (i.e. if one was dry), then the concentration was considered to be the concentration of the side with a water table. If both the north-facing and south-facing wells were dry, then the concentration was considered to be the average of the two well concentrations at the next upstream transect. The rationale behind this method is the likelihood of hyporheic flowpaths, evidenced by gross gain and loss results. The hydrologic mass balance results generally show bilateral exchange, as do the lateral hydraulic gradients. Thus, even if a well was dry at a particular point in the landscape, hyporheic flow is likely from upstream groundwater and/or surface water.

In the hydrologic mass balance calculations, we assumed that gross losses occurred before gross gains. This results in a minimum gross loss and gross gain calculation (see *Payn et al.*, [2009] for description). Using these same assumptions in the nitrate mass balance, we assumed that physical outflow fluxes of nitrate occurred before physical inflow fluxes, and thus used the upstream nitrate concentration as C_{loss}.

3.1 Lateral Hydraulic Gradients and Precipitation Response

Water tables (hydraulic heads) were analyzed relative to the stream bed elevation at each transect from August 2014 through late June 2015, capturing most of the 2014-2015 water year (Figures 9 and 10). From onset of monitoring through November, water levels on south-facing and north-facing riparian areas remain relatively constant. Climatically, throughout this period, the regime changes from primarily dry conditions, to snow and snowmelt dominated, and finally to rainfall-dominated, with the wet period defined as springtime (Figure 8). Generally, all of the head values increase starting in late March to early April, and peak in early May. By the June experiment, the heads are already on their recession moving back towards baseflow conditions.

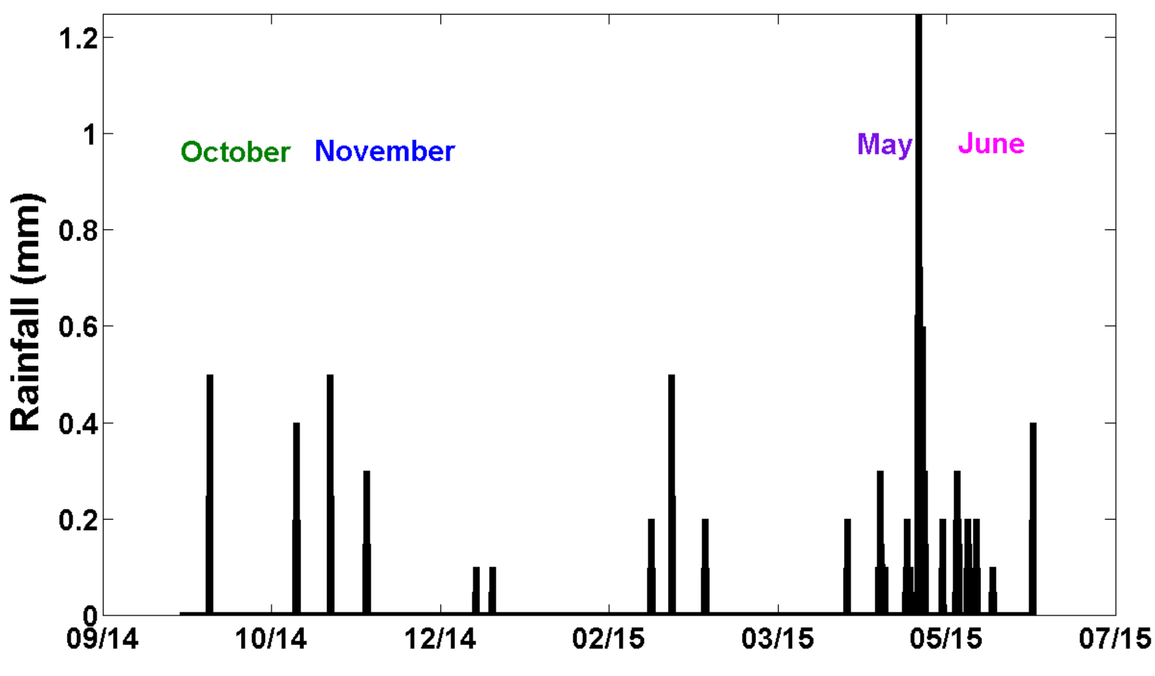

Figure 8: Rainfall (mm) measured in GGL at BcCZO south-facing met station during the study period.

During snowmelt, north-facing heads relative to the streambed are generally greater than south-facing heads, with the exception of transects 7 and 8. Transects 3 and 10 are missing data for the later part of the time series due to logger malfunctions. Despite some logger malfunctions, the results clearly indicate seasonality of water tables, and spatial variability in water tables throughout the catchment on both the north-facing and south-facing riparian areas.

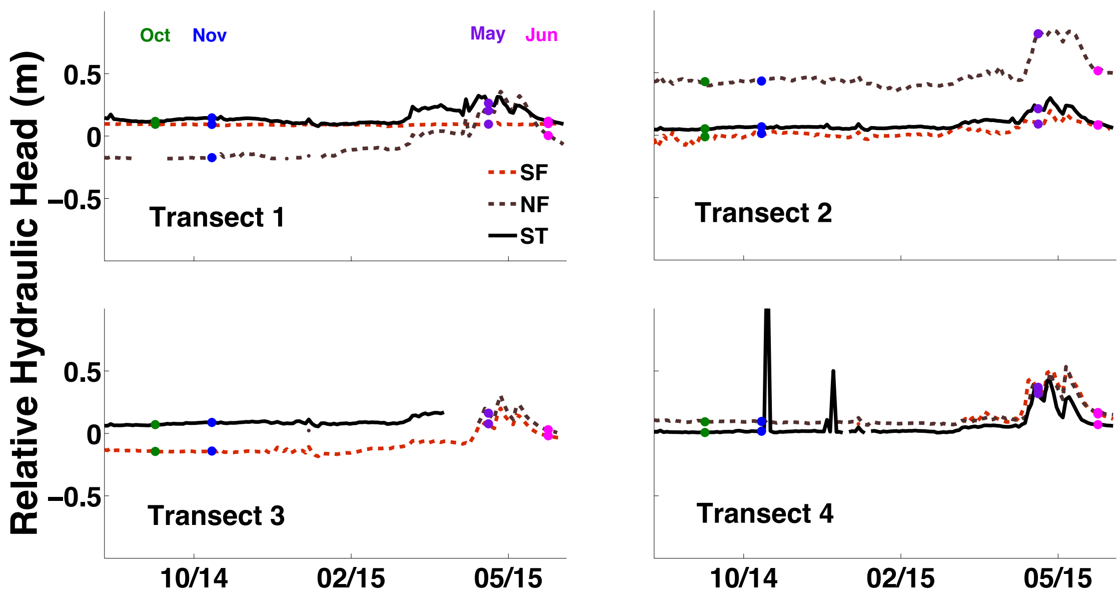

Figure 9: Hydraulic heads relative to the streambed elevation at transects 1-4 for the stream (ST), north-facing groundwater well (NF), and south-facing groundwater well (SF) through the majority of the 2014-2015 water year (encompassing all 4 study dates). Colored dots represent heads for the stream, north-facing, and south-facing locations during each of 4 dates in the study (October, November, May, June). Note there are missing data at Transect 3 for the months of May and June due to logger malfunction. Other locations of no data represent no water table or ice-over periods.

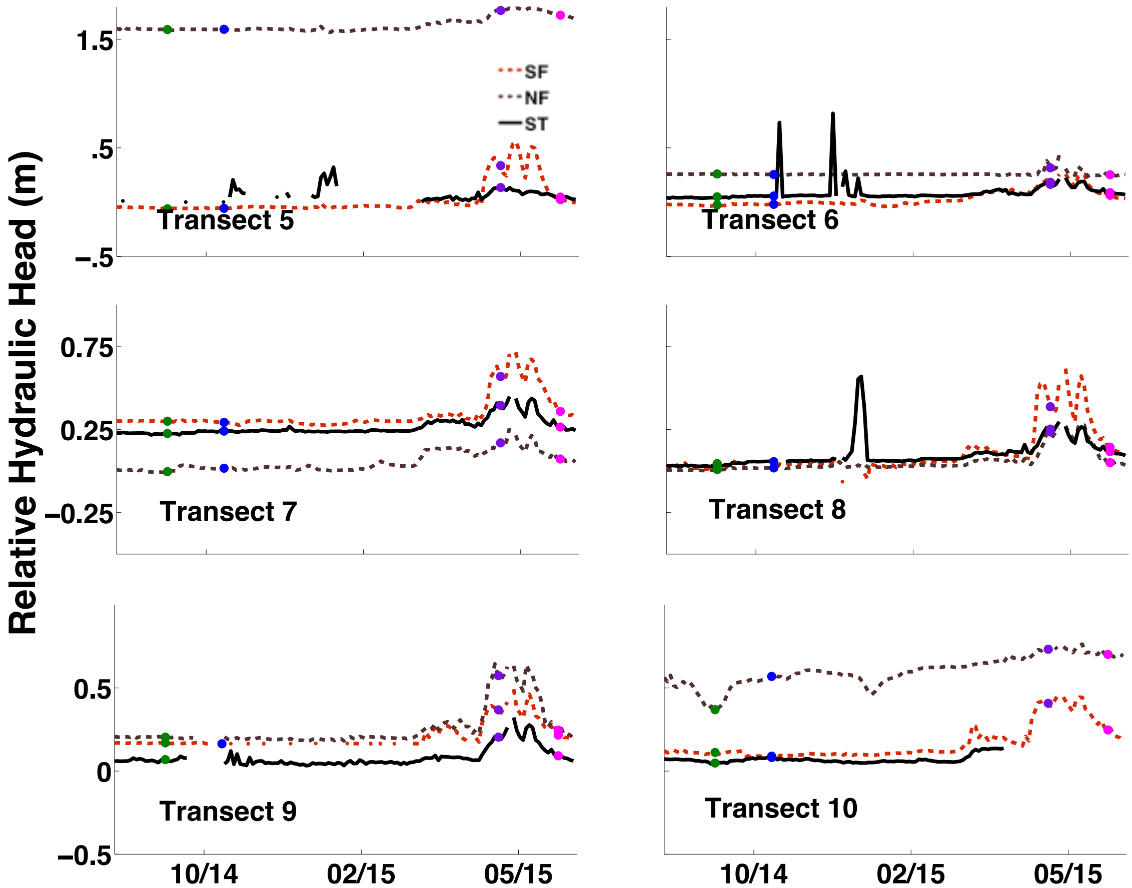

Figure 10: Hydraulic heads relative to the streambed elevation at transects 5-10 for the stream (ST), north-facing groundwater well (NF), and south-facing groundwater well (SF) through the majority of the 2014-2015 water year (encompassing all 4 study dates). Colored dots represent heads for the stream, north-facing, and south-facing locations during each of 4 dates in the study (October, November, May, June). Note there are missing data at Transect 10 for the months of May and June due to logger malfunction. Other locations of no data represent no water table or ice-over periods.

3.2 Hydrologic Mass Balance

Results show variable discharge patterns from upstream to downstream during dry (October and November) versus wet (May and June) periods (Tables 1 and 2). In October and November, discharge is at near-baseflow conditions, with values all less than or equal to ~1.5 L/s. There is a consistent, subtle increase in discharge from upstream to downstream for both October and November, but there are reaches all along the catchment that indicate losses. Net losing reaches, such as the well transect between 300 and 400 meters, are likely indicative of rapid exchange with the subsurface. Bidirectional exchange is evident during baseflow, as well, as indicated by the concurrent gains and losses along each reach. For both months, experimental results show gross losses and gains to be on the order of 5-10 times the overall net change in discharge, showing that an increase or a decrease in discharge does not just mean solely gains or solely losses. In one reach for both October and November, the hydrologic mass balance produces negative losses, which essentially means the reach is strictly gaining. While this has been attributed to experimental error [*Payn et al.*, 2009], the pattern persists for one location for both experiments. This may also be due to discharging springs in the area, some of which may be supplying groundwater to the surface and maintaining streamflow during low-flow conditions.

The October and November results show losing lateral hydraulic gradients during times when the water balance indicates gross gains (Figures 11 and 12). This may be due to the point measurement nature of wells, in that only one location within the groundwater flowpath is analyzed, which may not capture true variability. If we deem this to be the true nature of the gradients during that time, however, this may be indicative of upstream hyporheic flowpaths that circumvent well locations and reach the stream. In order to fully confirm this, further analyses and mixing models need to be employed.

Table 1: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and net change in Q [ΔQ]) as well as gain and loss proportions of the net change in discharge along 1000 m reach for October and November experiments.

Transect	October			November		
	Q_{gain} [L/s]	Q_{loss} [L/s]	ΔQ [L/s]	Q_{gain} [L/s]	Q_{loss} [L/s]	ΔQ [L/s]
1	0.283	-0.494	-0.211	0.471	-0.429	0.042
2	-0.006	-0.240	-0.246	0.178	-0.503	-0.325
3	0.883	-0.321	0.562	1.099	-0.147	0.952
4	NaN	NaN	NaN	0.231	-0.780	-0.549
5	NaN	NaN	NaN	0.376	-0.210	0.166
6	0.363	-0.311	0.052	0.408	-0.247	0.161
7	0.378	-0.297	0.081	0.240	-0.323	-0.083
7	0.248	-1.068	-0.820	0.331	-0.908	-0.577
9	0.973	0.000	0.973	0.883	0.000	0.883
10	0.235	-0.210	0.025	0.222	-0.276	-0.054

Transect	October			November		
	$Q_{gain}/\Delta Q$	$Q_{loss}/\Delta Q$	ΔQ [L/s]	$Q_{gain}/\Delta Q$	$Q_{loss}/\Delta Q$	ΔQ [L/s]
1	-1.340	2.340	-0.211	11.219	-10.219	0.042
2	0.023	0.977	-0.246	-0.548	1.548	-0.325
3	1.571	-0.571	0.562	1.154	-0.154	0.952
4	NaN	NaN	NaN	-0.421	1.421	-0.549
5	NaN	NaN	NaN	2.264	-1.264	0.166
6	6.975	-5.975	0.052	2.535	-1.535	0.161
7	4.670	-3.670	0.081	-2.889	3.889	-0.083
7	-0.302	1.302	-0.820	-0.573	1.573	-0.577
9	1.000	0.000	0.973	1.000	0.000	0.883
10	9.392	-8.392	0.025	-4.113	5.113	-0.054

Table 2: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and net change in Q [ΔQ]) as well as gain and loss proportions of the net change in discharge along 1000 m reach for May and June experiments.

Transect	May			June		
	Q_{gain} [L/s]	Q_{loss} [L/s]	ΔQ [L/s]	Q_{gain} [L/s]	Q_{loss} [L/s]	ΔQ [L/s]
1	4.484	-4.660	-0.176	0.383	-0.373	0.010
2	4.662	-0.725	3.937	2.374	-2.228	0.146
3	6.958	0.000	6.958	0.000	-0.957	-0.957
4	7.432	-3.527	3.905	2.230	-0.555	1.675
5	0.000	-4.952	-4.952	0.878	-1.003	-0.125
6	8.415	0.000	8.415	0.614	-0.175	0.439
7	7.390	0.000	7.390	2.364	-1.354	1.010
7	3.673	-1.536	2.137	0.639	-0.715	-0.076
9	0.000	-1.119	-1.119	0.000	-0.286	-0.286
10	7.337	0.000	7.337	3.025	-0.079	2.946

Transect	May			June		
	Q_{gain}/ΔQ	Q_{loss}/ΔQ	ΔQ [L/s]	Q_{gain}/ΔQ	Q_{loss}/ΔQ	ΔQ [L/s]
1	-25.474	26.474	-0.176	38.340	-37.340	0.010
2	1.184	-0.184	3.937	16.259	-15.259	0.146
3	1.000	0.000	6.958	0.000	1.000	-0.957
4	1.903	-0.903	3.905	1.331	-0.331	1.675
5	0.000	1.000	-4.952	-7.026	8.026	-0.125
6	1.000	0.000	8.415	1.398	-0.398	0.439
7	1.000	0.000	7.390	2.340	-1.340	1.010
7	1.719	-0.719	2.137	-8.401	9.401	-0.076
9	0.000	1.000	-1.119	0.000	1.000	-0.286
10	1.000	0.000	7.337	1.027	-0.027	2.946

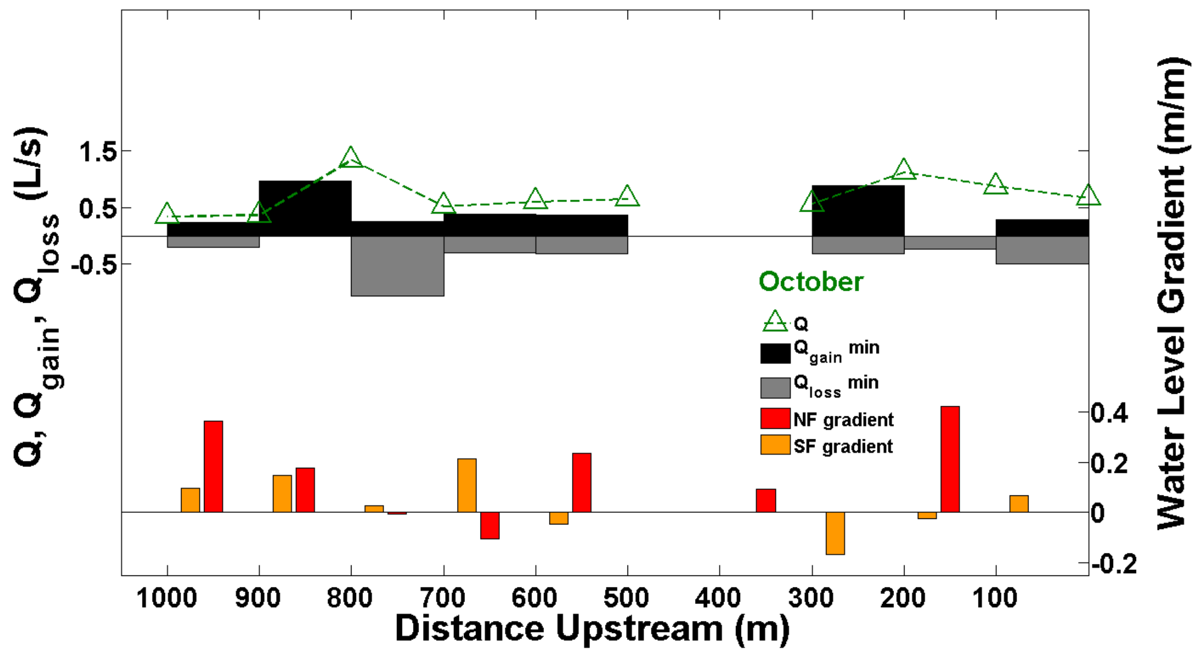

Figure 11: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and in-stream Q) and water table gradients for ten transects along 1000 m reach during October 2014 experiment. Positive gradient indicates higher water tables in riparian areas on the north-facing or south-facing sides relative to the stream. Negative gradients indicate the opposite.

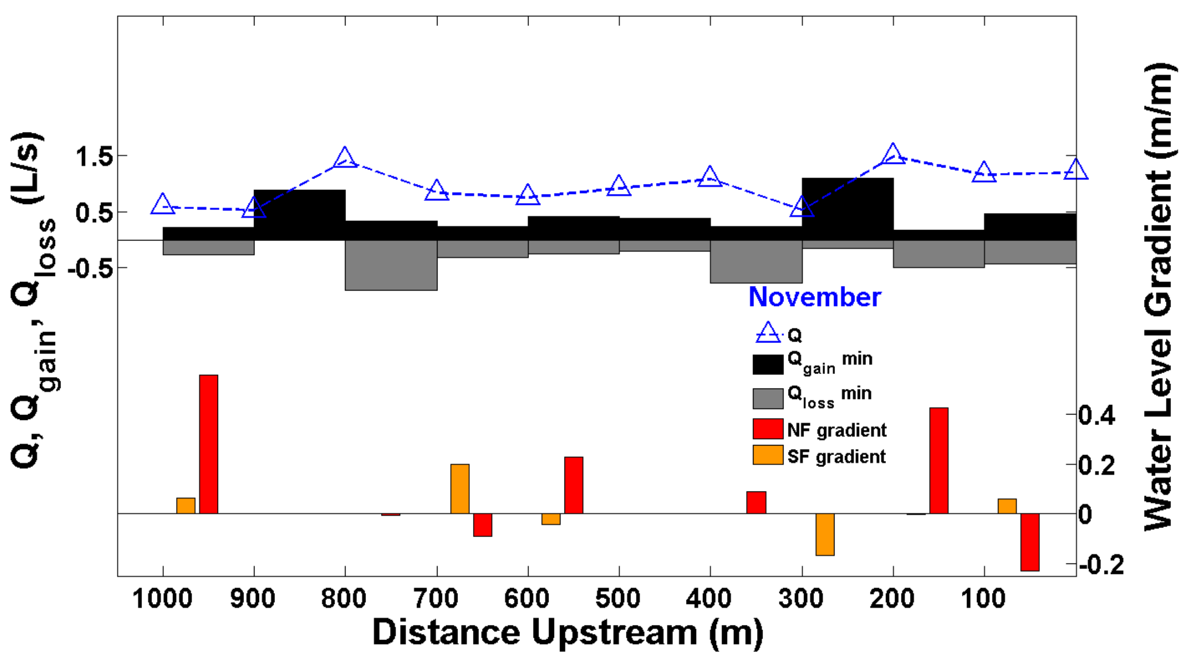

Figure 12: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and in-stream Q) and water table gradients for ten transects along 1000 m reach during November 2014 experiment.

Springtime results during wetter periods (May and June) show much higher discharge (Figures 13 and 14) relative to baseflow. The uncertainty in the measurements is also higher during this period, however, likely due to springs turning on, variable background EC, and incomplete mixing. Note that the June results are a combination of two field days due to some issues with equipment. The discharge measurement at transect 1 (0 m upstream) is the average of discharge measurements 6/10 and 6/12 (which were ~3 L/s apart), and the discharge measurement at transect (100 m upstream) is from 6/12. There may be variability in discharge during that time and moderate amounts of rainfall between the two dates, yet overall catchment response and bidirectional exchange is likely not very different over a 48 hour time period. Note also that in May and June, due to some uncertainty in background EC and mixing, values of zero gains or zero losses are locations where the mass balance produced the opposite sign in either the gain or loss (i.e. a negative gain or a positive loss). These were "corrected" to show either all gains or all losses in problematic reaches, which allows for easier analysis of the data. Negatives gains occurred once in October, but were minimal (i.e. not very negative), and thus were not corrected.

In May, discharge increases more significantly from upstream to downstream, and the catchment is generally generating much greater streamflow. Thus, gross gains and losses are much greater than in October and November, and overall, the reaches indicate mostly gains as opposed to concurrent gains and losses. June results show bidirectional exchange in much greater proportions compared to May, which is likely due to significant recession following peak snowmelt. The rapid increase in discharge from upstream to downstream is less pronounced for June relative to May, as well. For both May and June, once again, in locations of bilateral exchange, gross gains and losses can be orders of magnitude greater than the net change in discharge. This is particularly pronounced for the downstream-most reach, which is consistent for each month in the study. Other hotspots of exchange appear to occur approximately midway through the catchment, which is also the case for the other months.

In May, if present, the lateral hydraulic gradients are always directed toward the stream. In other words, during this experiment, the groundwater table appears to be higher than the stream surface, thus generating groundwater to stream water flow directions at all locations. This is likely indicative of the combined snowmelt and rainfall during the month of May that infiltrates the hillslopes and moves down-gradient toward the stream. In June, the lateral hydraulic gradients are also almost always directed towards the stream for both sides of the stream. The lateral hydraulic gradients in the NF riparian aquifer at transects 1 and 7, however, were slightly sloped away from the channel. Note that the scales for the lateral hydraulic gradients during the two wetter months (May and June) are much greater than the scales during October and November, displaying the observed greater magnitude gradients.

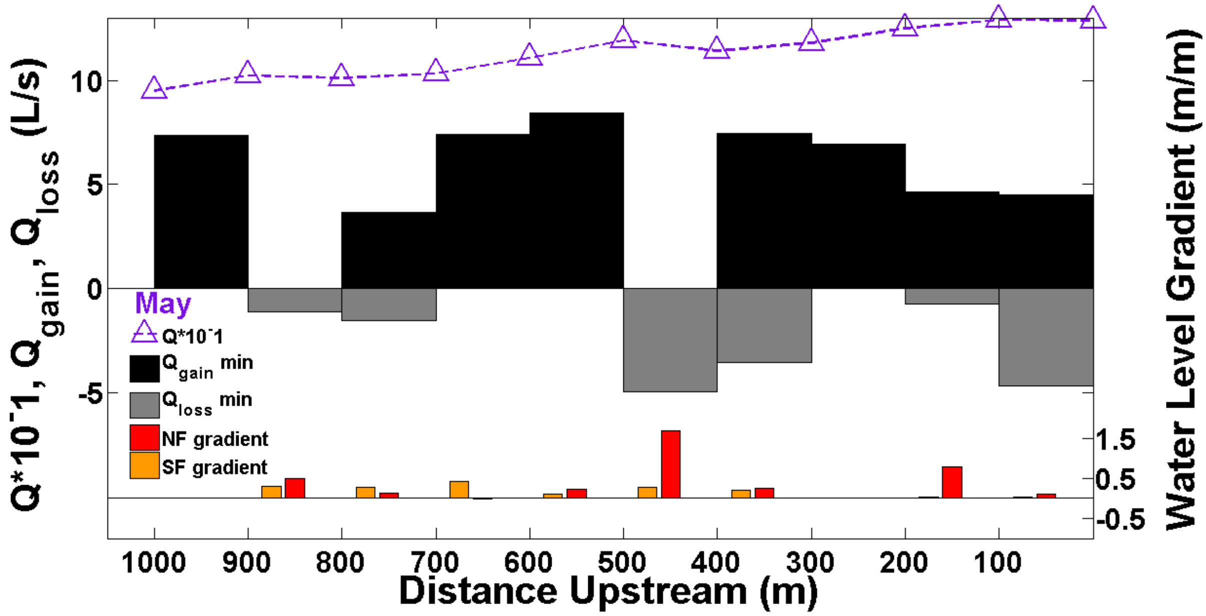

Figure 13: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and in-stream Q [scaled by a factor of 10]) and water table gradients for ten transects along 1000 m reach during May 2015 experiment following snowmelt. Note that discharge from US to DS is scaled by a factor of 10 to allow for better visualization.

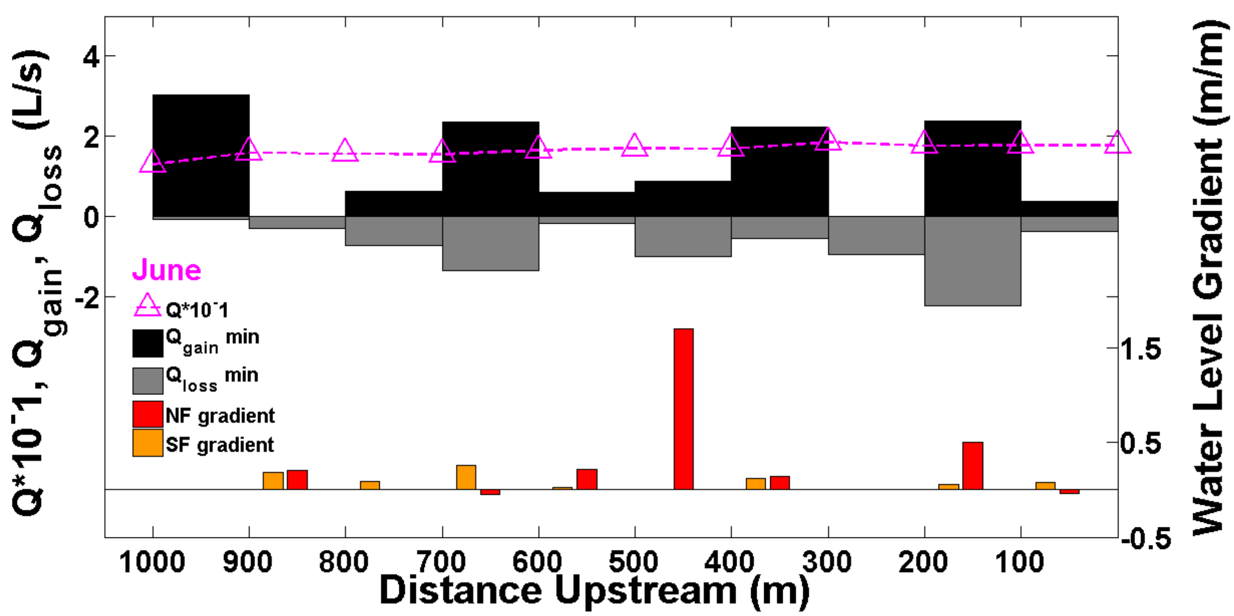

Figure 14: Hydrologic mass balance results (Q_{gain}, Q_{loss}, and in-stream Q [scaled by a factor of 10]) and water table gradients for ten transects along 1000 m reach during June 2015 experiment. Note that discharge from US to DS is scaled by a factor of 10 to allow for better visualization.

3.3 Nitrate Concentrations

In-stream nitrate concentration and in-stream nitrate flux, calculated as the discharge times the nitrate concentration, show a decrease from upstream to downstream for the drier months in the study (Figure 15). In October and November, concentration drops off fairly uniformly, whereas flux increases initially (upstream) quite rapidly, before decreasing. The changes in concentration and flux are quite pronounced during these low flow conditions due to increases and decreases acting as a large proportion of the total change. The abrupt increase in flux measured in October and November towards the upstream end of the reach is likely due to the measured large increase in discharge (greater than other increases farther downstream), which corresponds to the location in the catchment near a prominent spring.

For October and November, the results show that the catchment is most likely acting as a net sink for nitrate rather than a net source, given the decreasing concentration from upstream to downstream. Concentration is generally predicted to decrease with increasing streamflow (such as moving upstream to downstream along a reach), due to the dilution effect. If there were a great enough source of nitrate flowing into the stream, whether it be from draining hillslopes, overland flow, or some sort of runoff, concentration might remain closer to constant, decrease at a less rapid pace, or might even slightly increase.

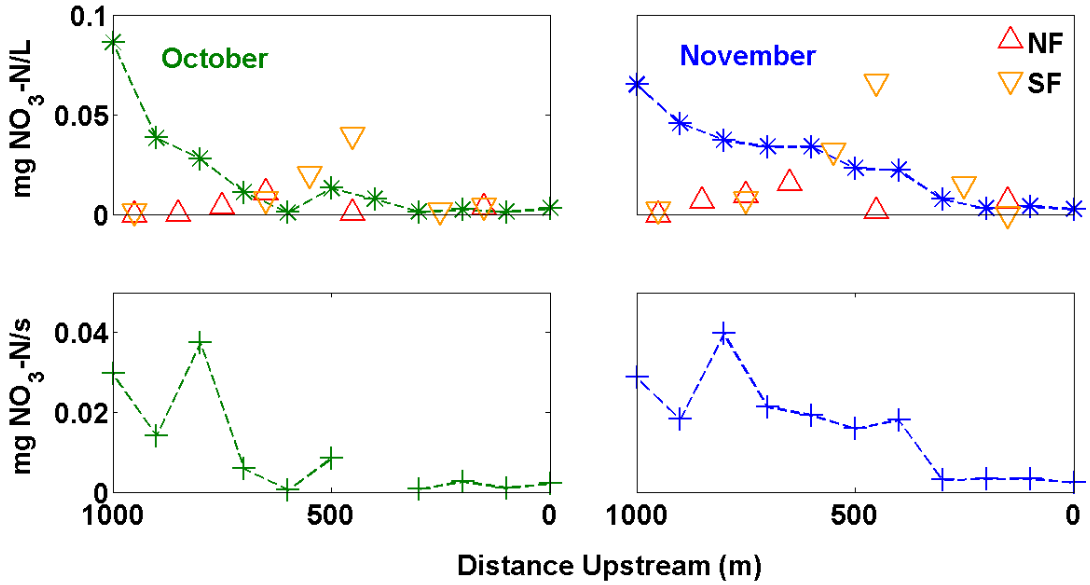

Figure 15: In-stream nitrate concentration (stars) and flux (plus signs) from upstream to downstream along 1000 m study reach for October and November 2014. Red and yellow triangles indicate groundwater concentrations of nitrate measured along each transect after sampling of north-facing and south-facing riparian wells.

When addressing the groundwater concentrations of nitrate, determined from the water sampling in the wells, groundwater nitrate is generally less than stream water nitrate for October and November. For this period, there are a few exceptions, in which groundwater nitrate concentrations appear to be elevated in certain locations relative to in-stream nitrate concentrations. Approximately midway through the catchment during both the October and November experiments, the south-facing groundwater concentration of nitrate is significantly higher than both the stream and north-facing nitrate concentrations. In general, between October and November, the groundwater concentrations on the north-facing and south-facing slope are similar, with November groundwater and in-stream concentrations being slightly greater.

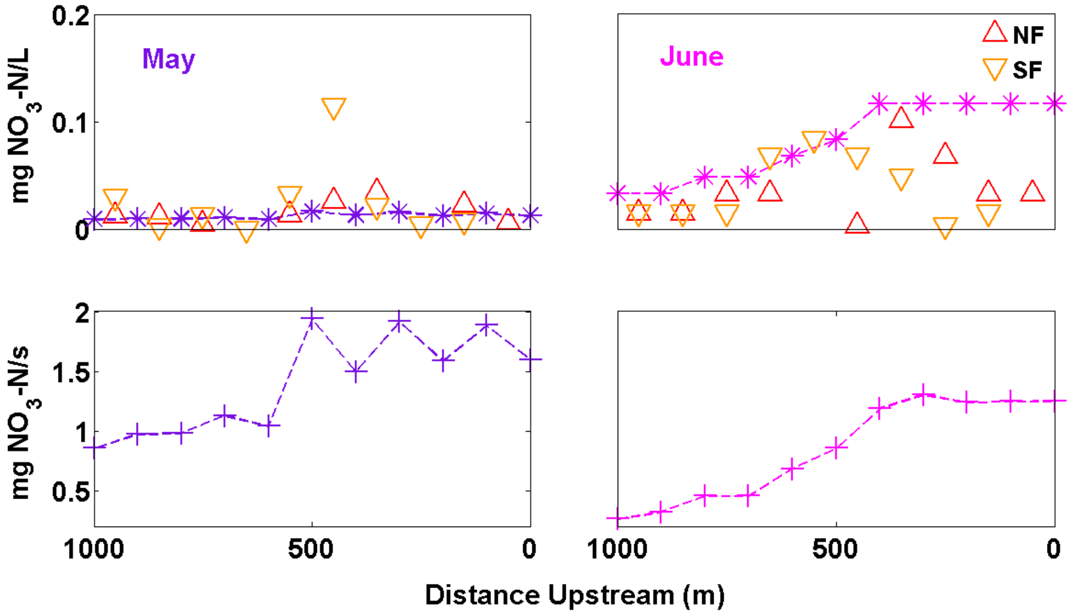

Figure 16: In-stream nitrate concentration (stars) and flux (plus signs) from upstream to downstream along 1000 m study reach for May and June 2015. Red and yellow triangles indicate groundwater concentrations of nitrate measured along each transect after sampling of north-facing and south-facing riparian wells.

For May (Figure 16), the resulting concentration and flux from our measured samples and discharge values tell a different story. In-stream concentration remains fairly constant from upstream to downstream, and in-stream flux increases from upstream to downstream. These two findings suggest that there must be sources of nitrate along the catchment to combat the dilution effect. The groundwater samples from May for both the north-facing and south-facing wells corroborate these findings, as groundwater nitrate concentrations are generally on the same order of magnitude as in-stream nitrate concentrations. At the same transect location as seen in October and November results (between 400 and 500 meters upstream), the groundwater concentrations of nitrate are once again noticeably elevated on the south-facing side relative to the in-stream and the north-facing concentration at the same transect. The rapid increase in flux from upstream to downstream is likely more indicative of the rapid increase in discharge from upstream to downstream during the sampling event.

The June results (Figure 16) are the only set of samples from the four experiments that show an increase in in-stream nitrate concentration and flux from upstream to downstream. The increase in concentration is most rapid midway through the catchment, and then appears to level off towards the downstream end. Groundwater concentrations of nitrate are the highest of all four experiments, especially for transects 1-5. As opposed to the October, November, and May results, north-facing groundwater concentrations are equally as elevated if not more elevated compared to south-facing groundwater concentrations.

3.4 Nitrate Mass Balance

Following application of equation (2), the contribution of hydrologic and biological fluxes of nitrate to the overall change of nitrate fluxes in the stream is determined. The hydrologic component includes both hydrologic gains and losses, or inflowing nitrate from groundwater and outflowing nitrate in the stream to the groundwater. October and November results show variable hydrologic fluxes (both gains and losses) moving from upstream to downstream along the catchment. The hydrologic loss term is the dominant component for both October and November (Figure 17), which likely means that the apparent decrease in the in-stream nitrate flux is due to nitrate moving out of the system via hyporheic flowpaths. Water flowing into the system containing nitrate is most pronounced lower in the catchment, especially for November, where the third transect exhibits a large gain flux to the stream. The biological component, meant to represent all biological sources or sinks, such as nitrification, denitrification, assimilation, or fixation, show sources of nitrate for all of October, and sources of nitrate downstream and sinks of nitrate downstream for November. In a cumulative sense, the October results show an overall source of nitrate from upstream to downstream, whereas the November results show an overall sink of nitrate, although that change does not occur until lower in the catchment (Figure 18)

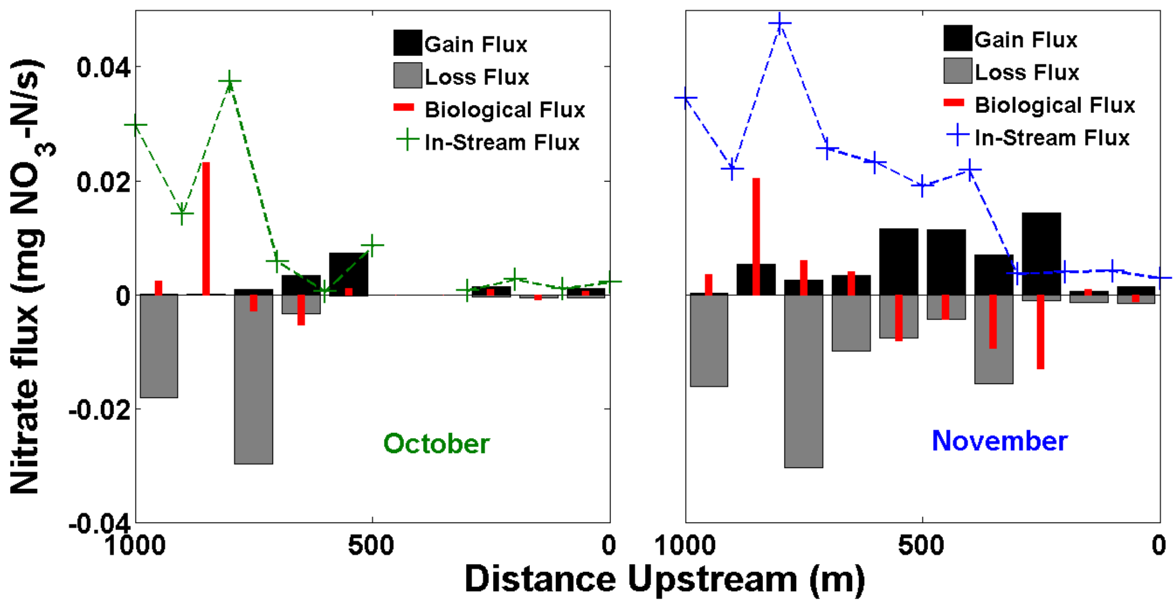

Figure 17: Nitrate mass balance results (hydrologic gain and loss fluxes, and biological source or sink flux) as well as in-stream nitrate flux for ten transects along 1000 m reach during October and November 2014 experiments. Positive fluxes indicate an increase in nitrate or a source, whereas negative fluxes indicate a removal or sink of nitrate via either physical or biological mechanisms.

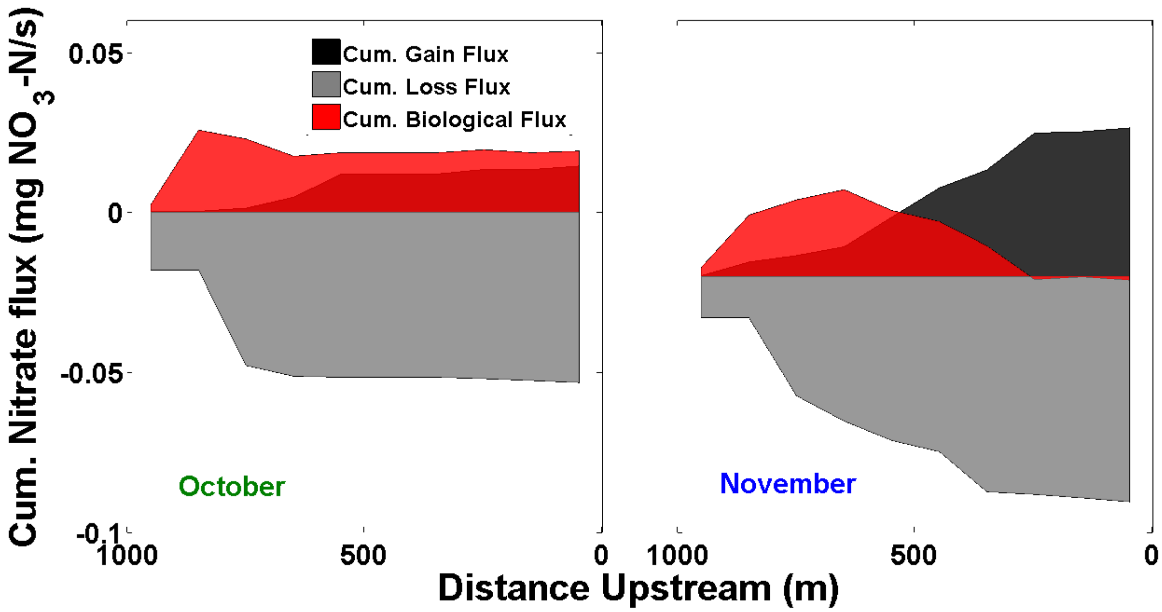

Figure 18: Cumulative hydrologic gain and loss fluxes and cumulative biological fluxes summed from upstream to downstream following application of the nitrate mass balance approach for October and November 2014.

The nitrate mass balance results for May and June show the catchment acting as a net source of nitrate as opposed to a net sink of nitrate (Figure 19). The hydrologic loss flux is the least dominant or important term for May (relative to the other fluxes), and greatly diminished for June, a stark contrast from October and November results. For May, both the hydrologic gain flux and the biological flux act to increase the flux of nitrate from upstream to downstream, according to model results. Biological sinks of nitrate appear to occur in the upstream portion (if at all) of the catchment during this period (following snowmelt), and the remainder of the catchment appears to be a biological source. The biological source term increases rapidly midway through the catchment, which is approximately the same location where the biological sink term increased during baseflow period. Hydrologic losses are limited, as well, at all points in the catchment. Relative to baseflow results (October and November), snowmelt results (May) show fluxes of approximately 1 order of magnitude (10 times) greater. This is true for the cumulative fluxes as well, with the exception of the cumulative hydrologic loss flux (Figure 20). For May, this cumulative flux is very close to the cumulative flux seen in baseflow.

For June, the increase in nitrate concentration and flux appears to be primarily due to the biological component. The biological gain flux is the dominant term, according to model results, and the hydrologic gain flux and hydrologic loss flux are nearly balanced in a cumulative sense. At no point along the study reach does the June model show the catchment acting as a sink of nitrate. Each transect appears to be a biological source of nitrate, which may be indicative of nitrification following the period of snowmelt and rainfall in May and June.

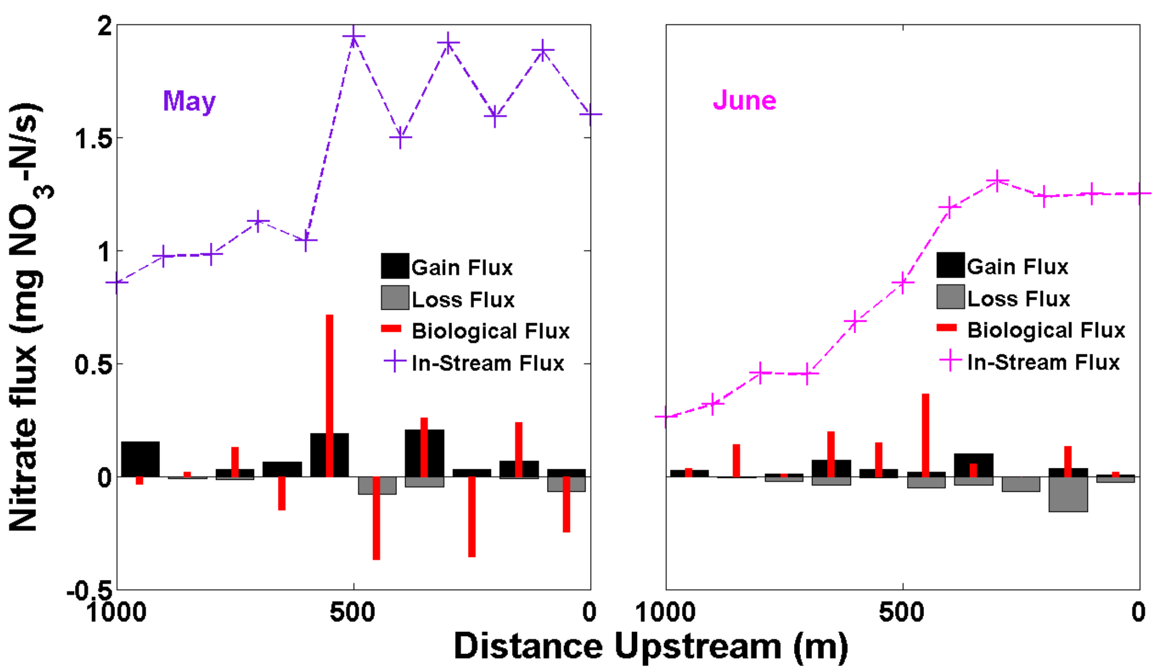

Figure 19: Nitrate mass balance results (hydrologic gain and loss fluxes, and biological source or sink flux) as well as in-stream nitrate flux for ten transects along 1000 m reach during May and June 2015 experiments.

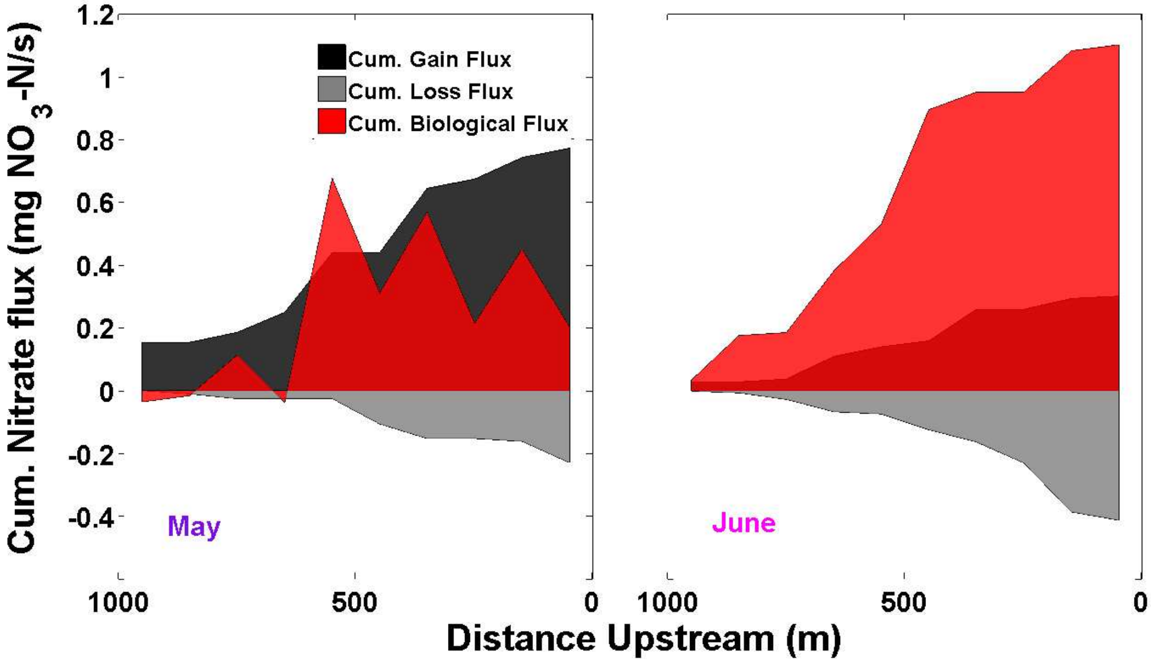

Figure 20: Cumulative hydrologic gain and loss fluxes and cumulative biological fluxes summed from upstream to downstream following application of the nitrate mass balance approach for May and June 2015.

CHAPTER 4: DISCUSSION

Results from the four experiments conducted along Lower Gordon Gulch during the 2014-2015 water year clearly demonstrate the role of the hydrologic cycle and catchment wetness in biogeochemical cycling of nitrate along headwater streams. From the onset of monitoring in August 2014, through the winter and into the spring snowmelt and rainfall period, the shifting climatic regime is evident in the changing lateral hydraulic gradients and streamflow patterns along our 1000 m reach. Within GGL, snowmelt and rainfall both act to influence the quantity and composition of water observed at the catchment outlet, which is the case for most montane streams given their elevation along Colorado's Front Range. The hydrologic and nitrate mass balance results from this study show bidirectional hydrologic exchange (hydrologic gains and losses) along each of our 10 study transects, spaced approximately 100 m apart. Moreover, our application of a nitrate mass balance that explicitly links the hydrologic and biological component of nitrate cycling allows us to analyze hydrologic and biological processes acting at each transect, which paints a fuller picture of biogeochemical potential in GGL with respect to nitrate.

4.1 Biological Removal Rates from Hydrologic and Nitrate Mass Balance Results

Contrary to our initial expectations, all four experimental and model results show that there is always at least one portion of the catchment that produces nitrate via biological processes, and that the majority of the catchment follows this trend, with minimal transects showing biological removal of nitrate. While the October and November results show fewer biological source terms than May and June results, the cumulative results show that during October, along with May and June, the catchment acts as a net source of nitrate, yet the biological mechanisms behind this are not known. For November, the catchment acts as a net sink, but the magnitude of removal is not nearly as large as hydrologic losses. In sum, the biological component of nitrate retention does not seem to play a large role for any month in the study. Given that the four experiments in the study span nine months and capture variability in the water year, with baseflow, snowmelt-dominated, and rainfall-dominated periods, the results show that the hydrology of the system resulting from varying climatic conditions does not necessarily turn on or turn off nitrate removal via biological mechanisms such as denitrification. In fact, hydrologic pathways generally appear to be the direct source and sink of nitrate throughout the water year, which has been found in previous studies that attempt to separate flushing from biogeochemical activity [*Covino et al.*, 2010].

There is a noticeable switch, however, in the relative importance of the fluxes, determined via the nitrate mass balance, between dry and wet periods. In-stream nitrate concentrations and groundwater samples show the manifestation of these fluxes in overall nitrate concentration and flux patterns in the stream moving from upstream to downstream. During drier periods (October and November), nitrate concentration and flux in the stream decreases from upstream to downstream, and groundwater nitrate concentrations are relatively less than in-stream concentrations. The decrease in flux is predominantly due to hydrologic flushing, as opposed to biological removal. Despite an overall lack of apparent wetness within the catchment during this time, subsurface processes appear to be exporting stream water, which reduces the nitrate concentrations and fluxes.

During wetter periods (May and June), nitrate concentration and flux increase from upstream to downstream, although May's concentration is more chemostatic than noticeably increasing. Still, these findings indicate sources of nitrate along the catchment, which are received either via hydrologic or biologic processes. Mass balance results provide insight regarding the importance of both source terms for May and for June. In May, the hydrologic gain flux is the most dominant (10 times greater, on average, than the two fluxes from the October and November model runs). In June, the biological gain flux is the most dominant. Such results suggest that between snowmelt and late-spring rainfall, montane zone catchments switch from hydrologic-dominated transport of nitrate to biological processing such as nitrification.

While our models results provide some stimulating insights that are in part in line with past studies in the catchment [*Hinckley et al.*, 2014a, 2014b], it is important to consider the uncertainty in the hydrologic mass balance and the nitrate mass balance methods. The hydrologic mass balance approach relies on the assumption of fully mixed flowpaths, which may not always be the case despite our careful efforts for complete mixing. Our method of obtaining gross gains and losses had not been previously applied during high flow conditions, and thus further work to understand the application of this method under a variety of hydrologic regimes is necessary to understand any error terms. The nitrate mass balance relies on the results of the hydrologic mass balance and the sampling results. In-stream and groundwater samples are point measurements, which may not fully capture spatial heterogeneity. Moreover, by lumping all biological sources and sinks into one term, it is difficult to differentiate specific processes such as denitrification and the generalization thus may not provide a thorough understanding of catchment cycling of nitrate at different times of the water year. While it would be possible to derive a potential overall error from the propagation of these uncertainties [*Schmadel et al.*, 2010]., the focus of this thesis is not on the intricacies of the method, but on the potential for the method to be used to understand nutrient dynamics at the reach to catchment scales. The hope is that these results can provide insight into the hydrology of GGL, which has not been studied in great extent, and that they also foster discussion and desire to apply the dual approach to other sites to understand its use and potential.

4.2 Role of Groundwater Inputs in Nitrate Cycling

Groundwater inputs to the stream appear to be important in regulating nitrate levels, as model results show greater biological sources when groundwater nitrate concentrations are elevated. The mechanism by which these sources of nitrate reach the stream, however, are not as well understood, and the lateral hydraulic gradients measured in this study are only a small snapshot of the groundwater movement with GGL and its importance in nitrate retention and export. Despite different soil content, vegetation patterns, and radiation balances, the lateral hydraulic gradients between the north-facing and south-facing riparian zones and the stream are similarly variable. In general, the results show no set pattern in north-facing versus south-facing groundwater tables along the riparian zone, and generally connectivity between the stream and the riparian zone is evident for both sides of the stream. The flow patterns that move water from the hillslopes down-gradient to the riparian zones may be different for north-facing versus south-facing slopes in timing and magnitude, however, and wells along the riparian zone would not capture this variability. Perhaps wells installed higher up on the hillslopes would better capture differences in groundwater flow, but this was not attempted in this study.

As our study focuses on the near-stream riparian zones, an obvious question is whether the noted bidirectional exchange can elucidate the extent and role of the hyporheic zone in groundwater-surface water interactions along GGL. Are the gross gains and losses indicative of lateral, vertical, and longitudinal exchange through the hyporheic zone? To attempt to answer this, we can analyze the lateral hydraulic gradients on both sides of the stream, which are not always in line with the hydrologic mass balance results. For instance, gains and losses measured in the streams are not always at locations with exceptional gaining or losing lateral hydraulic gradients. In October and November, variable hydraulic losing and gaining gradients are evident yet not always located at the same transects displaying similar magnitude gains and losses determined via the hydrologic mass balance. In May and June, despite the results showing purely gaining lateral hydraulic gradients, the hydrologic mass balance shows both gross gains and losses along the reach. This is likely in part due to spatial variability in groundwater flowpaths, which is not captured in a single well installation.

Conflicting mass balance results and well gradients may also be indicative of hyporheic flowpaths that move water out of the stream at an upstream location, and back into the stream at a downstream location via primarily lateral and longitudinal connections along the hyporheic corridor. The size or presence of the hyporheic zone (or storage zones) would be difficult to quantify after the fact without an end-member mixing model method such as seen in *Covino and McGlynn* [2007], however, despite our evidence of bidirectional exchange. A tracer study combined with transient storage modeling would likely also lend valuable information, yet it is always necessary to consider the window of detection for the tracer used (in our case KBr and NaCl), as not allowing for upstream tracers to reach downstream loggers may not completely capture the tail (and thus the inflows and outflows) of the tracer [*Ward et al.*, 2013]. Without the use of a transient storage model with our results, we cannot say with certainty if short-term and long-term storage or short-term and long-term hyporheic flowpaths are captured in our method. Since we cannot directly equate gross gains and gross losses to transient storage or hyporheic exchange via our methods, we can only extend our findings to infer that groundwater to surface-water interactions seem to facilitate both nitrate removal and nitrate export, depending on the timing of the interaction and the direction (away from the stream or towards the stream). Bidirectional hydrologic exchange is certainly in part dependent on local lateral hydraulic gradients, which may be a good indicator of whether groundwater nitrate from adjacent riparian zones can reach the stream.

4.3 Conceptual Model of Nitrate Transport in Montane Streams

With respect to nitrate transport within Lower Gordon Gulch, many of our findings are in line with previous studies performed in GGL following snowmelt. Notably, *Hinckley et al.* [2014b] found that nitrate was rapidly transported via preferential flowpaths on south-facing slopes with less developed soils and greater incident radiation, whereas matrix flow dominated north-facing soils with a more sustained snowpack, which thus retained nitrate for longer timescales. In our conceptual model results, nitrate concentrations during the May experiment show higher groundwater concentrations of nitrate along the south-facing riparian corridor, perhaps indicative of preferential flow from higher on the hillslopes. Preferential flow, although not directly studied during the four experiments, is more likely to occur in poorly developed soils that are unable to move water via matrix flow. In addition to *Hinckley et al.* [2014a, 2014b]'s work within Lower

Gordon Gulch, *Clow and Fleming* [2008] explored controls on runoff and water chemistry Rocky Mountain National Park alpine and subalpine basins. Their findings corroborate the work of *Hinckley et al.* [2014a, 2014b], as they found steeper slopes with less dense vegetation to be positively correlated with runoff and nitrate concentration. The south-facing slopes in Gordon Gulch are generally more incised near the stream and are certainly less vegetated compared to north-facing slopes. It is therefore likely that our findings from the May snowmelt experiment show this phenomenon in GGL at most points along the study reach, which extends *Hinckley et al.* [2014b]'s findings for their single transect, which was situated toward the upper end of our study reach.

In June, groundwater concentrations of nitrate along the north-facing riparian corridor are noticeably elevated, and the biological source term is dominant in the nitrate mass balance. It is certainly possible that such results are a manifestation of matrix flow (of water, ammonium and organics, and nitrate) on north-facing slopes between May and June, and that the biological source shows the transformation of organics to nitrate along the valley bottom. The consistently moist north-facing soils are more likely to provide an environment for organic-rich soil and increased microbial activity relative to the south-facing slopes [*Fisk et al.*, 1998]. Moving into lower flow conditions (October and November), with less direct precipitation, the catchment appears to effectively transport the bulk of organics from wet-season sources through groundwater pathways on both the north-facing and south-facing slopes. During this period, nitrate cycling results in reduced nitrate concentrations at the downstream end relative to the upstream end, primarily due to losing lateral hydraulic gradients along the reach. It is unknown what occurs in the late growing season, as this period was not included in this study.

It is possible that late growing season dynamics exhibit far more nitrate removal via biological mechanisms than other times of the water year. This makes sense theoretically, as the growing season combined with slightly slower discharges provides an environment that is conducive to denitrification and assimilation as well as increased hyporheic exchange. *Campbell et al.* [2000] found reduced nitrate export from forested ecosystems during the growing season, attributed to biologically active zones. Once again, although not directly measured in this study, bidirectional hydrologic exchange is conducive to facilitating hyporheic interactions, and numerous studies have focused on the importance of the hyporheic zone in nitrate removal. Many have found a positive correlation between the extent of the hyporheic zone and the residence time of surface water or groundwater parcels in storage with nitrate removal [*Gooseff et al.*, 2004; *Zarnetske et al.*, 2011; *Sawyer*, 2014]. Enhanced exchange between surface water and groundwater has been found to be negatively correlated with discharge in many previous studies [*Zarnetske et al.*, 2008; *Payn et al.*, 2009; *Voltz et al.*, 2013], likely due to enhanced contact with geomorphic in-stream drivers [*Hester and Doyle*, 2008]. Further work along montane zone catchments throughout the entire summer and into the early autumn would be necessary to understand biological removal and whether GGL is also most retentive during lower flows.

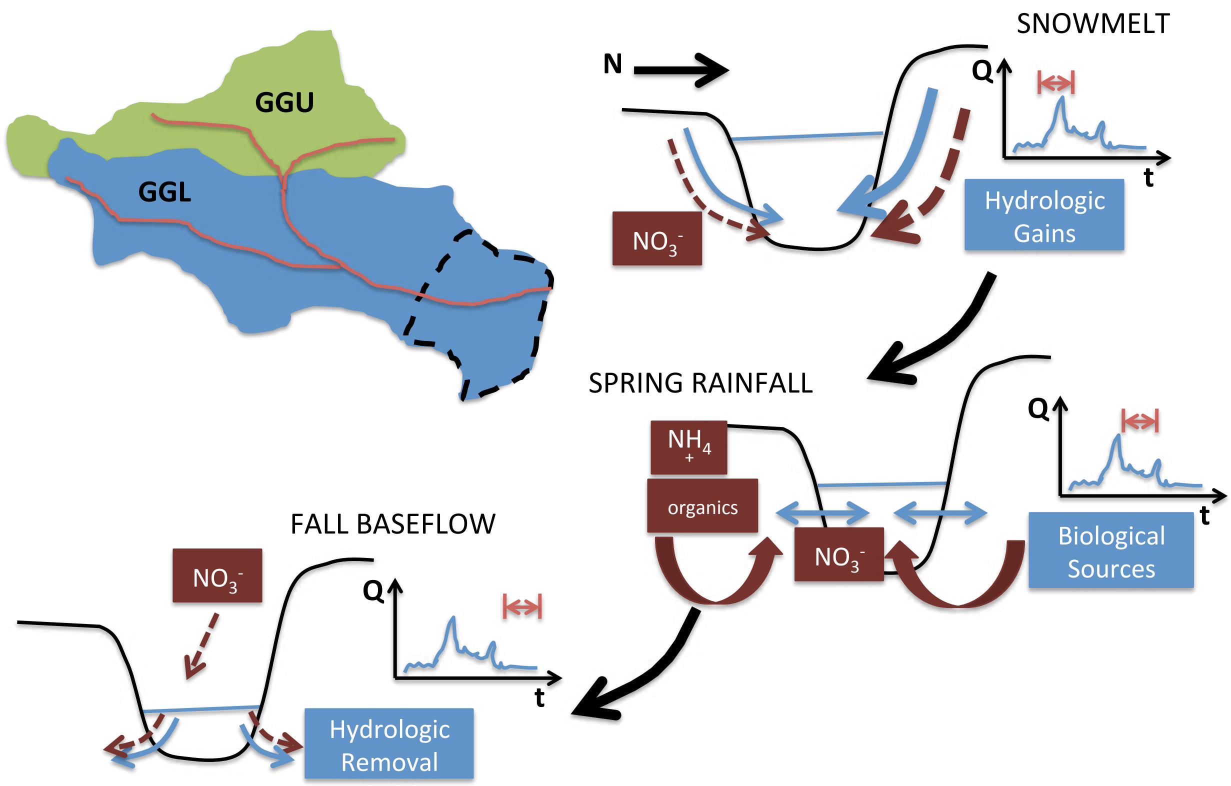

Figure 21: Conceptual diagram for nitrate transport within our study reach of Lower Gordon Gulch (outlined area). Starting from the top right and working clockwise: snowmelt-dominated with hydrologic gains of nitrate, rainfall-dominated with biological sources of nitrate, and baseflow with hydrologic removal of nitrate. Note that late growing season was not studied and is thus not pictured.

Given our conceptual model, it is interesting to think about GGL and potentially other montane catchments along Colorado's Front Range in a cyclical fashion. The "filter" of the stream-riparian corridor changes the composition of water that moves from upland sources to the valley bottom, and the filter's abilities change in different hydrologic conditions throughout the water year (Figure 21). In baseflow periods, when much of the snowmelt and early melt has moved from the hillslopes and drained through the catchment, both groundwater concentrations along the north-facing and south-facing riparian corridor are low in nitrate, and in-stream nitrate concentrations decrease when moving from upstream to downstream. The nitrate mass balance suggests that the reduction is due to hydrologic outflows from the stream, and overall discharge does not increase substantially from upstream to downstream. Thus the catchment's filter is mostly dry and clear, and small inputs of nitrate are easily removed. On the contrary, in wet periods following snowmelt, groundwater concentrations of nitrate increase and eventually are greater than in the stream. Lateral hydraulic gradients and hydrologic mass balance results suggest net gains along the reach, and nitrate mass balance results suggest first hydrologic and then biological nitrate fluxes towards the stream. Thus the catchment's filter is mostly wet and likely clouded from a substantial increase in nutrient loading, and inputs of nitrate are not easily removed until later in the seasonal cycle.

Understanding the catchment's filtering abilities is exceptionally important when addressing changes in climate and anthropogenic influence within all headwater stream catchments, and montane zone streams are no exception. Headwater streams have been found in previous studies to contribute over half of the nitrogen flux in lower order streams [*Alexander et al.*, 2007]. With the potential for lower regional aquifer levels, lower overall snowpack accumulation, and higher frequency floods, climate change can affect stream ecosystems in diverse ways. With drier years, less snow and lower aquifers may manifest in less snowmelt and also less potential for microbial buffering in subnivial soils. With drier years, there may be less overall catchment scale and watershed scale connectivity. Without watershed connectivity, catchments such as GGL may become isolated from upstream processes, such as snowmelt in alpine areas, or larger nitrate concentrations. In this context, N saturation may not be a concern for these ecosystems, but rather N limitation. In a different light, nitrogen deposition may continue to increase over the years with increased fossil fuel combustion and fertilizer use from increased agricultural demands. Increased rainfall relative to snowmelt in alpine and subalpine catchments, then, may elevate N levels without a means to flush or cycle nitrate due to decreased catchment to stream connectivity. If fertilizer levels increase drastically in springtime, our results suggest that nitrate levels in montane zone streams may increase due to a "clouded filter". Such a thought exercise has been explored in modeling efforts in the past, and results have shown that forested ecosystems, in addition to alpine areas are sensitive to increased N deposition [*Baron et al.*, 1994] with rapid changes in productivity. Continued monitoring of montane zone catchments such as GGL, especially during the growing season in Colorado, can help us begin to understand the current state of the catchment with respect to nitrate levels and cycling, and the means by which increased or decreased N availability may affect the ecosystem.

CHAPTER 5: CONCLUSION

We utilized a coupled hydrologic and nitrate mass balance modeling framework to assess nitrate removal and generation for Lower Gordon Gulch (GGL), a montane zone stream along Colorado's Front Range. We collected data during four synoptic stream tracer and sampling campaigns along a 1000 m study reach during the 2014-2015 water year, and also analyzed near-stream riparian lateral hydraulic gradients to assess groundwater to surface water interactions from a second perspective. Three distinct hydrologic regimes are captured in our results, including two experiments during baseflow, one experiment following snowmelt, and one experiment following late-spring rainfall. Hydrologic mass balance results indicate bidirectional hydrologic exchange for all four months in the study, with greatest bidirectional exchange during baseflow. Nitrate mass balance results indicate nitrate removal via hydrologic pathways out of the surface stream during baseflow, nitrate inputs via hydrologic pathways from the hillslopes during snowmelt, and nitrate inputs via biological transformations during late-spring. Our conceptual model explains the changing face of GGL's "filter" with respect to nitrate cycling abilities, and the clear role of the hydrology, or the catchment wetness in nitrate export and/or retention. Lateral hydraulic gradients coupled with bidirectional exchange show the likelihood of hyporheic exchange, which may be greatest during baseflow, yet we cannot confirm that our exchange results exhibit movement through the hyporheic zone. Further work should consider the mid- to late-summer growing season dynamics, and whether biological removal of nitrate is evident, and also should consider employing techniques to "image" hyporheic interactions. Our novel modeling framework provides a new method to assess nitrate dynamics in catchments, and our results corroborate findings from previous experiments conducted in GGL. Our findings can assist Colorado scientists and environmental managers in understanding the potential of ecosystem eutrophication and reduced water quality in forested montane catchments due to increased industrialization (and increased N deposition) and/or the potential for reduced snowpack and catchment connectivity due to climate change in the Mountain West.

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APPENDIX A

October and November Water Quality Results

Item	October			November		
	NO_3^- [mg N/L]	NH_4^+ [mg N/L]	TDN [mg N/L]	NO_3^- [mg N/L]	NH_4^+ [mg N/L]	TDN [mg N/L]
INJ 1	0.003	0.024	0.079	0.002	0.084	0.067
INJ 2	0.001	0.014	0.069	0.004	0.075	0.025
INJ 3	0.002	0.030	0.103	0.003	u	0.062
INJ 4	0.001	0.024	0.083	0.007	0.089	0.102
INJ 5	0.008	0.062	0.130	0.020	0.151	0.068
INJ 6	0.013	0.022	0.082	0.021	0.076	0.083
INJ 7	0.001	0.015	0.070	0.031	0.045	0.102
INJ 8	0.011	0.042	0.082	0.030	0.020	0.096
INJ 9	0.028	0.076	0.092	0.034	0.016	0.090
INJ 10	0.038	0.079	0.112	0.041	0.014	0.079
INJ 11	0.086	0.093	0.146	0.059	0.005	0.094
1_NF	NSS	NSS	NSS	NSS	NSS	NSS
1_SF	NSS	NSS	NSS	NSS	NSS	NSS
2_NF	0.004	0.058	0.293	0.006	0.021	0.194
2_SF	0.004	0.062	0.198	u	0.208	0.288
3_NF	NSS	NSS	NSS	NSS	NSS	NSS
3_SF	0.002	0.139	0.345	0.0131	0.076	0.161
4_NF	NSS	NSS	NSS	NSS	NSS	NSS
4_SF	NSS	NSS	NSS	NSS	NSS	NSS
5_NF	0.001	0.017	0.129	0.001	0.055	0.135
5_SF	0.040	0.041	0.176	0.059	0.156	0.140
6_NF	NSS	NSS	NSS	NSS	NSS	NSS
6_SF	0.020	0.013	0.073	0.028	0.054	0.117
7_NF	0.011	0.066	0.209	0.014	0.059	0.172
7_SF	0.007	0.072	0.164	NSS	NSS	NSS
8_NF	0.004	0.382	1.230	0.009	0.168	0.215
8_SF	NSS	NSS	NSS	0.007	0.122	0.186
9_NF	0.000	0.125	0.309	0.006	0.133	0.307
9_SF	NSS	NSS	NSS	NSS	NSS	NSS
10_NF	u	0.471	1.403	u	0.020	0.095
10_SF	0.001	0.136	0.366	0.002	0.046	0.197

EQCL=exceeds quality control limits
NSS=no sample submitted
u=undetected

APPENDIX B

May and June Water Quality Results

Item	May			June		
	NO_3^- [mg N/L]	NH_4^+ [mg N/L]	TDN [mg N/L]	NO_3^- [mg N/L]	NH_4^+ [mg N/L]	TDN [mg N/L]
INJ 1	0.012	0.008	0.190	0.070	<0.001	0.029
INJ 2	0.015	0.022	0.244	0.070	0.002	0.033
INJ 3	0.013	0.010	0.222	0.070	<0.001	0.034
INJ 4	0.016	0.022	0.218	0.070	0.004	0.037
INJ 5	0.013	0.013	0.178	0.070	<0.001	0.039
INJ 6	0.016	0.011	0.243	0.050	<0.001	0.034
INJ 7	0.009	0.011	0.209	0.041	0.002	0.035
INJ 8	0.011	0.010	0.209	0.029	<0.001	0.034
INJ 9	0.010	0.016	0.210	0.029	<0.001	0.027
INJ 10	0.009	0.017	0.185	0.020	<0.001	0.031
INJ 11	0.009	0.017	0.179	0.020	<0.001	0.030
1_NF	0.007	0.017	0.198	0.020	0.017	0.042
1_SF	NSS	NSS	NSS	NSS	NSS	NSS
2_NF	0.023	0.020	0.232	0.020	0.007	0.039
2_SF	0.007	0.041	0.327	0.009	0.013	0.067
3_NF	EQCL	0.008	0.174	0.041	0.002	0.044
3_SF	0.004	0.039	0.226	<0.002	0.006	0.031
4_NF	0.034	0.016	0.143	0.061	<0.001	0.025
4_SF	0.021	0.011	0.220	0.029	<0.001	0.035
5_NF	0.026	0.032	0.153	<0.002	0.004	0.037
5_SF	0.114	0.033	0.317	0.041	0.012	0.048
6_NF	0.013	0.010	0.363	NSS	NSS	NSS
6_SF	0.032	<0.006	0.164	0.050	0.007	0.041
7_NF	EQCL	<0.006	0.196	0.020	0.010	0.046
7_SF	u	0.013	0.210	0.041	0.003	0.039
8_NF	0.005	0.016	0.159	0.020	0.010	0.046
8_SF	0.012	0.186	0.432	0.009	0.017	0.062
9_NF	0.011	0.092	0.345	0.009	0.024	0.072
9_SF	0.002	0.020	0.227	0.009	<0.001	0.026
10_NF	0.012	0.052	0.244	0.009	0.013	0.067
10_SF	0.030	0.055	0.362	0.009	0.013	0.083

EQCL=exceeds quality control limits
NSS=no sample submitted
u=undetected