NITRATE DYNAMICS UNDER UNSTEADY AND INTERMITTENT FLOW IN AN ANTARCTIC STREAM

by

JOEL GREENE SINGLEY

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written by Joel Greene Singley

has been approved for the Environmental Studies Program

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Eve-Lyn S. Hinckley, Ph.D.

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Michael N. Gooseff, Ph.D.

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William Kleiber, Ph.D.

Date_______________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Singley, Joel Greene (M.S., Environmental Studies Program)

Nitrate Dynamics Under Unsteady and Intermittent Flow in an Antarctic Stream

Thesis directed by Assistant Professor Eve-Lyn S. Hinckley, Ph.D.

Abstract

Low order streams are a primary vector and modulator for the transport of anthropogenically derived reactive nitrogen, especially as nitrate (NO_3^-). A large proportion of low orders streams experience short-term unsteady and intermittent flow conditions, and the prevalence of these dynamics is likely to increase due to climate change and human management. While such hydrologic variability is recognized as an important first-order control on the transport of NO_3^-, prior reliance on manual sampling has resulted in a disparity between our understanding physical and hydrochemical dynamics at short-timescales, such that a large gap exists in our understanding of how unsteady and intermittent sub-daily discharge affects instream NO_3^- transport patterns. To address this challenge, I used *in situ* sensors to collect high-frequency (i.e., 15 minute) NO_3^- concentration and discharge data in an ephemeral, oligotrophic glacial meltwater stream in the McMurdo Dry Valleys, Antarctica. I analyzed concentration-discharge relationships using a power-law framework to identify a flow threshold that governed NO_3^- transport dynamics. I observed relative chemostasis of NO_3^- during large magnitude diel flood pulsing events. This suggests that biological and physical processes controlling the transport and transformation of NO_3^-, and N more generally, are likely to exhibit spatial and temporal variability at very short timescales in response to extreme hydrologic variability. Such spatiotemporal variability in N processing dynamics has not been included in prior conceptual models of N cycling in MDV streams. As such, I propose a conceptual model in which short-term flow pulsing and cessation shift sediment redox conditions and microbial processes such

that the shallow hyporheic zone temporally becomes a net source and storage zone for a spatially distributed pool of NO_3^-. The results of this approach will inform understanding of how highly variable hydrological conditions measured at very short timescales interacts with instream biogeochemical processes to control N transport.

Dedication

This work is for my parents,

who taught me to find joy while standing in streams

and asking questions.

Acknowledgments

While I use the personal pronoun "I" throughout this work, I must acknowledge the tremendous assistance and intellectual investment that I have received from my committee, colleagues, family, and friends. I am greatly indebted to many people, without whom this project would not have been completed. Specifically, I would like to thank my advisor, Eve-Lyn Hinckley, for her persistent encouragement, high expectations, and ability to advise me as an individual. It has been a great honor to work with her and see our lab grow. I would also like to thank my secondary advisor, Michael Gooseff, for accepting me into his lab and offering me the opportunity to work in Antarctica with an amazing group of people. Finally, I would like to thank my loving partner and fiancé, Annie Gettinger, for the essential role you have played in helping me find success and confidence as a scientist. The support and encouragement you so generously provide are boundless, no matter where my dreams (or research) take me or for how long we must be apart. I am always grateful that you are by my side.

With the utmost gratitude,

Joel G. Singley

Longmont, CO

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1. Introduction

Humans have greatly altered the global availability and cycling of reactive nitrogen (N_r) [*Davidson et al.*, 2011; *Galloway et al.*, 2008; *Galloway et al.*, 2004; *Vitousek et al.*, 1997]. Large additions of N_r via the combustion of fossil fuels, fertilizer application, and livestock production have resulted in extensive impacts to terrestrial and aquatic ecosystems, as well as human health [*Davidson et al.*, 2011; *Sobota et al.*, 2015]. N_r is easily mobilized and atmospherically deposited many kilometers from the initial source [*Burns*, 2004; *Davidson et al.*, 2011], especially in landscapes with high topographic relief [*Benedict et al.*, 2013]. Streams and rivers are a major vector for the transport of excess N_r from terrestrial systems to lakes, reservoirs, and oceans, yet they are not passive pipes. Instead, important biogeochemical and physical processes in streams control the transport and retention of N including determination of the forms, timing, and magnitude of N fluxes to downgradient systems [*Alexander et al.*, 2007; *Boyer et al.*, 2002; *Boyer et al.*, 2006; *Duff and Triska*, 2000; *Howarth et al.*, 1996; *Mulholland et al.*, 2004; *Triska et al.*, 2007].

Low order streams are the starting point of larger river networks. They exert a strong influence on the downstream transport of N_r [Alexander 2007] and are vulnerable to human modification and global climate change [*Larned et al.*, 2010]. Particularly in mountainous regions or semiarid climates, low order streams are characterized by unsteady discharge at sub-daily to seasonal timescales, often with periods of ephemeral or intermittent flow throughout much of the drainage network [*Jensen et al.*, 2017; *Larned et al.*, 2010; *Robinson et al.*, 2016]. Past research on the role of hydrologic variability on N_r transport has focused disproportionately on catchment export to streams rather than on the processes occurring in low order streams themselves. In particular, the influence of short-term, periodic drying and re-wetting of hyporheic and streambed sediments under short-term intermittent flow on N_r transformations and transport has only been partially constrained [*Jones et al.*, 1995; *Martí et al.*, 1997].

Motivated by this knowledge gap, I asked: how do short-term, persistently unsteady and intermittent flow conditions affect nitrate transport dynamics? I addressed this question by analyzing high-frequency discharge and nitrate concentration data from an ephemeral glacial meltwater stream located in the McMurdo Dry Valleys, Antarctica (MDV) that experiences short-term flow intermittency (i.e., 15 min to 2 d) and diel meltwater pulse events. While seemingly singular, such stream systems are ideally suited to answer questions about the response of instream processes to short-term unsteady and intermittent flow because they lack hillslope and groundwater connectivity, receive nearly all water inputs from dilute glacial meltwater, host diverse benthic and hyporheic microbial communities, and experience sub-daily flood pulsing and intermittent flow. Thus, MDV streams allow consideration of instream processes without obscuring catchment influences under unsteady flow conditions that are relevant to stream systems in other regions.

To address my research question, I analyzed concentration-discharge (C-Q) relationships using a power-law framework, assessed evidence for low-flow and temporal thresholds in C-Q relationships, and compared C-Q relationships between short-term, high-frequency data and long-term, low-frequency sampling. Last, I developed a conceptual model based on inferences from my results and prior studies to explain the importance of short-term flow cessation and re-initiation on the transport, temporary storage, and transformation of NO_3^- in the sediment of low order streams. The results of this approach will inform understanding of how highly variable hydrological conditions measured at very short timescales interacts with instream biogeochemical processes to control N transport. Furthermore, by addressing the primary research question, this study will inform future work that seeks to determine how spatial and temporal patterning of in-stream biogeochemical and hydrological processes control the transport and retention of nitrate under such flow conditions.

2. Background

2.1 Reactive Nitrogen and Low Order Streams

The strong hydrological and biogeochemical linkages between low order streams and headwater catchments make them a critical link in the global cycling of N with implications for distant, downgradient systems [*Alexander et al.*, 2007]. Once excess N reaches a stream, changes in flow may alter rates of biogeochemical processes that retain or remove N through the effects of water velocity on uptake processes [*Webster et al.*, 2003] or indirectly through changes in residence time and temporary storage [*Briggs et al.*, 2014; *Gooseff et al.*, 2004; *Koch et al.*, 2010; *Lautz and Siegel*, 2007; *McKnight et al.*, 2004]. For example, *Briggs et al.* [2014] found that shifts in hyporheic residence times on the scale of minutes to hours resulted in the hyporheic zone shifting from a net source to a net sink of NO_3^- in snowmelt driven, beaver dam impacted streams.

While it has been possible to collect high-frequency hydrological datasets (i.e., channel *Q*) in low order streams for decades, the hydrochemistry of low order streams tends to be measured infrequently (≤1 per week) due to difficulty in accessing remote and numerous catchments and the reliance on labor intensive manual sampling. This disparity in sampling rates, where the resolution of hydrochemical data does not match rates of hydrological variability, potentially obscures important water quality dynamics at short timescales [*Kirchner et al.*, 2004; *Rode et al.*, 2016b]. At minutes to hours, for example, variation in sourcing from multiple streams and terrestrial contaminant pools following a rainfall event can rapidly alter water quality [*Wyer et al.*, 2010]. This is especially true in flashy systems, where the majority of mass fluxes for contaminants and nutrients may occur during relatively short hydrograph peaks, which would not be adequately characterized by low-frequency sampling [*Cassidy and Jordan*, 2011].

Meanwhile, stream biota can alter the magnitude and form of nutrients at sub-daily timescales [*Cohen et al.*, 2013; *Halliday et al.*, 2013b; *Heffernan and Cohen*, 2010; *Pellerin et al.*, 2012], with consequences for downstream loading. Thus, there remain gaps in understanding the variability of N transport dynamics in unsteady, low order systems.

Recently, increasing attention has been given to ephemeral and intermittent streams, which are often low order, and represent the most extreme case of unsteady flow. Periods of streambed drying occur frequently in temperate headwater catchments [*Jensen et al.*, 2017] and may be increasing throughout Europe due to both climate change and extractive management of surface waters [*Krysanova et al.*, 2008; *Sabater*, 2008; *Wilby et al.*, 2006]. These conditions are already common and may occur in up to 69% of headwater streams [*Raymond et al.*, 2013]. Even so, the prevalence of intermittent flow has probably been underestimated due to the difficulty in capturing rapidly variable flow conditions across spatially distributed drainage networks [*Arce et al.*, 2014; *Jensen et al.*, 2017].

Intermittent flow dynamics are particularly prevalent across much of the Mediterranean (and regions with Mediterranean climate) due to seasonal contrasts in precipitation and relatively hot, dry atmospheric conditions. For example, over 45% of Greece is composed of intermittent drainage networks. Given the prevalence and importance as water resources throughout the region, non-perennial Mediterranean streams are particularly well-studied [e.g., *Arce et al.*, 2015; *Arce et al.*, 2014; *Merbt et al.*, 2016; *Skoulikidis et al.*, 2017]. Periodic drying and inundation are important drivers of stream hydrochemistry and microbial activity in intermittent Mediterranean and semiarid streams. In particular, flow fluctuations and cessation affect N availability, sediment redox conditions, and dissolved organic carbon concentrations [*Gómez et al.*, 2009; *Koch et al.*, 2010; *von Schiller et al.*, 2011]. These factors are important controls on the rates of microbial N transformations, such as denitrification and nitrification, in intermittent streams at both seasonal and event based timescales [*Arce et al.*, 2015; *Arce et al.*, 2014; *Martí et al.*, 1997; *Merbt et al.*, 2016; *Skoulikidis et al.*, 2017; *Stanley and Valett*, 1992]. Thus, streambed drying due to cycles of flow intermittency strongly impact the forms and amounts of N_r that are mobilized when flow returns, often with the preferential production and subsequent mobilization of NO_3^- [*Arce et al.*, 2014; *Bernal et al.*, 2013; *Skoulikidis et al.*, 2017; *von Schiller et al.*, 2008].

The onset of flow following dry periods in most of the systems considered in the aforementioned studies (i.e. Mediterranean and semiarid streams), results from seasonal to interannual shifts in precipitation. As a result, flow onset is accompanied by increases in hydrologic connectivity to source waters and hydrological flow paths within a catchment that are likely to obscure the impact of rewetting of hyporheic and streambed sediments on water quality and N transport, even though dry streambeds may contribute up to 50% of the NO_3^- mobilized in first flush events [*Merbt et al.*, 2016]. Additionally, intermittency in many of the systems previously considered occurs at seasonal to annual timescales, which may not be indicative of the short-term intermittency likely to occur as previously permanent reaches respond to the contracted and intensified precipitation regimes projected under global climate change or intensive management [*Krysanova et al.*, 2008; *Larned et al.*, 2010; *Sabater*, 2008]. Thus, while we have some understanding of the effects of periodic drying on pool hydrochemistry and microbial N transformations in streambeds, our understanding of the importance of these in-channel processes on water quality during periodic and rapid flow re-initiation is confounded by the event-responses that occur throughout catchments and the timescales of intermittency previously considered.

Unlike many other non-perennial streams, ephemeral and intermittent streams in the McMurdo Dry Valleys, Antarctica (MDV) are largely disconnected from the surrounding landscape due to the presence of continuous permafrost, lack of precipitation, and the absence of groundwater inflow or losses from streams. Thus, MDV streams offer ideal hydrologic conditions that aid in unravelling the importance of instream processes and short-term flow intermittency to N transport dynamics that are obscured or difficult to capture elsewhere due to more complex catchment connectivity.

2.2 McMurdo Dry Valley Streams

The MDVs (approximately 78°S, 162°E), which cover an area of 22,700 km^2 between the Transantarctic Mountains and the Ross Sea, are composed of glacially carved valleys, perennially ice-covered lakes, and expanses of ice-free glacial till (4,500 km^2) [*Levy*, 2013]. Climatically, the MDVs are a polar desert with average annual air temperatures of -18°C [*Doran et al.*, 2002] and minimal precipitation (3–50 mm snow water equivalent yr^{-1}, all of which occurs as snow) [*Fountain et al.*, 2010]. Continuous permafrost exists throughout the landscape with a seasonally thawed active layer that extends to a maximum depth of approximately 50 cm [*Bockheim et al.*, 2007; *Conovitz et al.*, 2006].

Despite the cold, dry conditions in the MDVs, ephemeral meltwater streams flow from glaciers to closed-basin, perennially ice-covered lakes, for approximately 4-8 weeks per year during the Austral summer [*Wlostowski et al.*, 2016]. Flow in MDV streams is highly unsteady and frequently intermittent due to the generation of diel meltwater pulses from source glaciers, with discharge varying by 5- to 10-fold in less than an hour [*Conovitz et al.*, 1998]. The lack of significant precipitation and the presence of continuous permafrost beneath the landscape

[*Bockheim et al.*, 2007; *Conovitz et al.*, 2006] act to decouple streams from adjacent hillslopes and prevents groundwater inflows or outflows [*Fountain et al.*, 2010; *Gooseff et al.*, 2004; *Gooseff et al.*, 2011]. As a result, the only major interaction between the stream channel and the landscape is through the hyporheic zone, which consists of loosely consolidated glacial till and is, itself, bounded by permafrost.

While MDV streams remain dry for most of the year, they host a rich microbial ecosystem composed of well-developed benthic cyanobacterial mats and hyporheic microbial communities [*Alger*, 1997; *Kohler et al.*, 2015; *McKnight et al.*, 1999; *Stanish et al.*, 2011]. Microbial mats exist in a freeze-dried state throughout the winter and are capable of reactivating within 20 min to 1 week once flow is re-initiated, even after decades of desiccation [*McKnight et al.*, 2007; *Vincent and Howard-Williams*, 1986]. Once active, these microbial communities and mats rapidly drive instream biogeochemical processing, especially nitrogen removal and transformation (i.e. denitrification and uptake), along the stream corridor and hyporheic zone during periods of flow [*Gooseff et al.*, 2004; *Koch et al.*, 2010; *McKnight et al.*, 2004]. Benthic algal mats account for the majority of N processing via assimilatory uptake and dissimilatory processes including denitrification, which occurs over very short spatial and temporal scales [*Gooseff et al.*, 2004; *McKnight et al.*, 2004]. Benthic algal mats are nitrogen limited resulting in NO_3^- uptake rates of 16 nmol N cm^{-2} h^{-1}, which is partially fueled by net releases of NO_3^- from hyporheic sediments (7 nmol cm^{-2} h^{-1}) following desorption of NH_4^+ [*Gooseff et al.*, 2004]. Denitrification occurs at a similar rate, though, notably, the availability of NO_3^- rather than dissolved organic matter derived from microbial mats, was the rate limiting factor [*Gooseff et al.*, 2004]. Based on two reach-scale nutrient injection studies, *Gooseff et al.* [2004] calculated a whole stream net NO_3^- uptake rate under ambient conditions of approximately 0.004 μM N m^{-2}, which integrates hyporheic and benthic microbial processes. As in other studies, uptake rates increased with nutrient concentrations, but were lower than for temperate systems, likely due to the very low ambient NO_3^- concentrations in MDV streams. Importantly, the conceptual model of nitrogen cycling in MDV streams based on these lines of evidence only includes processes that retain or remove NO_3^- [Figure 2 in *Gooseff et al.*, 2004]. Other N_r forms or related transformations (i.e., mineralization of DON to NH_4^+) have not been considered, nor are any production processes (i.e., nitrification) included. However, it is reasonable to expect that the N cycle in MDV streams is more complex than prior studies, which have focused particularly on NO_3^-, is more complex than the available evidence suggests.

Overall, these biologic features, hydrologic constraints, relatively simple and dilute inputs from glaciers, and highly periodic structure of flow in MDV streams make them ideal natural laboratories for this study.

2.3 The Sensor Revolution & Solute Dynamics

As foreseen by *Kirchner et al.* [2004] and recently summarized by *Rode et al.* [2016b], advances in the precision and temporal resolution of *in situ* water quality sensors (i.e., nutrient concentrations, dissolved gases, algal pigmentation, cytometers, etc.) have enabled researchers to assess watershed and instream biogeochemical processes on the time scales over which they and hydrological drivers often vary (i.e., minutes to hours). Such *in situ* sensing technology can overcome the limitations to understanding short-term N transport dynamics imposed by prior reliance on low-frequency sampling as described above (Section 2.1).

The availability of multiple solute time series at fine temporal resolutions has enabled more detailed understanding of how watersheds and streams function physically, hydrologically, and biogeochemically. In particular, integrated, high-frequency solute datasets have made it possible to unravel variation in nutrient sources and flow pathways [*Bowes et al.*, 2015]; quantify coupled instream metabolic and nutrient transformations at sub-daily timescales [*Cohen et al.*, 2013; *Hensley et al.*, 2014; *Kurz et al.*, 2013; *Rode et al.*, 2016a]; disentangle the interactive effects of biological, physical, and hydrochemical drivers of water quality variability [*Bowes et al.*, 2016]; and analysis of multi-timescale solute concentration variability to assess travel time distributions, transfer functions, and the detection of spurious trending behaviors due to fractal scaling patterns [*Dupas et al.*, 2016; *Gisiger*, 2001; *Godsey et al.*, 2010; *Halliday et al.*, 2013b]. Thus, a widening array of high-frequency sensing technology enables researchers to disentangle coupled hydrological and biological processes that control water quality parameters (especially N_r concentrations) over time and space.

As adoption and operation costs of high-frequency *in situ* sensors decline, one area that requires further development is in the deployment of high-frequency water quality sensors in streams that experience highly unsteady, short-term flow variations. Few studies have considered such conditions [e.g., *Pellerin et al.*, 2012] given the non-periodic nature of discharge fluctuations in most systems, usually due to highly variable episodic precipitation patterns. Thus, it can be difficult to strategically deploy high-frequency sensors to capture these dynamics if few are available. However, systems in which, predictable periodic flow variations occur (i.e. glacial meltwater streams) provide an important stepping stone for such investigations. The predictable, yet variable conditions present in glacial meltwater systems will aid in advancing understanding of coupled hydrological and biological processes affecting N (and other solute) transport and transformation processes in response to short-term flow fluctuations.

3. Study Site and Methods

I focused my investigation on Von Guerard stream, a relatively long stream (5.2 km) in Taylor Valley, McMurdo Dry Valleys, Antarctica (Figure 1). Von Guerard stream flows from the glaciated Kukri Hills to Lake Fryxell with an average gradient of 0.078 m m^{-1} [*Wlostowski et al.*, 2016]. Near the source glacier the channel is incised and steep, though the bed, composed of loose gravel and sand embedded in cobbles and boulders, remains fairly wide and flat throughout its entire length. A relatively broad plane, over which shallow, ephemeral ponds form and drain during diel flood events, is located just below the upstream gauge (F21). Further downstream, the stream re-channelizes as it descends towards the outlet to Lake Fryxell, where a second gauge and field camp (F6) are located. I selected Von Guerard Stream for this study given its seasonally variable hydrograph, highly intermittent flow patterns with frequent flow cessation [*Wlostowski et al.*, 2016], and proximity to laboratory facilities at the F6 camp. I collected the primary data for this study during the 2016-2017 flow season for Von Guerard Stream and is complimented by historical water chemistry and hydrological data from the MCM LTER database.

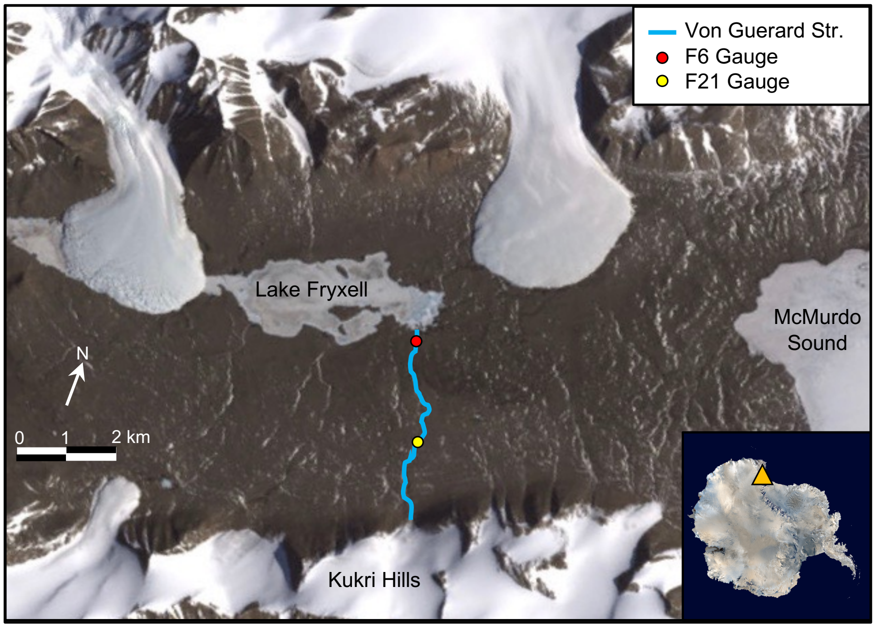

Figure 1. Map of the Lake Fryxell Basin, Taylor Valley, Antarctica. Von Guerard Stream is shown (blue line) along with upstream (F21; yellow circle) and downstream (F6; red circle) gauging and nitrate sensor deployment locations. Map inset (bottom right) depicts location of the McMurdo Dry Valleys with respect to Antarctica. Other streams in the Lake Fryxell Basin are omitted for clarity.

3.1 Data Collection

I utilized *in situ* sensors and stream control structures to measure stage at both upper and lower Von Guerard stream (F21 and F6, respectively). At F21, in-channel stage was measured by a Hobo U20 Water Level Logger (Onset, Massachusetts, USA) at 15 min intervals. I corrected raw pressure readings for barometric pressure variations using another Hobo U20 pressure transducer located on the adjacent streambank (within 4 m). At F6, stream stage was measured using an Accubar Gauge Pressure Sensor (Sutron Corporation, Virginia, USA) and collected with a Campbell Scientific CR1000 data logger at 15 min intervals. Depending on stage, I used either a pygmy meter or Baski Cutthroat portable flume to obtain discharge measurements (about 1-2 times wk^{-1}) that were then paired with a gauge-derived stage measurement. Concurrent discharge and stage measurements were subsequently used to develop a rating curve for F6 through the AQUARIUS (Aquatic Informatics, British Columbia, Canada) software package.

Continuous discharge measurements were then derived from the rating curve and stage records. Due to high sedimentation and a rapidly shifting channel morphology at the control structure, I did not develop a rating curve or continuous discharge measurements for F21.

I also used existing infrastructure and removable sensors to major specific electrical conductance (EC) and water temperature (WT) at 15 min intervals at both F6 and F21. For F6, WT and EC data were recorded by a Campbell Scientific CS547A probe and A547 interface. I periodically validated and corrected gauge measurements with handheld EC and WT probes (YSI). At F21, I collected EC and WT data using a HOBO U24 (Onset, Massachusetts, USA) probe deployed in the main channel just below the control structure throughout the duration of the study.

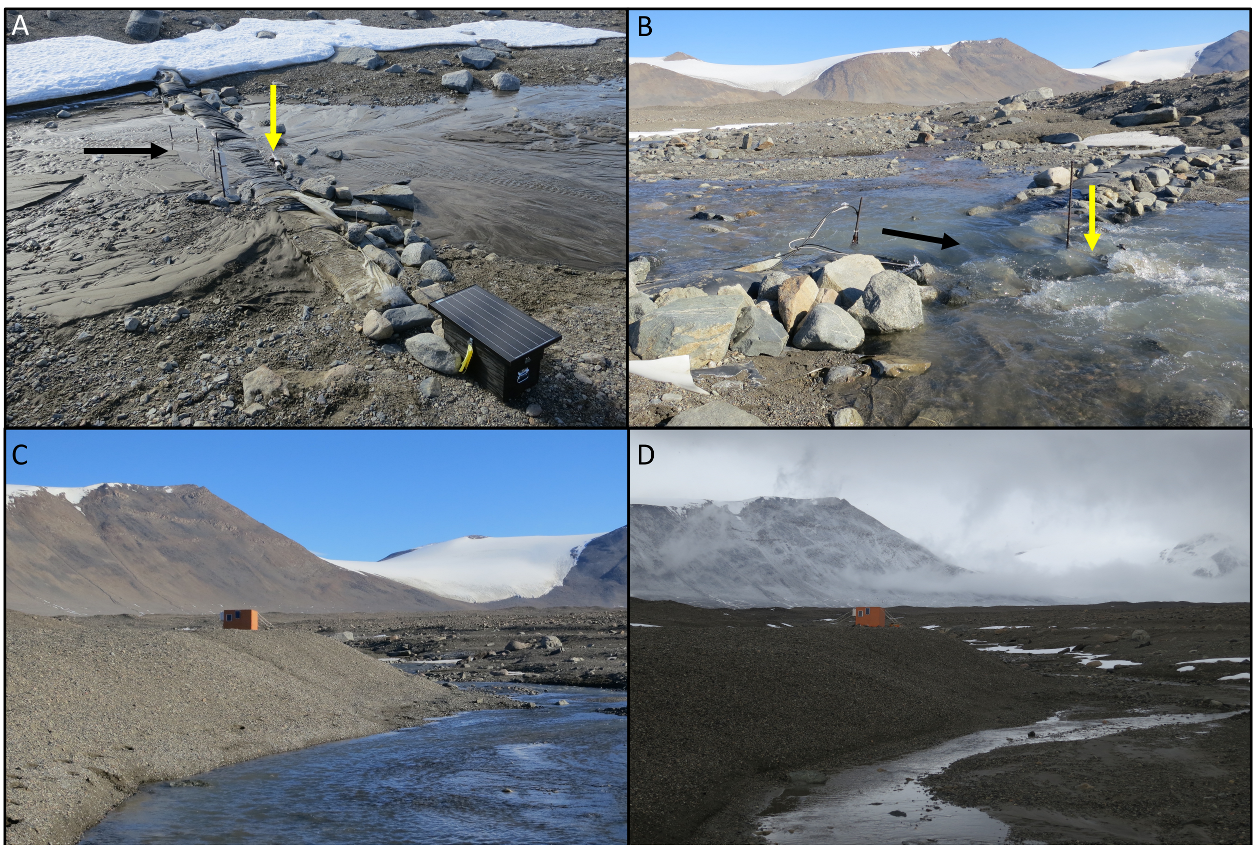

Figure 2. Stream gauge controls at (A) F21 and (B) F6 with SUNA V2 locations in pools below controls indicated by yellow arrows. Direction of flow is indicated by black arrows. Channel width variability below F6 (gauge box visible) is shown during (C) high and (D) low flow conditions (148.6 and 6.6 L s^{-1}, respectively).

I installed submersible ultraviolet nitrate analyzers (SUNA V2, Satlantic, Halifax, Nova Scotia, Canada) in small pools below the control structures at both F6 and F21 (Figure 2). The SUNAs measured NO_3^- concentration (μM N L^{-1}) at 15 min intervals simultaneously with stage, WT, and EC data collection by stream gauges. Similar to *Cohen et al.* [2013], the SUNAs made measurements in bursts of 5, which were subsequently averaged to a single data point. An anti-biofouling wiper swept the optical path each hour to prevent interference by algal growth or sedimentation. The limit of quantification for SUNA V2 sensors with freshwater calibration was approximately 1.0 μM NO_3^- with a precision of ±0.03 μM. Manual grab samples were collected opportunistically (1-2 wk^{-1}) by myself and fellow field team members for instrument validation in 250 ml acid-washed (1% HCl) HDPE bottles. We immediately transported grab samples to the field laboratory at F6 and filtered them using 0.47 μm Whatman GF/C pre-combusted (450°C for 4-5 hours) glass fiber filters. Once filtered, samples were frozen and transported to the University of Colorado Boulder (USA) and USGS Colorado Lab, where they were analyzed for nitrate concentration by ion chromatography on a (Dionex ICS-5000 with an AS4-A RFIC 4x250 mm analytical column and an AG4-A RFIC 4x50 mm guard column). The detection limit for laboratory analysis was 2.0 μM NO_3^- L^{-1}.

I also analyzed low-frequency, historical data for Von Guerard stream (1994-2017) from the MCM LTER database (mcmlter.org/streams-data-sets). Hydrological data (Q, WT, and EC) were collected at F6 as described above during this period by various field team members. Historical NO_3^- data from F6 were obtained by opportunistic grab samples (n= 87) and processed by the same protocol as described above for the SUNA validation from 1994-2017 and analyzed using a Lachat QuikChem 8500 Flow Injection Analyzer at the Arikaree Environmental Laboratory at the University of Colorado Boulder.

3.2 Data Processing and Validation

I inspected the resulting high-frequency NO_3^- time series for F6 and F21 for general patterns or abnormalities. I identified outliers during data inspection and removed anomalous NO_3^- values (replaced with a missing value indicator, NA), leaving gaps in the data record. These amendments focused on singular spikes to unrealistically high or low values (i.e. single values more than 5 times preceding and subsequent measurements, values above historically detected limits, as well as those below the limit of instrument detection), negative values, and periods when interference occurred due to high sedimentation or instrument burial. I thus justified the removal of data points based on known historical concentrations, temporally adjacent solute dynamics, and problems directly observed during data collection. Where possible, only single measurements within a 5-sample burst were removed allowing the remaining 4 samples to be used to calculate an average for that time point.

For the F6 NO_3^- concentration time series, I manually omitted 0.3% off all measurements during data inspection, while 31.6% were omitted or confirmed as gaps (i.e. no reading when buried) from the F21 time series. The higher percentage of omissions from F21 is due to the high sedimentation rates during daily hydrograph recession, which frequently buried the instrument. Missing or omitted values for the NO_3^- time series from F6 were infilled by averaging the preceding and following nitrate data points. No infilling was performed on the F21 data given the much longer duration of gaps.

Next, I compared the distribution of data from the in situ NO_3^- sensor at F6 to that of validation grab sample data using a two sample Kolmogorov-Smirnov Test (as per *Halliday et al.* [2012] for similar purposes).

3.3 Net Concentration Difference Analysis

I constructed a concentration difference time series between upstream and downstream sites according to the methods presented by *Halliday et al.* [2012] as:

$$C_d(t_i) = C_l(t_i) - C_u(t_{i-h}) \tag{1}$$

The concentration difference (C_d) at time t_i is the difference between the concentration at the upstream site (C_u) and downstream site (C_l) at time points t_{i-h} and t_i, *respectively*. The value of h, the average flood wave travel time between upper and lower time points, was defined as:

$$h = \frac{\sum_{d=1}^{d_n}(t_{Qpl}(d) - t_{Qpu}(d))}{d_n} \tag{2}$$

The lag (h) is the average difference in the timing of peak daily discharge for the lower (t_{Qpl}) and upper (t_{Qpu}) sites on each day divided by the total number of days (d_n) considered. For F21, I used stage records in lieu of discharge as a rating curve was not developed at this site. I selected 19 days (d_n) during which diel flood waves were clearly present with maximum discharge occurring at a single data point (15 min resolution) for both locations.

I also assessed whether the calculated flood wave travel times varied as a function of observed daily peak discharge at F6 to confirm whether utilization of an average travel time (as from Equations 1 and 2) would introduce systematic bias into concentration difference calculations. To accomplish this, I performed a Kendall rank correlation between flood peak travel time and peak discharge. Given the large gaps in the F21 dataset, additional analyses performed on high-frequency NO_3^- focus solely on the F6 time series.

3.4 Nitrate Concentration-Discharge Relationships

3.4.1 C-Q Power-Law Analysis

Power-law analysis of concentration discharge (C-Q) relationships has proven to be a useful empirical tool for assessing the response of solute mobilization and transport dynamics over a wide range of discharge values across a range of catchments and solute types [*Clow and Mast*, 2010; *Godsey et al.*, 2009; *Haygarth et al.*, 2004; *Vogel et al.*, 2005]. Following visual inspection of the high-frequency NO_3^- data in C-Q space, I fitted power-law relationships of the form:

$$C=aQ^b \tag{3}$$

Where a and b are constants, with b representing the slope of the fitted line in log-log space. A number of shifts in C-Q relationships due to temporal patterning and discharge thresholds were identified, such that separate power-law relationships were fitted to better describe NO_3^- C-Q dynamics. The b parameter of power-law C-Q relationships has a physical basis and can be interpreted to characterize solute sourcing patterns as either chemostatic (b = 0), enrichment (b > 0; transport limited), or dilution (b < 0; source limited) [*Godsey et al.*, 2009]. I used the same method to analyze historical, low-frequency grab sample data from 1994-2017 from the F6 site on Von Guerard Stream.

3.4.2 Concentration Probability Exceedance Curves

In addition to assessing C-Q relationships through power-law fitting, I constructed concentration probability exceedance curves for both the high-frequency NO_3^- data for the 2016-2017 season and the historical, low-frequency data. I utilized these curves to assess how sampling interval affects the frequency of detection across a range of concentrations under a diel flow pulsing regime in MDV streams. I applied Kolmogorov-Smirnow two sample tests to assess whether the continuous distributions (based on empirical cumulative distribution functions) from which samples were drawn differed by method.

3.4.3 Explanatory Factors for Historical C-Q Relationships

To provide broader temporal context on solute transport dynamics, I calculated summary statistics and performed an initial visual exploration of relationships between NO_3^- and other major hydrochemical constituents and parameters (antecedent flow, EC, Si, Cl^-, DOC, NO_2^-, NH_4^+, SO_4^{2-}) obtained from 1994-2017 at the F6 stream gauge. Again, following visual observations, I selected and applied a power-law framework for analysis, from which log-log slopes and coefficients were obtained to identify the strength, directionality, and significance of relationships to NO_3^- concentrations.

4. Results

4.1 High-Frequency Nitrate Time Series

The NO_3^- concentrations that I observed from high-frequency *in situ* sensors remained low relative to temperate systems characterized by unsteady discharge [*Alexander et al.*, 2007; *Pellerin et al.*, 2012], though were typical for MDV streams [*Fortner et al.*, 2013], while high-frequency data on physical parameters (Q, EC, WT) exhibited strong diel periodicity driven primarily by meltwater pulse events (Figure 3). Flow was observed at the downstream site (F6) beginning on December 13, 2016 (Figure 3A). Large magnitude diel flow pulsing (from 0 to more than 200 L s^{-1}) occurred along with periods of low or zero flow conditions, until sensors were removed and data downloaded on January 26, 2016. The maximum discharge (Q_{pk}) for this period was 286 L s^{-1}. The duration of zero flow conditions ranged from 15 min to 2 d and cumulatively represented 1.65% of the period of record. Flows below 3.0 L s^{-1} occurred during 24.94% of the study period.

The F6 [NO_3^-] time series exhibited relative stability about a mean of 2.92±0.23 µM throughout periods of diel flow pulsing, though notable positive excursion with rapid decreases (approximately 11 µM to 3 µM in less than 15 min) occurred during low and zero flow periods (Figure 3B). Nitrate concentrations varied with diel periodicity while flood waves rose and receded, especially in the F6 time series, though the magnitude of variance during these periods (s^2=0.054 µM, range of 2.45 to 6.38 µM) was relatively small compared to the variability in concentrations under low to zero flow conditions (s^2=7.33 µM, range of 2.52 to 11.57 µM). Under flowing conditions, the variance in [NO_3^-] at F21 (s^2=0.275 µM) was nearly 5 times larger than at F6.

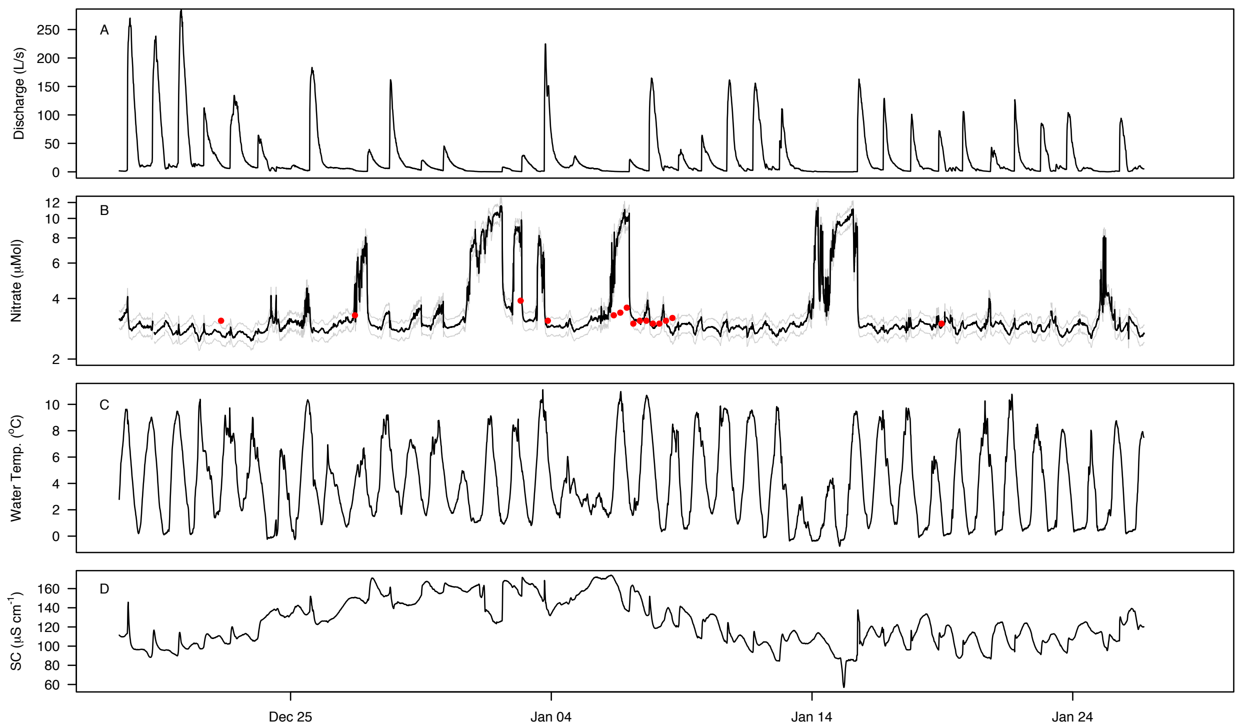

Figure 3. High-frequency (15-min resolution) data obtained from lower Von Guerard stream gauge (F6) and *in situ* NO_3^- sensor from December 14, 2016 to January 26, 2017 including (A) discharge, (B) nitrate concentration with precision bounds (gray) and adjusted validation samples (red), (C) water temperature, and (D) specific electrical conductance.

Water temperature fluctuated by approximately 6ºC, primarily due to the periodic influx of relatively cold glacial meltwater (Figure 3C). Specific electrical conductivity initially increased throughout the first half of the flow season, then decreased and stabilized (Figure 3D). As with [NO_3^-], relatively small diel fluctuations in EC occurred within long-term patterns due to daily meltwater flood events.

I matched manual grab samples (N=17) collected throughout the flow season an analyzed in the laboratory to *in situ* measurements by SUNA V2 sensors (Table 1) for validation and correction purposes. On average, the *in situ* measurements were 2.1±0.54 µM N L^{-1} greater than those analyzed in the laboratory. For samples where *Q* was low (below 1% of seasonal maximum *Q*), the *in situ* measurements were shifted positively by 1.0±0.12 µM L^{-1}, on average. When corrected for (subtraction of mean shift from *in situ* measurements) the remaining mean difference between validation and *in situ* measurements was 0.02 µM N L^{-1}, which is within the precision specifications of the SUNA V2 sensor (±0.03 µM L^{-1}).

Table 1. Discharge and paired *in situ* sensor and laboratory observations of nitrate concentrations at the lower stream gauge (F6) on Von Guerard Stream during the 2016-2017 flow season.

Date	Time (GMT+13)	Discharge (L s^{-1})	In Situ NO_3^- (µM N L^{-1})	Laboratory NO_3^- (µM N L^{-1})
22 December 2016	08:00	12.93	2.7	2.1
27 December 2016	11:15	3.01*	4.5	2.3
2 January 2017	19:45	0.59*	7.2	2.9
5 January 2017	17:45	5.55	3.2	2.1
6 January 2017	09:30	0.82*	4.6	2.3
6 January 2017	15:30	0.45*	8.5	2.4
6 January 2017	21:30	0.41*	9.8	2.6
7 January 2017	03:30	13.75	3.2	2.0
7 January 2017	09:30	5.86	3.0	2.1
7 January 2017	15:30	1.90*	3.4	2.1
7 January 2017	21:30	154.07	2.9	2.0
8 January 2017	03:30	32.26	2.9	2.0
8 January 2017	09:30	8.28	3.1	2.1
8 January 2017	15:30	7.13	2.7	2.2
8 January 2017	21:30	30.00	2.9	NA
9 January 2017	03:30	17.75	3.0	NA
18 January 2017	23:15	51.90	2.9	2.0

*Denotes discharge values at or below 1% of the seasonal maximum discharge.

I constructed [NO_3^-] probability exceedance curves (Figure 4) from the low-frequency, historical grab samples (N=69, 1994-2017) and the high-frequency, *in situ* data (N=4105) for the downstream site, which were above their respective detection limits. The *in situ* sensor detected concentrations below approximately 3.75 µM and above approximately 8.0 µM less frequently during the 2016-2017 flow season relative to the grab samples collected over 23 years. The probability of exceedance for each method was similar for concentrations between these two values. A Kolmogorov-Smirnov two-sided test found that the low-frequency, historical grab samples and high-frequency, *in-situ* data were from statistically different continuous distributions ($p<0.001$), which was also true ($p<0.001$) for the 2016-2017 grab samples and *in situ* measurements. I obtained the same results ($p<0.001$) from Kolmogorov-Smirnov two-sided tests using *in situ* data that was corrected for the mean difference between *in situ* and laboratory samples.

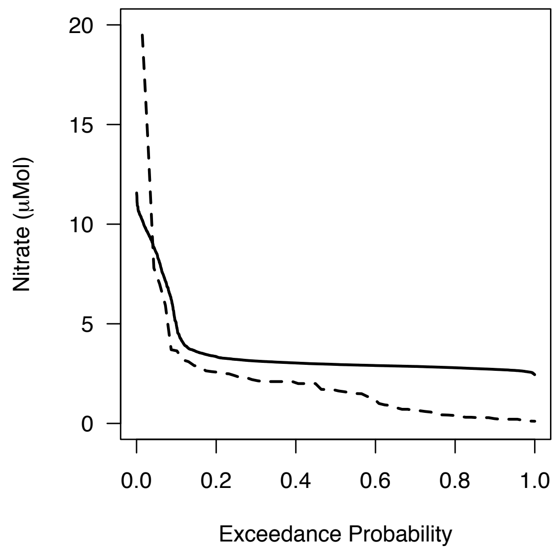

Figure 4. Probability exceedance curves for [NO_3^-] at F6 from (dashed line) historical, low-frequency nitrate data from manual grab samples (N= 69, 1994-2017) and (solid line) uncorrected high-frequency, *in-situ* data from SUNA V2 sensor (N=4105, December 2016-January 2017). The data presented include only samples above the respective detection limit for each dataset.

Mean flood peak travel time (h) between F21 and F6 was 1.95±0.014 hr, which I adjusted to 2 hr given the 15-min resolution of each dataset. Peak discharges for the subset of Q data used in this calculation ranged from 13.8% to 67.1% of seasonal peak discharge with a median value of 39.3%. A Kendall rank correlation test showed a significantly negative linear relationship between flood magnitude and the calculated flood peak travel time ($\tau = -0.46$, $p = 0.0174$), which was confirmed by a simple linear regression (R^2=0.42, p=0.005; Figure 5). Based on an approximate reach length between F21 and F6 of 2.5 km, I found that these travel time estimates correspond to a water velocities ranging from 0.69 down to 0.25 m s^{-1}.

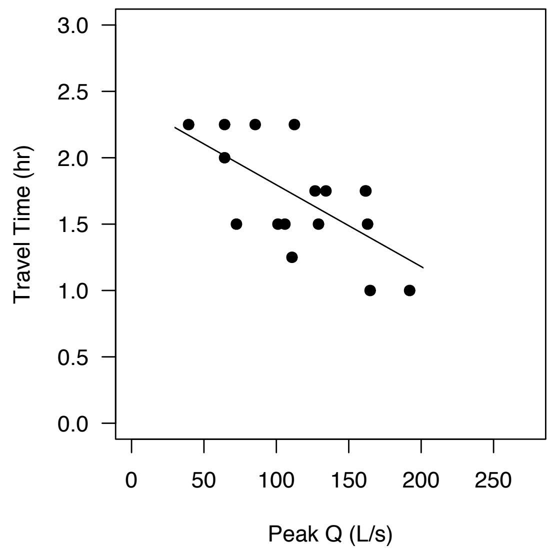

Figure 5. Flood peak travel time between upstream and downstream sites of Von Guerard Stream by diel peak discharge (measured at F6) for a subset of the 2016-2017 flow season. Travel time was calculated as the difference in time between detection of diel flood peaks at the upstream and downstream site. A trend line from a simple linear regression (R^2=0.42, p=0.005) is also presented.

Based on the mean flood peak travel time, I calculated a net [NO_3^-] difference time series for the reach between F21 and F6 was calculated using Equation 1 (see Figure 6). The concentration difference time series was negative for all time points where calculation was possible, indicating that the reach from F21 to F6 remained a net sink for NO_3^- throughout the study period. The mean concentration difference between the two sites, utilizing a constant travel time of 2 hr, was –1.84 ±0.49 μM with an autocorrelation (γ_1=0.95) corrected standard error on the mean of ±0.09 μM. Similar to the individual site data, the concentration difference time series exhibit diel periodicity, though the strength of this dynamic is obscured by gaps in the data due to incomplete records from the upstream site. No seasonal trends were observed in the concentration difference time series, though it is notable that concentration differences were only calculated for part of the month of January and had many gaps.

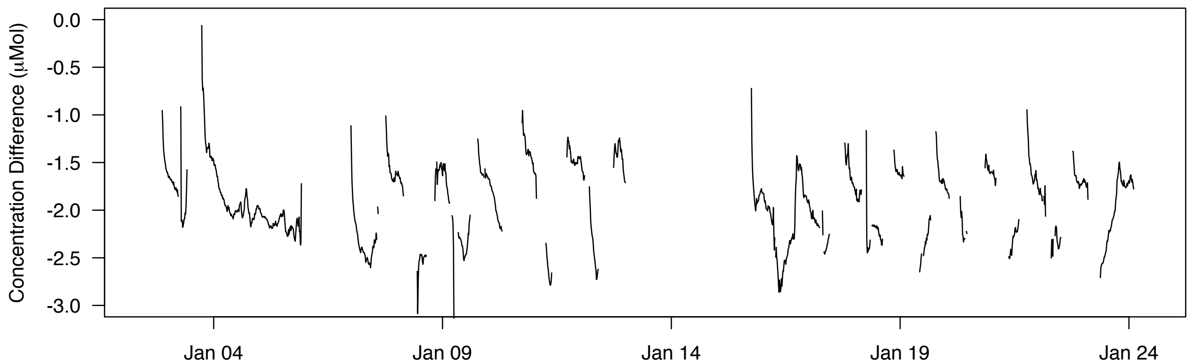

Figure 6. Travel time adjusted nitrate concentration difference between upper and lower sites on Von Guerard Stream during the 2016-2017 flow season. Gaps in data are primarily due to frequent sediment deposition at F21, which resulted in burial of the sensor. Periods of low flow ($Q_t < 0.01*Q_{pk}$) have been removed due to limited advective transport between the two sensor locations under those conditions.

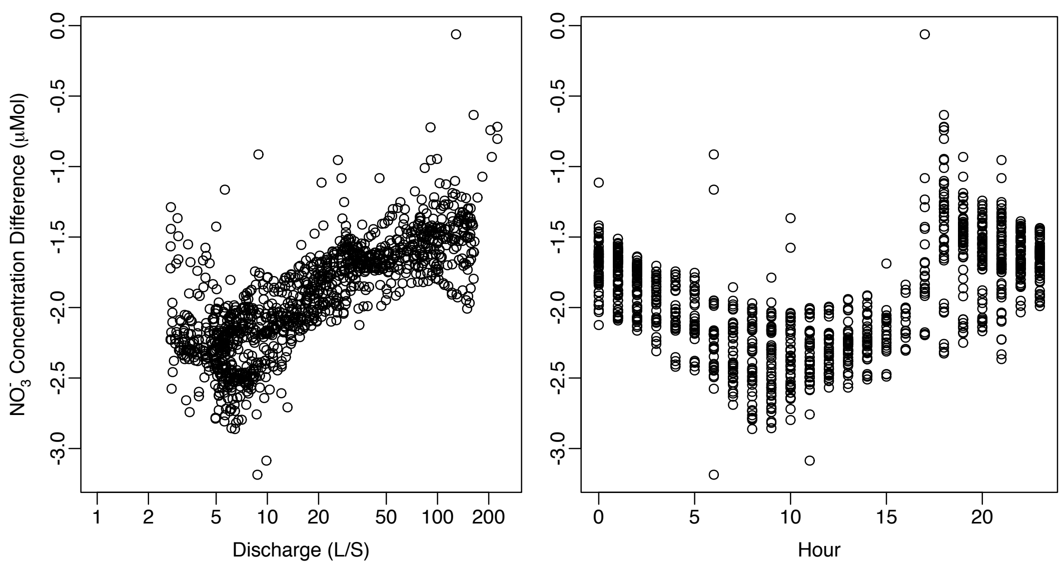

Figure 7. Nitrate concentration difference by (A) discharge and (B) time of day. Periods of low flow ($Q_t < 0.01*Q_{pk}$) have been removed due to limited advective transport between the two sensor locations under those conditions.

I also found that the magnitude of concentration differences decreased as Q increased (Figure 7A). This led to sub-daily patterning in the net change of $[NO_3^-]$ along the study reach such that the least change in [NO_3^-] occurred overnight and the greatest net removals (approximately –2.0 to –2.75 μM) occurred during diel flood recession (Figure 7B), from morning to midday.

4.2 Nitrate Concentration-Discharge Relationships

High-frequency [NO_3^-] data showed three distinct patterns in log-log C-Q space, related to temporal and discharge thresholds (Figure 8). I identified a flow threshold at 2.86 L s^{-1} or 1% of the max discharge (Q_{max} = 286 L s^{-1}) for the study period. I define this as a low flow threshold (Q_{low}) for subsequent analysis. Nearly all notable deviations from low variability diel periodicity in NO_3^- occurred at discharge values below Q_{low} (Figure 3 and Figure 8). For $Q(t) > Q_{low}$, I fitted a power-law C-Q relationship of the form $C=aQ^b$ due to the linear relationship in log-log space. From this, I obtained a log-log slope (b) of –0.0178 ±0.00133. For $Q(t) < Q_{low}$ two distinct power-law patterns are present. Prior to January 14, 2017, I found a log-log C-Q slope of –0.421 ±0.0113, while data after this date had a log-log C-Q slope of –0.221. None of the log-log slopes I obtained were within 2 SEs of either 0 or -1, though all were closer to 0.

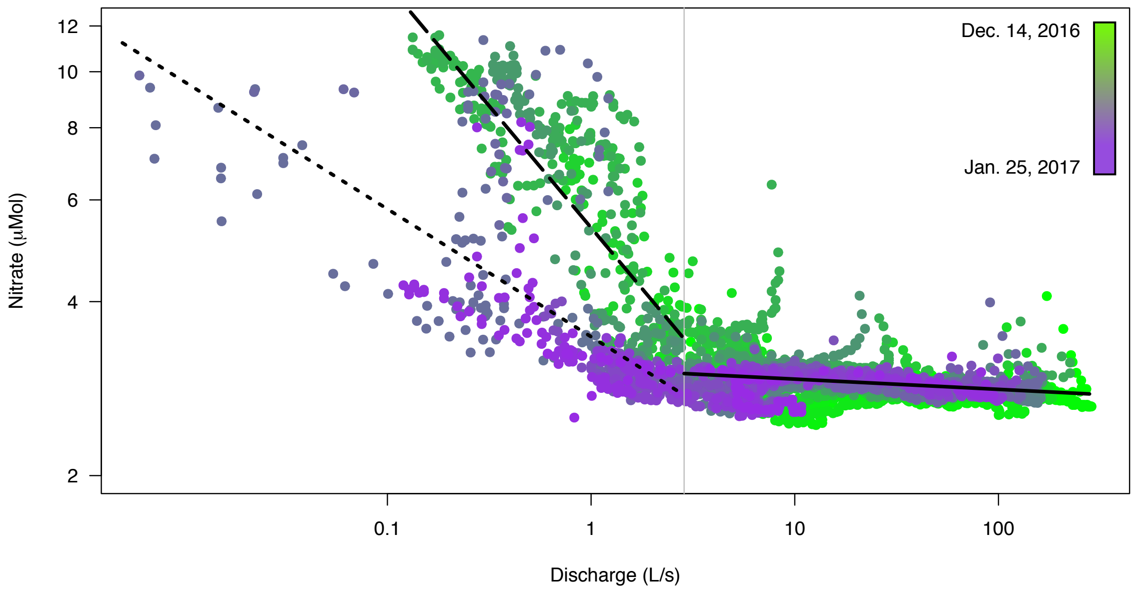

Figure 8. High-frequency nitrate concentration measurements from the downstream site by discharge for the 2016-2017 flow season in log-log space. Vertical gray line denotes low-flow threshold (Q_{low}). For low flow conditions (Q_t<Q_{low}), power-law C-Q relationships ($C=aQ^b$) are shown before (long dash) and after (short dash) January 14, 2017. Solid line denotes power-law C-Q relationship for $Q_t > Q_{low}$.

I found a positive power-law relationship ($p<0.001$, $R^2=0.47$) between the duration of low flow (T_{low}, *when* $Q_t > Q_{low}$) and NO_3^- concentration (C), of the form $C=aT_{low}^{\ b}$, where b=0.244±0.0084 (Figure 9). I identified temporal patterns in the relationship between [NO_3^-] and the T_{low}. Increases in [NO_3^-] did not occur until after at least 1 h of low flow conditions. This threshold shifted later in the season, with increases in [NO_3^-] occurring only after 3 hr for data collected after January 14, 2017.

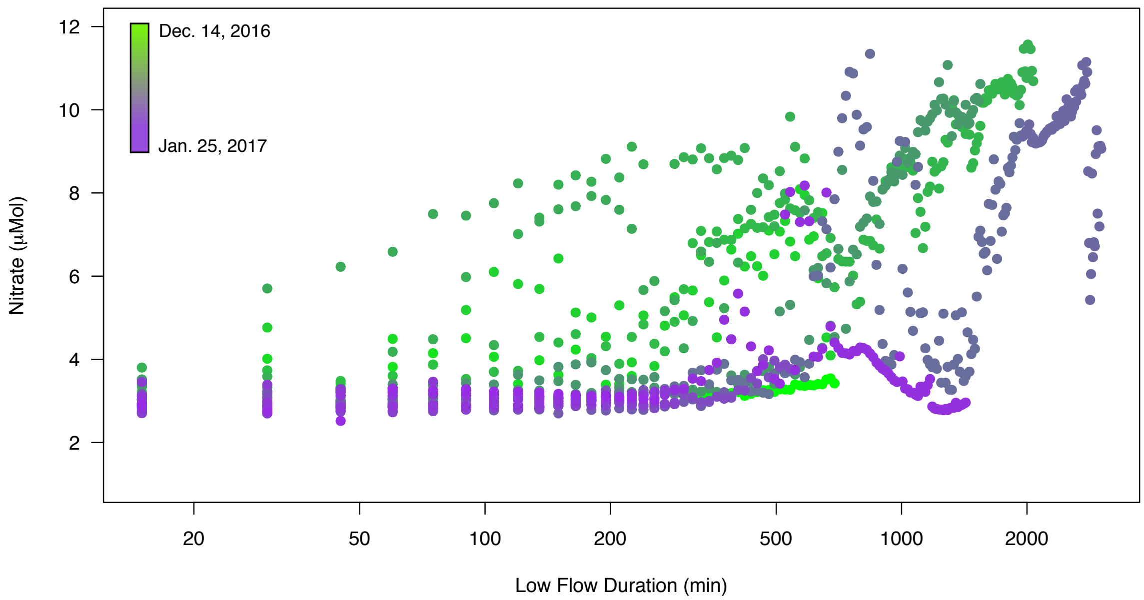

Figure 9. Nitrate concentration at F6 by duration of low flow conditions ($Q_t < Q_{low}$) from high-frequency data for the 2016-2017 flow season.

4.3 Historical Patterns in Low-Frequency Nitrate Data

In addition to high-frequency in situ NO_3^- measurements made during the 2016-2017 flow season, I analyzed historical (1994-2017), low-frequency grab samples from F6. For these data, [NO_3^-] ranged from 0.11 to 19.49 µM, with a mean and standard error on the mean of 2.12±0.36 µM. All except one of the historical NO_3^- concentrations were below 10 µM. The historical samples were collected over Q conditions ranging from 0 to 313.0 L s^{-1}. For these historical data, I found a weakly negative C-Q power-law relationship ($p=0.027$, $R^2=0.066$), with a log-log slope (b) of –0.15±0.069 (Figure 10).

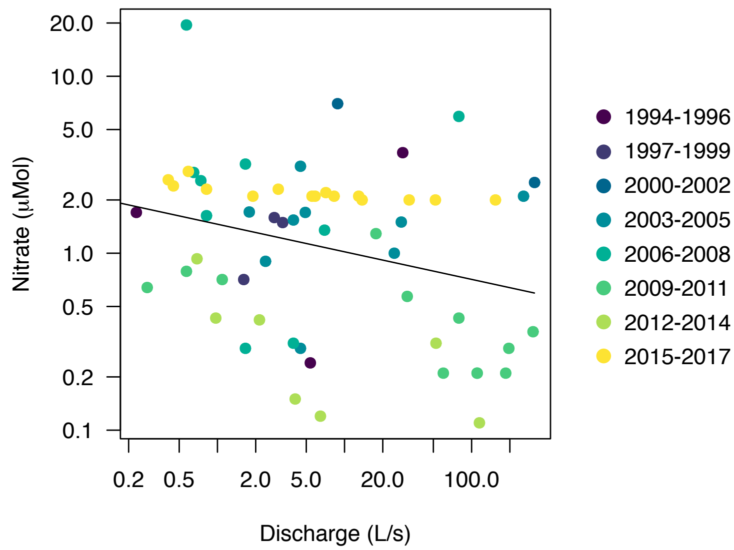

Figure 10. Historical (1994-2017), low-frequency grab sample nitrate concentration data from F6 by discharge. Weakly negative power-law relationship ($C=aQ^b$) is shown (solid line; p<0.027, R^2=0.066).

Based on apparent temporal shifting in the historical C-Q plot (Figure 10), I also examined the temporal patterns in the log-log slope parameter (*b*) for three-year periods (Figure 11). For most periods, the log-log slope was not significantly different from 0, which is indicative of chemostasis or relatively balance between transport and supply of solutes. While the log-log slope for the 1997-1999 flow seasons was markedly positive (1.16±0.33) it was not significantly different from 0 (p=0.18) due to high variance relative to sample size. The log-log slope for the 2015-2017 flow seasons was significantly less than zero (-0.049±0.0098, p<0.001), due to the low variability and higher sample size during the 2016-2017 flow season (see Table 1).

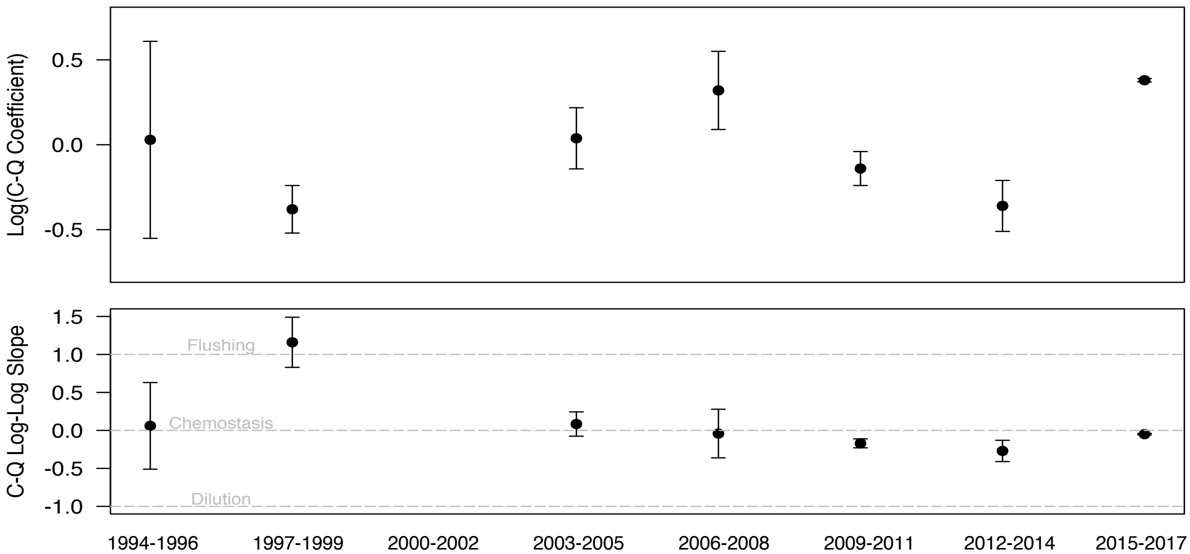

Figure 11. Concentration-discharge (top) coefficients and (bottom) log-log slopes with standard errors for power-law fits ($C=aQ^b$) from low-frequency, historical nitrate data collected at F6. Flow season is designated by the year in which flow ceases (e.g., 1994 is approximately December 1993 to February 1994). Multiple flow seasons were combined to achieve adequate sample sizes for power-law analysis.

Additionally, I analyzed historical relationships between concentrations of NO_3^- and major ions (Cl^-, Si, SO_4^{2-}), other inorganic N species (NO_2^-, NH_4^+), dissolved organic carbon, electrical conductivity, and cumulative flow metrics (seasonal cumulative and 3-day antecedent cumulative flow). Based on visual inspection, power-law relationships were fitted between these parameters and [NO_3^-]. I present the data with power-law fit lines in Figure 12 and power-law fit statistics in Table 2. Power-law coefficients (*a*) and log-log slopes (*b*) were significantly non-zero ($p<0.01$) for each relationship, except for NO_3^- to Si. However, removal of four outliers ([Si]<60 μM) resulted in a significantly positive ($p<0.01$) log-log slope and power-law coefficient. Log-log slopes were positive for all relationships except 3-day cumulative flow, which was negative.

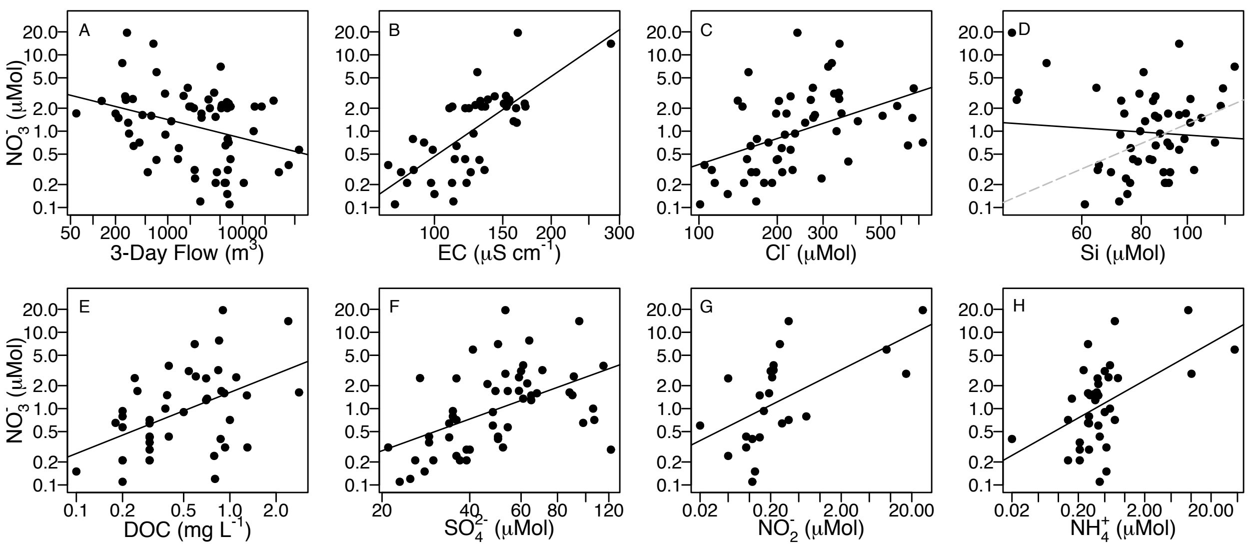

Figure 12. Historical relationships at F6 between nitrate concentration and physical and hydrochemical parameters. Fit lines represent power-law relationships. Dashed line in panel D represents Si-NO_3^- relationship with removal of 4 outliers ([Si]<60 μM).

Table 2. Power-law relationship ($C_{NO3}=aX^b$) fit values between historical, low-frequency nitrate data (C_{NO3}) and various hydrochemical and physical parameters (X). Standard error on parameter values is given in parenthesis. R^2 values are derived from the fitting of a linear model to log-transformed variables.

Parameter (X)	Power-Law Coefficient (a)	Log-Log Slope (b)	R^2
3-Day Flow (m^3)	0.89 (0.30)**	–0.26 (0.08)**	0.09
EC (μS cm^{-1})	–7.20 (1.1)***	3.50 (0.52)***	0.51
Cl^{-1} (μM)	–2.70 (0.75)***	1.10 (0.31)***	0.19
Si (μM)	0.79 (1.4)	–0.42 (0.74)	0.01
Si Adjusted†	–5.20 (1.8)**	2.70 (0.93)**	0.13
DOC (mg L^{-1})	0.21 (0.10)*	0.80 (0.23)**	0.21
SO_4^{2-} (μM)	–2.30 (0.57)***	1.40 (0.34)***	0.23
NO_2^- (μM)	0.37 (0.13)**	0.46 (0.14)**	0.32
NH_4^+ (μM)	0.22 (0.090)*	0.49 (0.14)**	0.24

*p<0.05, **p<0.01, ***p<0.001

†Si concentrations below 60 μM (N=4) removed as outliers

5. Discussion

In this study, I sought to determine how short-term (i.e. sub-hourly to daily), unsteady and intermittent flow conditions affect patterns in NO_3^- transport dynamics in a glacial meltwater stream. To accomplish this goal, I collected and analyzed high-frequency [NO_3^-] data along with discharge from two locations in Von Guerard Stream, Taylor Valley, Antarctica during the 2016-2017 Austral summer. I utilized the high-frequency data to assess C-Q relationships and identify threshold behaviors using a power-law framework. The results of this analysis informed the development of a revised conceptual model describing the temporal and spatial influence of hydrological and biological processes operating during diel flood pulsing and intermittent flow, which will inform future process-oriented investigations. To assess instrument performance and predictions of the conceptual model, I also analyzed historical low-frequency hydrochemical data collected by the MCM LTER (1997-2017).

5.1 Nitrate C-Q Patterns Under Short-Term Unsteady and Intermittent Flow

In many low order systems, dissolved inorganic nitrogen (especially NO_3^-) concentrations vary in response to short-term, unsteady discharge. Many systems showing increasing concentrations with rising Q as N is flushed from relatively enriched terrestrial or instream sources [*Heffernan and Cohen*, 2010; *Rusjan et al.*, 2008; *von Schiller et al.*, 2011]. Nitrate concentrations may also vary at sub-daily timescales due to temporally variable biotic processes under both steady [*Rusjan and Mikoš*, 2010] or unsteady flow conditions [*Halliday et al.*, 2013a; *Pellerin et al.*, 2012].

Interestingly, I found that for $Q>Q_{low}$, NO_3^- C-Q relationships were relatively chemostatic (concentration remains relatively stable compared to variations in Q such that b=0,

Figure 8) and that this pattern persisted at F6 even under large magnitude, repeated diel flood pulsing for up to 1 week. This is surprising given that meltwater from MDV glaciers is highly dilute in NO_3^- [*Fortner et al.*, 2005], marginal hillslopes are decoupled and lack subsurface waters [*Fountain et al.*, 2010; *Gooseff et al.*, 2004; *Gooseff et al.*, 2011] that may contribute to increased NO_3^- fluxes during flow events, and microbial communities in MDV streams have been shown to rapidly deplete instream NO_3^- [*Gooseff et al.*, 2004; *McKnight et al.*, 2004]. Therefore, the source of relatively large mass fluxes of NO_3^- in Von Guerard Stream at high Q is not readily apparent. Additionally, while chemostatic C-Q relationships are prevalent for non-reactive, geogenic solutes [*Godsey et al.*, 2009], N_r solutes rarely exhibit chemostasis, except for instances in agricultural catchments where a legacy of long-term fertilizer application provides a very large, spatially distributed subsurface mass of easily mobilized DIN [*Basu et al.*, 2010]. In contrast, [*Dubnick et al.*, 2017] found that [NO_3^-] scaled positively with Q in Garwood Stream (Garwood Valley, McMurdo Dry Valleys, Antarctica) during a period of dynamic but sustained flow. However, occasional flushing of a large pond at high Q likely drove this result, as the pond was relatively enriched and served as a source of NO_3^-. No such permanent pond contributes to flow in Von Guerard Stream, though zones of ponding do form and drain periodically. Even so, observed chemostasis in the both the high-frequency and low-frequency sampling at F6 during the 2016-2017 flow season suggests that there must be spatial and temporal variability in N cycling within MDV streams. By examining coupled Q and [NO_3^-] data at higher temporal resolution than was previously possible, we find there is a need to reassess and revise the complexity of our prior conceptual models of N cycling in this highly dynamic system.

For sustained flow conditions where $Q<Q_{low}$, [NO_3^-] increased as Q fell (Figure 8), thereby deviating from chemostasis. However, the magnitude of these increases was less in the

manual grab sample data (i.e., January 6, 2017; Table 1), which raises questions about the accuracy of the *in situ* sensor as well as the importance of spatial variability in NO_3^- dynamics at low flows. Also, the relative increase in $[NO_3^-]$ to a unit fall in Q decreased later in the season (b parameter was less negative). Furthermore, positive increases in $[NO_3^-]$ did not occur instantaneously for low flow conditions, but rather exhibited a lagged response whereby longer durations below the low flow threshold resulted in higher $[NO_3^-]$. This could be indicative of either direct lags in the response of processes driving increases in $[NO_3^-]$ or as a lag in the propagation of instantaneous distal responses to the sensor location relative to the propagation of hydrologic signals down the channel.

As with chemostasis above Q_{low}, potential increases in $[NO_3^-]$ below Q_{low} defy expectations based on prior studies, particularly in that MDV streams are sinks for DIN [*Dubnick et al.*, 2017; *Gooseff et al.*, 2004; *McKnight et al.*, 2004] and nutrient removal processes typically become more effective at lower flows and water velocities due to the shortening of uptake lengths [*Webster et al.*, 2003]. However, these typical expectations are supported by the data from higher flow conditions in which the reach between F21 and F6 remains a net sink for NO_3^- (Figure 7) and that smaller net removals of NO_3^- occur at higher flows, while the greatest removals occur as Q declines towards Q_{low} (Figure 8A). Yet, the deviation from these patterns below the flow threshold suggest that there is a change in the processes that control NO_3^- dynamics as a result of sustained low flows. Despite the fact that the accuracy of the high-frequency data during these low flow conditions may be called into question, the possible patterns that exist therein are indicative of the same type of spatiotemporal variability in N processing as is suggested by chemostasis at higher flows. Thus, regardless of whether we accept or remove increases in NO_3^- below Q_{low}, I still find that the conceptual model of N cycling in MDV streams must be updated to better capture spatiotemporal variability in N transformations.

Overall, these findings present two complications relative to our understanding of the hydrology and biogeochemistry of MDV stream systems. First, given the highly constrained hydrologic inputs to MDV streams, there is not a clear source from which a sufficient mass of NO_3^- could be mobilized to maintain chemostasis and high mass fluxes during large pulsing events. Second, prior research indicates that stream microbial processes in both benthic algal mats and the hyporheic zone rapidly remove and retain NO_3^- via dissimilatory processes (especially denitrification) and assimilatory uptake [e.g., *Gooseff et al.*, 2004 and *McKnight et al.*, 2004]. Thus, I would expect NO_3^- to decrease as flow decreases to Q_{low}, rather than remain relatively stable as I observed, due to increased travel times (Figure 5), which would increase opportunities for uptake along the stream. In the following section, I propose a conceptual model for the spatial and temporal dynamics of hydrological and biological processes that addresses these problems and explains observed flow-related threshold shifts in NO_3^- transport dynamics in MDV streams.

5.2 High-Frequency *In Situ* Nitrate Sensor Performance

For discharge above 1% of the seasonal maximum, the high-frequency *in situ* measurements showed a consistent positive shift relative to validation grab samples (Table 1; mean of 1.0±0.12 μM L^{-1}). Below this flow threshold, [NO_3^-] in validation samples remained low (2.1-2.9 μM L^{-1}) while high-frequency *in situ* measurements varied over a larger range of elevated concentrations (3.4-9.8 μM L^{-1}). The disagreement between validation and *in situ* sensor samples at low flows is potentially attributable to the slight difference in sampling points, as validation samples were manually collected from water flowing over the gauge control structure, whereas *in situ* sensor measurements were obtained from the pool beneath the control structure (Figure 2). As described above, the patterns in the high-frequency NO_3^- data above Q_{low} are indicative of spatiotemporal variability in N processing and NO_3^- source/sink dynamics, yet cannot indicate the scales over which variability occurs. It is, therefore, possible that differences between lotic and (relatively) lentic sampling points at low flow contribute to discrepancies in validation and sensor measurements at low flows, while under higher flow conditions ($Q>Q_{low}$) advection homogenizes NO_3^- dynamics between the sensor and grab sample locations. While the magnitude of variation at low flow conditions differs between the sensor and grab sample data, the general structure of rising concentrations throughout low flow periods with a rapid decrease upon flow re-initiation is present in both datasets (Figure 3).

The differences in probability exceedance curves between historical, low-frequency data and single-season high-frequency *in situ* measurements (Figure 4) and results from Kolmogorov-Smirnov tests indicating that the two data sets belong to different continuous $[NO_3^-]$ distributions ($p<0.001$) are also attributable to sampling from spatially distinct locations under different flow conditions as well as long-term (i.e. interannual) variation in NO_3^- dynamics (Figures 10 and 11). The *in situ* and manual measurements were taken concurrently from locations in close proximity (<2 to 5 m) such that one would expect them to be drawn from the same continuous distribution. However, my analysis demonstrates that C-Q power-law fit parameters shift at interannual timescales (Figure 11). Therefore, that the data from the distribution of concentrations occurring during the 2016-2017 flow season and their relationship to flow may not be entirely representative of those found during prior seasons. This would then result in the differences between the concentration exceedance probability curves.

Though it is possible that the *in situ* sensor is systematically biased towards detecting a narrower range of [NO_3^-] values relative to laboratory analysis of grab samples, it is unclear that this was the case as far more grab samples were collected during the 2016-2017 season, yet [NO_3^-] varied over a much smaller range than for the whole historical record. Thus, disregarding shifts in the *in situ* sensor data itself, disregarding interannual alterations to [NO_3^-] distributions would require accepting the counterintuitive premise that increasing the frequency of manual grab sampling introduced a selective bias against the detection of relatively rare low and high concentrations.

For these reasons, I have accepted the high-frequency data from periods where $Q>Q_{low}$, where there exists good agreement with the validation samples. The positive excursions in [NO_3^-] that occurred for $Q<Q_{low}$ could be accepted based on arguments of spatial variability at low flows, though this is not necessary to the central argument that such variability exists, which is supported adequately by the observations of chemostasis for $Q>Q_{low}$. Importantly, the conceptual model presented below could be derived based on data from either of those periods independently, but is also consistent if with the entire dataset.

5.3 Process Controls on Nitrate Dynamics Under Short-Term Flow Intermittency

Based on the observed high-frequency NO_3^- patterns, I propose a conceptual model (Figure 13) in which cycles of lateral expansions and contraction of the stream channel shift sediment redox conditions and microbial processes such that the shallow hyporheic zone temporally becomes a net source and storage zone for a spatially distributed pool of NO_3^-, which may be mobilized by hyporheic exchange during hydrograph rise and channel expansion. Prior nutrient injections and mesocosm studies demonstrate that denitrification occurs in the hyporheic zones of MDV streams [*Gooseff et al.*, 2004], which indicates the presence of a reduced environment in the subsurface pore spaces. However, oxygenated water fluxes occur from the channel into the shallow hyporheic zone (especially at the lateral margins) during hydrograph rise due to hydraulic pumping [*Gerecht et al.*, 2011; *Hucks Sawyer et al.*, 2009]. This influx of oxygenated water into the hyporheic zone is likely to vertically shift redox conditions, specifically by increasing the depth into the sediment beneath which denitrification may occur. Dissolved organic carbon is also transported from benthic microbial mats, the main source of organic matter, which may later be utilized during denitrification. Then, as flood recession and channel contraction proceed lateral sediments are exposed and begin to drain. Consequently, shallow sediment pore spaces become unsaturated, thereby allowing for greater oxygen penetration into the shallow subsurface. Dissimilatory denitrification among hyporheic microbes in this zone will be suppressed by these oxic conditions, though such processes may persist at greater depth due to sustained saturation and relatively less exchange with highly oxygenated channel water at depth. Additionally, net (and potentially gross) nitrification by hyporheic microbes would increase within shallow unsaturated hyporheic pore spaces. These exchange processes establish a vertical redox gradient in which the oxic zone where denitrification will be suppressed and nitrification favored expands during the hydrograph rise and initial recession. Effectively, NO_3^- will be consumed less and, potentially, generated in the shallow sediments that most rapidly exchange with channel flow. Thus, an increased mass flux of NO_3^- from the hyporheic zone will be induced by, and coincide with, highly unsteady Q at short timescales.

Additionally, low advection rates between brief periods of inundation in oxic and unsaturated sediments will provide a spatially distributed pool of temporarily stored NO_3^- that will be incrementally accessed due to channel expansion at the onset of flood events. During sustained low and zero flow conditions, draining of lateral sediments into lower-elevation pools (i.e. where sensors were located) potentially results in temporally lagged increases in [NO_3^-] (Figure 9). Increases in NO_3^- within the shallow subsurface will be reinforced by the lack of exchange with most exposed benthic microbial mats, which are the primary biological sink for NO_3^- in MDV streams [*Gooseff et al.*, 2004; *McKnight et al.*, 2004]. However, NO_3^- in water that continues to flow in the narrowed channel will remain available to a subset of benthic microbial mats, such that for locations where advection still dominates, NO_3^- concentration may not peak as it does in pools. As such, I would expect a deviation between manual grab samples on the gauge control structure and *in situ* sensor measurements within the pool below (Figure 3 and Table 1).

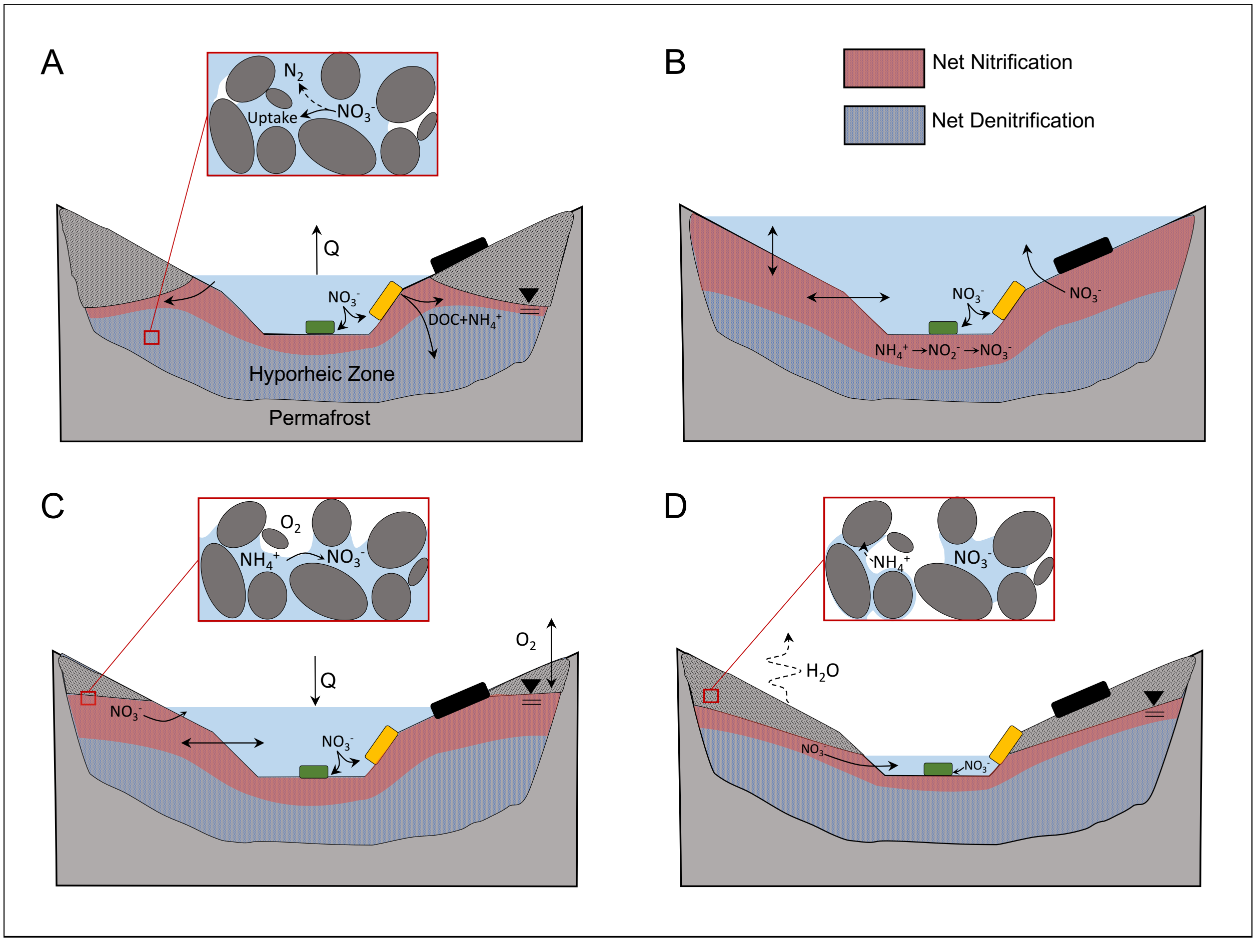

Figure 13. Revised conceptual model of nitrate (NO_3^-) transformation, storage, and mobilization under unsteady and intermittent flow in MDV streams. Shifts in vertical and lateral redox gradients and associated N transformations occur due to unsteady flow conditions. This model serves as a hypothetical revision of the prior conceptual model [Figure 2 in *Gooseff et al.*, 2004] to include the type of spatiotemporal variability and additional N processing that are necessary to maintain NO_3^- chemostasis, which was observed during highly unsteady and intermittent flows using high-frequency *in situ* sensors.

The effect of the biological processes described above on increasing [NO_3^-] in briefly inundated stream sediments is likely to be reinforced by physical processes, such as evapoconcentration due to hyper-arid atmospheric conditions. Evapoconcentration could further elevate NO_3^- (and other solute) concentrations as shallow sediments dry between flood pulses, as has been observed in pore water along the wetted margin of MDV lakes [*Barrett et al.*, 2009]. In an open pan experiment, *Gooseff et al.* [2003] found an evaporation rate of 7.1 x 10^{-5} L m^{-2} s^{-1} in the MDVs. While evaporation is unlikely to raise stream solute concentrations appreciably under moderate to high flow conditions [*Gooseff et al.*, 2002], it may be more important from standing pools and wetted sediments that may only be inundated for a few hours or less during a flow pulse event. Observations of surficial salt crusts along the wetted margin of stream channels (Figure 14) further support this expectation.

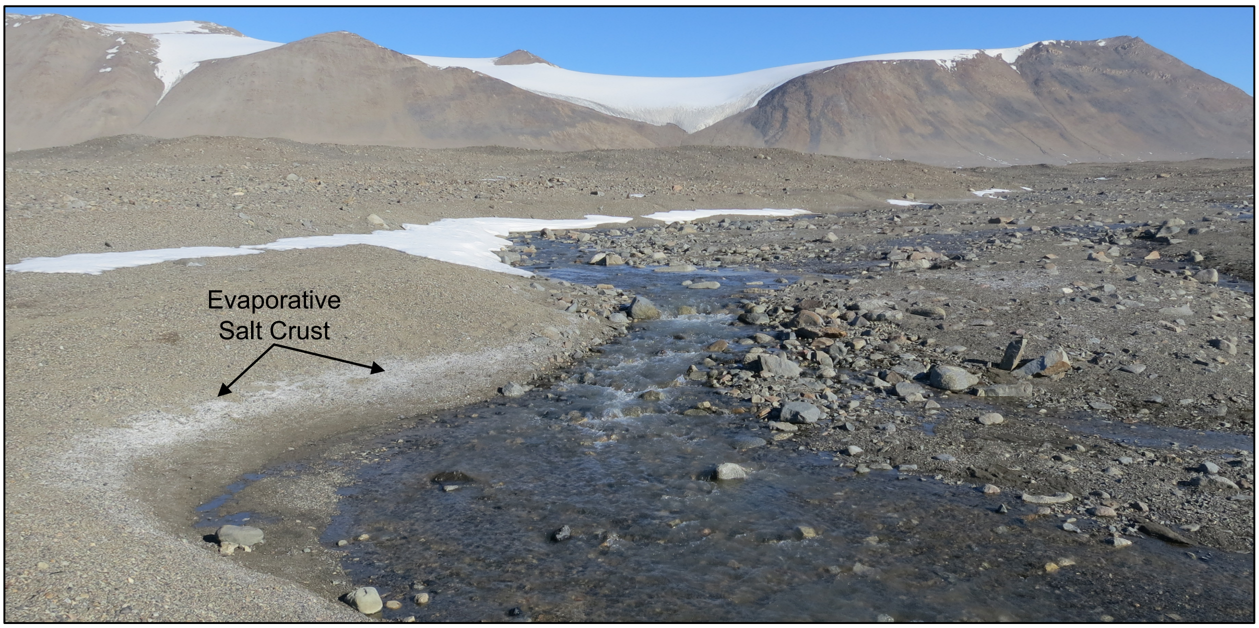

Figure 14. Surficial salt crusts along the wetted margin of Von Guerard stream.

As I would predict from this conceptual model, a negative relationship exists between three-day antecedent flow and [NO_3^-] (Figure 12A). This shows that prior low flow conditions likely play a role in enhancing the availability of NO_3^-. Furthermore, [NO_3^-] is positively related to EC, [Cl^-] and [Si] (Figure 12B-D), which are derived primarily from and indicative of exchange with the hyporheic zone [*Gooseff et al.*, 2002]. Thus, higher NO_3^- concentrations are observed as stream water interacts more with the hyporheic zone, suggesting that the hyporheic zone may temporarily act as a source of NO_3^-. The same positive relationships to these parameters would be observed if NO_3^- concentration in the shallow subsurface was driven primarily by evapoconcentration. Although the relative contribution of biological versus physical processes to the concentration of NO_3^- in the shallow subsurface cannot be determined from currently available data, it should be explored by future studies.

While prior studies [*Dubnick et al.*, 2017; *Gooseff et al.*, 2004; *McKnight et al.*, 2004] have found that the hyporheic zones and benthic microbial mats in MDV streams operate as net sinks for NO_3^- via uptake and denitrification, these finding may only partially capture the variability and range of N-dynamics in this system. Specifically, the nutrient tracer injections described by *McKnight et al.* [2004] and *Gooseff et al.* [2004] in nearby Green Creek, where conducted under fairly stable, low and moderate flow conditions (3.0-0.3 and 23.0-28.0 L s^{-1}, respectively), that, for practical reasons, did not capture the unsteady flow that characterizes MDV streams considered by my conceptual model. Given the relatively stable flow conditions during both injections, it is possible that hydraulic pumping would not suppress denitrification as significantly as I describe above. Green Creek also has a lower gradient (0.037 m m^{-1}) [*Wlostowski et al.*, 2016] relative to Von Guerard Stream (0.078 m m-1), which may reduce turbulent reaeration, further reducing the flux of oxic waters into the shallow subsurface by hydraulic pumping. Similarly, a mesocosm study on net nitrate removal and denitrification potential for benthic mats and sediment [*Gooseff et al.*, 2004] may not have provided for representative turbulent mixing or oxygenation, the latter due to the sparging of vials with N_2 for the acetylene block technique. These conditions may result in an overestimation of the degree to which dissimilatory reduction and denitrification removes NO_3^- under unsteady and intermittent diel flow conditions, as were present throughout my study period. The conceptual model I propose does not refute the results or interpretation of prior studies – in fact they are included in the conceptual model – but rather suggests that processes controlling NO_3^- transport may be much more dynamic in MDV streams and that the shallow hyporheic zone may variously operate as both a net source or sink of NO_3^- over time and flow conditions.

The conceptual model that I have presented is based on both inferences of processes from observed patterns (i.e., the need for spatiotemporal variability in N transformation processes and possible instream sourcing of NO_3^- to maintain chemostasis) and findings from other systems (i.e., vertical redox gradient, hydraulic pumping, and amplification of nitrification) in which sediments undergo periodic inundation and draining at longer timescales. In seasonally intermittent Mediterranean streams, drying of surface sediments led to increases in ammonia oxidation activity and elevated sediment NO_3^- content [*Arce et al.*, 2014; *Merbt et al.*, 2016] in temporally and spatially heterogeneous patterns due to the reduction or loss of advective transport [*Bernal et al.*, 2013; *Gómez et al.*, 2009; *von Schiller et al.*, 2011]. Instream nutrient processing becomes more important due to reduced terrestrial connectivity during low flow conditions, but also changes directionality as denitrification is suppressed in lateral and high salinity zones [*Arce et al.*, 2013; *Bernal et al.*, 2013] and nutrient retention efficiency (i.e., assimilatory and permanent removal processes) decline [*von Schiller et al.*, 2008]. The response of instream microbial processes to low flow may contribute to temporary accumulation of more than half of the mass of N_r, primarily in the form of NO_3^-, that is rapidly flushed from shallow sediments upon the re-initiation of flow [*Arce et al.*, 2014; *Merbt et al.*, 2016; *von Schiller et al.*, 2011]. Thus, the general patterns in NO_3^- dynamics described in my conceptual model are well documented at longer timescales in ephemeral and intermittent Mediterranean streams.

Desert streams provide another potential analog due to the occurrence of rapid pulse events (i.e., flash floods) and sandy, loosely consolidated sediments that episodically experience drying-rewetting cycles and are limited in NO_3^- [*Fisher et al.*, 1982; *Grimm and Fisher*, 1986;

Valett et al., 1990]. Such streams offer prime examples of biogeochemical hotspots and hot moments for nitrification and denitrification due to the variable interaction of flowpaths and surfaces which are alternately enriched and depleted in reactive substrates [*McClain et al.*, 2003]. Nitrification in desert streams is highest in areas of down-welling and increases by approximately 10-fold during flood recession, resulting in larger mass fluxes of NO_3^- [*Jones et al.*, 1995]. As with Mediterranean streams, NO_3^- retention efficiency may also decline briefly in response to flood events, though microbial communities and retentive processes rapidly recover [*Martí et al.*, 1997]. Again, these observations agree with the dynamics that I present as controls on NO_3^- under diel flood pulsing in MDV streams.

Similarly, relative increases in nitrifier biomass and nitrification potential are also observed in soils that are subjected to frequent wetting-drying cycles, especially where rewetting induces a net release of NH_4^+ previously sorbed to sediment particles [*Fierer and Schimel*, 2002]. In the same study, *Fierer and Schimel* [2002] also found that C mineralization and the release of CO_2 upon rewetting increased with the frequency of drying-rewetting events (up to once every 4 d). Stream biofilms showed similar shifts in the coupling of C and N processes, with reductions in autotrophic activity while heterotrophic processes were maintained during dry periods [*Sabater et al.*, 2016], signaling a potential shift in the overall metabolism of streams towards heterotrophy under increasingly frequent short-term intermittency.

It is worth noting that these examples do not demonstrate that such processes can occur at much shorter timescales (i.e., sub-hourly to daily). However, pore water samples along vertical and lateral transects in the sediment and riparian aquifer of an incised tidal stream (White Clay Creek, Delaware) shows the same expansions and contractions of redox gradients, shallow suppression of denitrification, and vertical hydrochemical patterns in sediments due to tidal pulsing on 12-hr cycles [R. Barnes, *personal communication/in preparation*]. Thus, it is not unreasonable to expect that MDV stream microbial communities, which can shift between active and dormant states rapidly [*McKnight et al.*, 2007], could respond similarly to 24-hr cycles of inundation and draining. Taken alongside the aforementioned studies on N-cycling during intermittency in desert and Mediterranean streams, these results suggest that spatial and temporal variations in redox conditions due to cyclic drying and rewetting of sediments, especially via unsteady discharge, is likely to govern the coupling of C and N cycles, as well as the preferential mobilization of NO_3^- across a wide range of environments and timescales.

While the particular details of the revised and expanded conceptual model that I have proposed above provide an explanatory framework for observed NO_3^- chemostasis that is consistent with findings from other studies, I must emphasize that this model is largely based on inferences from high frequency NO_3^- data, which was previously unavailable. However, the patterns observed at these finer temporal resolutions strongly suggest that such revisions are necessary in models of N cycling within MDV streams. Thus, the proposed model depicts and provides a framework for designing future studies on testable spatiotemporal patterns in N cycling and NO_3^- availability that my observations indicate likely exist.

5.4 Future Research and Broader Considerations

The conceptual model I propose above offers a number of hypotheses that may be tested in order to better constrain the role of short-term, unsteady and intermittent flow on NO_3^- transport dynamics. Specifically, there is a need to better constrain the response of gross rates of various N transformations (i.e., denitrification, nitrification, mineralization, and assimilatory uptake) to various hydrologic conditions across benthic bacterial mat types and sediment microbes. *Gooseff et al.* [2004] approximated net transformation rates and denitrification potential across these groups, but did not consider gross rates, their response to drying-wetting cycles, or spatial heterogeneity. Under my conceptual model, I expect that gross nitrification and denitrification in MDV microbial communities, especially shallow hyporheic sediments, are variably suppressed and amplified during channel expansion and contraction. I also hypothesize that [NO_3^-] in hyporheic pore water is greatest in the shallow subsurface and decreases with depth due to increasing net denitrification. I expect that the depth of NO_3^- enrichment increases at peak Q and the onset of flood recession as denitrification is suppressed along a vertical redox gradient. These hypotheses are all readily testable and would inform assessment of the conceptual model I have proposed above.

Evaluating these hypotheses would be useful both for deepening understanding of the biogeochemistry of MDV streams as well as a range of systems in which similar short-term, unsteady and intermittent flow conditions occur. Such systems likely include low order streams in arid, semi-arid, and Mediterranean climates subject to flash flooding following intense precipitation events; gravel bed rivers in which shifting channel braids rather than flow cessation variably inundates and dries sediments; and urban streams. The latter connection may appear counterintuitive; however, MDV streams are arguably reminiscent of small urban streams affected by Urban Stream Syndrome insofar as they are both hydrologically flashy and intermittent, have relatively depressed or no terrestrial processing or retention of non-conservative constituents, and experience highly dynamic mass fluxes of biogeochemically important solutes due to short-term, unsteady flow [*Walsh et al.*, 2005]. Further developing and synthesizing our understanding of how coupled instream nutrient processing, retention, and transport dynamics respond to increasing unsteady and intermittent flow across such a range of systems represents a broadly relevant challenge.

6. Conclusions

In this study, I present and analyze high-frequency NO_3^- concentration data from an ephemeral Antarctic glacial meltwater stream that experiences diel meltwater pulse events and is largely decoupled from hillslope and groundwater interactions. I demonstrate that short-term unsteady and intermittent flow conditions result in threshold dependent shifts in concentration-discharge relationships due to instream processes. For flows ranging from 3 to nearly 300 L s^{-1}, NO_3^- behaved chemostatically. In contrast, NO_3^- concentrations may have increased throughout sustained low flow periods, though questions remain about the magnitude of these positive excursions. While the study reach remained a net sink for NO_3^-, net removal varied non-linearly with discharge, with the least removal occurring under the highest flows and water velocities. Low-frequency, long-term data revealed that concentration discharge relationships in MDV streams shift at interannual timescales, but are generally closer to chemostasis than simple dilution. Historically, NO_3^- concentrations were negatively related to 3-day antecedent flow and positively related to the concentrations of solutes derived primarily from the hyporheic zone.

Taken together, these observations across timescales complicate prior understanding of MDV streams insofar as benthic and hyporheic microbial communities have been shown to act as net sinks for NO_3^- and there is no recognized source of NO_3^- that would maintain chemostasis during large influxes of dilute glacial meltwater. To explain the observed patterns and resolve these complications, I propose a conceptual model in which redox conditions within the hyporheic zone shift in response to inundation and draining during diel meltwater pulse events. In agreement with prior studies of seasonally intermittent streams, I infer that the vertical distribution of net NO_3^- source and sink areas within the hyporheic zone shift due to unsteady discharge, but infer from the observed patterns that these dynamics occur at very short timescales (i.e., sub-hourly to daily). Such spatiotemporal variability in N cycling has not been integrated into prior conceptual models of N cycling in MDV streams, but is necessary given the patterns I detected in finer resolution [NO_3^-] data. This conceptual model provides a testable framework for assessing spatiotemporal variability in N cycling in MDV streams. This can be accomplished by measuring hyporheic pore water hydrochemistry along vertical and lateral transects at various stages throughout a flow pulse event and directly measure the effect of periodic drying-rewetting on gross N transformation rates in benthic algal mats and hyporheic sediments.

Overall, these observations highlight the potential for measuring water quality parameters (i.e., concentrations of N forms) at temporal scales that match short-term hydrologic variability to provide additional insight into linked hydrological and biogeochemical processes within streams. The observed patterns in NO_3^- transport and resulting revisions to our conceptual model reinforce the importance of low-order streams as vectors and modulators of N_r transport to downgradient systems, especially under unsteady flow conditions. Understanding the response of instream N retention and transport processes under increasing flow intermittency due to climate change, land cover alteration, and water resource management across a variety of systems remains an important challenge to mitigating the impact of human activities on the global N cycle. My findings underscore the importance of investigating nutrient transport dynamics and related instream process-based controls on short timescales (i.e., sub-hourly to daily) that reflect the rates of hydrologic variability in intermittent low-order streams.

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