DISSERTATION

GREENHOUSE GASES IN ARCTIC AND ALPINE STREAMS:

PATTERNS, DRIVERS, AND RESPONSES TO DISTURBANCE

Submitted by

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ABSTRACT

GREENHOUSE GASES IN ARCTIC AND ALPINE STREAMS:

PATTERNS, DRIVERS, AND RESPONSES TO DISTURBANCE

Streams have recently received attention as previously unaccounted for sources of greenhouse gases (GHG; CH_4, CO_2, and N_2O) to the atmosphere. While progress has been made at incorporating streams into global estimates of GHG flux, many spatial gaps remain, especially in remote regions of the Siberian Arctic and high elevation ecosystems worldwide. To address a critical gap in regional estimates of emissions and better understand the sources of variability of those emissions, we quantified the vertical flux of CH_4, N_2O, and CO_2 and examined the sources of variability and spatial-temporal patterns of those fluxes in Siberian streams and high elevation streams. Emissions to the atmosphere from Siberian streams were smaller than expected with mean fluxes of CH_4 (12.4 µmol CH_4 m^{-2} d^{-1}) and CO_2 (2.6 mmol m^{-2} d^{-1}). In contrast, downstream export of dissolved gas is three orders of magnitude larger than emissions to the atmosphere and the fate of this dissolved gas is ultimately unknown. Water column transit time, dissolved oxygen concentration, and specific conductivity explained the majority of variability in the emissions of both gases, but variability in CO_2 emission was equally influenced by biological and physical processes whereas variability in CH_4 emission is mainly influenced by biological variability. High elevation streams were, on average, net sources of CH_4, CO_2, and N_2O to the atmosphere over the course of the observations period. However, instances of net uptake of these gases from the atmosphere by streams were also recorded during this time. Variability in mountainous gas emissions is strongly influenced by variability in the concentration gradient and less so by the reaeration coefficient. However, some site characteristics, namely elevation and silt fraction of sediments, were also contributing factors to

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overall emission variability. We observed a concurrent increase in N_2O emission and stream dissolved organic carbon (DOC) during an algae bloom in an upstream lake which explained a large part of the seasonal variability and average emission rate. Stream sediments from these contrasting sites, some of which were adjacent to other aquatic systems, showed a range of responses to alterations of their chemical environment not unlike what occurred during the algal bloom. From these data we were able to observe that enhanced N_2O production was only possible under aerobic conditions, suggesting that inefficient nitrification, as opposed to enhanced denitrification, was the source of the increase in N_2O emissions.

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INTRODUCTION

Streams are ubiquitous landscape features that are integrators of the physical, chemical and biological activity within the catchments they drain [*Lovett et al.*, 2005]. Globally, streams often occupy three percent of the land surface of any given ecosystem, but are disproportionately active parts of the landscape with regards to their biogeochemistry [*Cole et al.*, 2007]. Streams are active producers, transporters, and transformers of their solute load and are critical components in many human disturbed and natural systems both as a source of drinking water and as sites for biogeochemical activity [*Fisher et al.*, 1998]. The relative contribution of the constituent parts of a stream to its overall biogeochemistry is difficult to parse, and varies widely across space and time with stream sediments [*Lansdown et al.*, 2015; *Shelley et al.*, 2015], biofilms [*Battin et al.*, 2016; *Freixa*, 2016], and interaction with the surrounding terrestrial ecosystem [*Fahey et al.*, 2005; *Burrows et al.*, 2013] all being contributing factors.

Stream ecology has long been concerned with the interaction between nutrient cycling and the hydrologic cycle [*Bormann and Likens*, 1967]. The river continuum concept, [*Vannote et al.*, 1980], framed the questions pursued in the last few decades by emphasizing the connection between the physicality of the water's flow and the potential biology possible, as well as the reliance of downstream biological communities on the export of materials from upstream. Nutrient spiraling [*Newbold et al.*, 1981; *Fisher et al.*, 1998] and the importance of flow regimes [*Poff and Zimmerman*, 2010] for stream biology are borne directly from Vannote's work and together have provided a rich literature detailing the importance and variability of streams worldwide. This conceptual framework continues to carry the field forward as more biogeochemical cycles, and specific mechanisms are described.

Stream ecosystems are under pressure from the effects of climate change worldwide [*Yamashita et al.*, 2011; *Lawrence et al.,* 2014]. This pressure is felt by streams both directly through warmer water temperatures and indirectly through shifting hydrological and biogeochemical regimes. Indirect effects on the surrounding terrestrial landscape are integrated by the streams that drain them and often have synergistic effects through changes to allochthonous loading of the stream [*Spencer et al.*, 2015] and the impacts of altered hydrology, both in magnitude and timing, and on in-stream communities [*Hood et al.*, 2006]. The most direct effect of warmer temperatures is faster processing of materials by microbes across entire watersheds, the long term impacts of which are still largely unknown. It is plausible that this warming and subsequent acceleration of microbial metabolic rates could have both positive outcomes, in the form of greater excess NO_3^- removal, and negative outcomes, in the form of increased greenhouse gas emissions.

Direct anthropogenic effects, namely N loading to streams, compound the effects of warmer water and more variable hydrology on stream biogeochemistry by alleviating the need for one or more limiting macronutrients [*Dodds and Smith*, 2016]. In many agricultural systems, N loading is partially offset by denitrification *[Beaulieu et al>*, 2011a], but in N or C poor systems such as high elevation ecosystems, this may not be the case [*Mast et al.*, 2014].

Greenhouse gases produced, consumed, and transported by streams are increasingly recognized as important components of C and N cycles [*Butman and Raymond*, 2011; *Stanley et al.*, 2015]. Emissions of trace gases to the atmosphere from a stream surface are a product of the streams ability to produce gas and the turbulence with which it flows. Chronic and acute disturbances in streams modify both the physical and biological components of gas emission and can significantly interact to modify overall emissions. Streams also export a large portion of their dissolved gas load downstream and the fate of it is still unknown for most ecosystems [*Kokic et al.*, 2014].

Cold biomes, such as the alpine and arctic, are experiencing greater relative changes to a host of their properties as a result of human activities than warmer temperate systems [*Frey et al.*, 2007; *Baron et al.*, 2009]. These changes in energy input and consequently warmer stream temperatures induce further changes in both the physical and biological behavior of streams and their resident microbes. Temperature effects on the terrestrial landscape also contribute to the streams that drain it and further alter their behavior both through alterations of the magnitude and quality of allochthonous input as well as the hydrology [*Bardgett et al.*, 2008]. Streams flowing through arctic and alpine systems contrast in the importance of physical and biological processes for driving gas emissions and represent extreme ends of the spectrum between the two. Arctic streams are heavily influenced by biological loading of gas into the water column [*Campeau et al.*, 2014]. Streams are therefore able to build and maintain high concentrations of dissolved gas. Alpine streams, in contrast, are heavily influenced by the physical reaeration of the water surface [*Crawford et al.*, 2014]. Alpine streams turnover their dissolved gas load quickly due to a great deal of interaction with the atmosphere.

In this dissertation I quantify the magnitude and sources of variability to greenhouse gas emissions from arctic and alpine streams experiencing both acute and chronic disturbances. I additionally determine the potential response of stream sediment microbes to possible biogeochemical disturbances in order to parse out the roles of different stream components for the overall behavior.

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CHAPTER 1

INTRODUCTION

Streams are common landscape features of the Arctic, but are relatively understudied compared to lakes due to their small size, remote location, and the associated difficulty of observing them with remotely sensed data [*Arp et al.*, 2015]. Arctic streams can have a beaded morphology due to the presence of permafrost [*Arp et al.*, 2015] and these do not behave in the same way as streams in temperate zones due to their steep banks and pool-run sequence [*Crawford and Stanley*, 2014]. Quickening or slowing flow rates have the ability to enhance or diminish fluxes of gases to the atmosphere independently of the dissolved gas concentration by respectively decreasing or increasing the residence time of water within a given length of stream and the degree of flow turbulence. The flow regime of Arctic streams, and their ability to transport and transform permafrost carbon [*Yi et al.*, 2015], will be impacted by the effects of climate change on the precipitation dynamics of the Arctic.

Stream systems, comprised of both the flowing water and the underlying sediments, produce, consume, and transport dissolved gases and solutes as they flow through a landscape and can process a significant portion of their solute load [*Hall et al.*, 2015]. Lower order Siberian stream systems degrade carbon leached into them from permafrost meltwater and the overlying organic active layer [*Spencer et al.*, 2015] and some fraction of this degraded carbon is converted directly to CO_2 or even CH_4, while much of the remaining fraction is susceptible to further metabolic breakdown by stream microbes [*Vonk et al.*, 2015]. Streams themselves also carry dissolved gases produced in the pore waters of their sediments or in adjacent riparian zones. Recent work suggests that these dissolved gases may be important sources of C to the local stream foodweb [*Shelley et al.*, 2015] and that the internal processing of dissolved gases by stream microbes is an unstudied, but potentially important, controlling factor of overall gas

flux in systems across the planet. Heterogeneity in stream slope, topography, and complexity impacts both the biological production and consumption of dissolved gas as well as the physical diffusion of these dissolved gases to the atmosphere, which combined represent the major sources of variability to the overall variability in flux magnitudes.

A recent synthesis by [*Stanley et al.*, 2015] implicates stream ecosystems as an important, highly variable, yet previously un-budgeted source of CH_4 to the atmosphere despite their relatively small share of the landscape. Lakes and wetlands have long been considered the primary aquatic ecosystems responsible for CH_4 emissions to the atmosphere [*Zhu et al.*, 2013], but in some cases, Arctic streams have been found to have gas fluxes comparable in magnitude to lakes on an areal basis [*Lundin et al.*, 2013]. The highly variable nature of trace gas fluxes from stream surfaces to the atmosphere from Arctic streams, and especially from streams across the globe, poses interesting questions about what specifically is driving this variability. Relatively high reaeration coefficients in streams and rivers, compared to standing water, enhances flux rates of gases from streams to the atmosphere [*Raymond and Cole*, 2001; *Tranvik et al.*, 2009]. Additionally, the low surface area to volume ratio of headwater streams allows for the rapid development of positive concentration gradients of dissolved gas between the surface and the atmosphere [*Kokic and Wallin*, 2014]. However, headwater streams are more likely to experience a broader range of dissolved O_2 availability that can in turn enhance or suppress certain biogeochemical reactions, further moderating or enhancing the magnitude of emissions. A paucity of observations of stream gas fluxes in Siberia, an area known for strong lake CH_4 fluxes [*Zimov et al.*, 1997], contributes uncertainty to the understanding of the role of streams in the global C cycle.

In this study, we quantified the downstream and atmospheric flux of CH_4 and CO_2 in 8 small stream reaches within a single watershed near the Siberian town of Cherskiy. We additionally examined the sources of variability in the fluxes of these gases as well as the

sources of variability in factors contributing to gas flux. Finally, we examined spatial and temporal relationships between physical stream parameters and proxies for biological activity to examine variability in the observed fluxes of these gases. We expected that emissions of these gases to the atmosphere would be on par with that per area emissions from nearby lakes and that variability of emission rates would be due to variability in the amount of dissolved gas present.

METHODS

SITE DESCRIPTION

"Y3" is a small watershed near the North East Science Station, in Cherskiy, Russia with an area of 16.8 km^2. It is underlain by continuous permafrost, has been the focus of a number of previously studied thermokarst lakes [*Zimov et al.*, 1997; *Walter et al.*, 2006], and is described in detail by a number of other works [*Zimov et al.*, 1997; *Spawn et al.*, 2015; *Spencer et al.*, 2015]. The watershed lies along the transition between boreal forest and tundra with streams occupying 0.8% (134,000 m^2) and lakes 1.2% (202,000 m^2) of the surface area in this watershed. First order streams were not consistently flowing during the sampling time and were excluded, so sample sites varied from 2nd to 4th order. At all sample sites, thermal erosion left the streams moderately (~1m) to deeply (>3m) incised with respect to the surrounding terrestrial landscape. Y3 streams are predominantly fed by snowmelt and exhibit a pronounced seasonal pattern with a sudden increase during peak snowmelt, the "freshet", followed by a long tapering off of discharge until a baseflow is reached.

STREAM CHARACTERISTICS

We established nine, 20m sample reaches and re-sampled them weekly over the course of three weeks during July and August of 2014. Specific conductivity (µS cm^{-1}), temperature, and dissolved O$_2$ (% saturation) were collected using YSI multiprobes at either end of the

sample reach and were calibrated for dissolved O_2 each field day. A salt slug addition [*Wallin et al.*, 2011] was performed at each reach during every visit to determine the transit time (τ) and mean velocity of water in the stream. Stream widths, depths, and active layer thaw depth below the stream were measured manually at each sampling event. At several site visits (n=6), we observed irregular up and downstream conductivity after the addition of salt and concluded that the added salt was being poorly mixed, thus leading to unreliable data for transit time. We omitted all flux data and reaeration coefficients from these particular site visits, but present dissolved gas chemistry data.

GAS COLLECTION METHODS

Dissolved gas samples were collected in triplicate using a headspace equilibration method. Thirty milliliters of stream water were collected from approximately the center of the stream, 5cm below the surface. These bubble-free samples were equilibrated with 30 mL of air in a 60mL syringe by vigorously shaking for 30s. The equilibrated headspace air was then transferred to field evacuated 20mL vials for storage until analysis. Air samples were collected immediately above the water surface prior to sampling the dissolved concentration, and stored in the same manner. At the time of air sample collection, we also stored standards of known CO_2 and CH_4 concentrations in vials following the same procedures as our environmental samples to evaluate for bias in gas storage and analysis. All samples along with check standards were transported to Colorado State University for analysis on a Los Gatos Research UGGA CH_4, CO_2 analyzer modified to receive injection samples. Dissolved gas concentrations were calculated using Henry's law following [*Stumm and Morgan*, 1995].

Additions of butane (commercially sold in Russia as "camping gas") were used to determine the reaeration coefficient (k_{gas}) following [*Wallin et al.*, 2011]. Butane was sparged approximately 3m upstream from the upstream collection point through a submerged set of aquarium air stones. Butane was added to the stream for a period of time roughly equivalent to

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the stream transit time (τ) derived from the salt slug additions. Upstream samples were collected every 3 minutes (n=3) beginning five minutes after the butane addition started. The downstream end of the reach was sampled (n=3) after 1 transit time (τ) had elapsed from the beginning of Butane sampling upstream in order to sample the same packet of water after it had traversed the sample reach. Dissolved Butane samples and appropriate check standards were transported back to the USGS laboratory in Boulder, CO for quantification on a Shimadzu GC-14B equipped with a Porapak-Q column under N_2 carrier gas using a FID detector.

CALCULATIONS

The reaeration coefficient (K_{Butane}) was calculated from tracer gas additions following [*Genereux and Hemond*, 1992] (Equation 1) and then corrected for temperature effects on each gas and converted to K_{CH4} and K_{CO2} using the appropriate Schmidt number [*Raymond et al.*, 2012] (Equation 2). Briefly, a solute and gas tracer were released into the stream and quantified at up and down stream ends. We corrected for any loss of gas tracer in Equation 1 by multiplying the up and downstream tracer concentrations by the solute tracer concentration with any other loss of tracer therefore due to evasion to the atmosphere. We assumed a value of -0.5 for n in equation 2 following [*Wanninkhof et al.*, 1990].

(1) $k_{Butane} = \frac{1}{\tau} * \left(\frac{[Butane]_{Up} * Salt_{Up}}{[Butane]_{Down} * Salt_{Down}} \right)$

(2) $k_{Gas} = \left(\frac{Sc_{Gas}}{Sc_{Butane}} \right)^{-n}$

(3) $F_{Gas} = K_{Gas} * ([Gas]_{Atm} - [Gas]_{Diss})$

We normalized the k_{Gas}(min^{-1}) to K_{Gas} (m min^{-1}) by multiplying by the mean depth at time of collection prior to calculating fluxes [*Raymond et al.*, 2012]. For calculations we used the appropriate K_{gas} value as described above, but we report K_{600} values in (Table 1) calculated by

assuming a Schmidt number of 600 and using equation 2 for the purposes of comparison with other studies.

Fluxes of CH_4 and CO_2 (mol Gas m^{-2} min^{-1}) were calculated using Equation 3. Gas fluxes were converted from per-minute fluxes to daily fluxes and are reported as such in (Table 1). We assume a 120-day open water season when making scaled up estimates of total watershed flux.

ANALYSES

Basic calculations were performed in MS Excel 2013 and then exported to R (3.2.3) for analysis. Partial R^2 values were determined from package {stats} (version 3.2.3).

DATA QUALITY

Our dataset includes observations from eight study reaches, sampled one to three times for a total of 17 reach-observations (summarized in Table 1). We successfully used a gas and solute tracer to quantify fluxes from the stream surface to the atmosphere in in five of our eight sites for a total of 14 observations. Overall, we found evidence of good data quality and behavior of the stream system with respect to discharge and other characteristics. We found little evidence of water gain over the length of individual experimental reaches based on changes in specific conductivity under ambient (i.e., not during salt slug) conditions between upstream and downstream sample points; mean percent change in specific conductivity (μS cm^{-1}) was 0.09% ± 1.8% (SD, n=17) and not statistically significant (paired t-test, n=34).There was a statistically significant decrease in butane tracer concentration (paired t-test, p<0.001, n=51) within all reach observations that averaged -28% ± 18% (SD, n=51) providing robust data from which to calculate the reaeration coefficients and flux rates for CO_2 and CH_4. We corrected for the storage of our tracer gas by quantifying the proportion of our solute tracer lost into the deep thaw pools during a release following [*Wallin et al.*, 2011].

RESULTS

MAGNITUDE OF FLUXES

All streams were sources of CH_4 and CO_2 to the atmosphere (Table 1). The watershed

means of these emissions were 12.4 (3.9) µmol CH_4 m^2 d^{-1} and 2.6 (0.7) mmol CO_2 m^2 d^{-1} (1

SE, n=17) respectively. Emission magnitudes varied greatly by stream reach with reach-specific

means ranging from 0.5-47.0 µmol CH_4 m^2 d^{-1} and 0.4-6.7 mmol CO_2 m^2 d^{-1}. When averaged

across the stream network area, Siberian streams contribute 1.7mol CH_4 and 348 mol CO_2,

respectively, to the atmosphere per day.

Siberian streams on average export downstream a significant amount (7.2 mmol CH_4 d^{-1},

and 1.5 mol CO_2 d^{-1}) of their dissolved gas load, but the ultimate fate of this is gas, emission to

the atmosphere, consumption in the stream, or further export, remains unknown (Table 1). The

downstream export of dissolved gas is on the order of 10^5 greater than vertical flux to the

atmosphere making downstream export the primary avenue for trace gases leaving this system

(Table 1).

CONTROLS OF FLUX VARIABILITY

We found that spatial and temporal variability in emissions of CH_4 to the atmosphere at

the watershed level can mostly be explained by variability in the concentration of dissolved CH_4

(Figure 1a). However, variability in the export of dissolved CH_4 downstream is primarily due to

variability in discharge (Q) and variation in the dissolved CH_4 is not statistically significant

(Figure 2a). At a deeper mechanistic level, we found that variability in the concentration of

dissolved CH_4 is best explained by the variability of dissolved O_2, the interaction between

dissolved O_2 and dissolved CO_2, and the specific conductivity of the stream (Figures 1,2 c).

In contrast to CH_4, we found that the variability in CO_2 fluxes both to the atmosphere and

downstream were explained by primarily by physical features of the streams flow and only

secondarily by the amount of dissolved CO_2 present. (Figures 1,2 d). We examined a series of

factors that could contribute to the variability in dissolved CO_2 and found that the it was best explained by variability in dissolved O_2 and dissolved CH_4 but not the interaction between dissolved O_2 and CH_4 (Figure 1f). The importance of dissolved CH_4 for explaining dissolved CO_2 is potentially due to a number of different, but not mutually exclusive, factors.

For the emission of both gases to the atmosphere, we examined the sources of variability to the reaeration coefficient by determining the relative contribution of all the components of Equation 2. Variability in the reaeration coefficient was primarily due to variation in the stream's transit time at time of sampling and the temperature and depth of the stream (Figure 1 b,e), but not stream discharge. Discharge and transit time are intrinsically linked and exhibit a hyperbolic relationship over the course of the season with lower discharge resulting in increasingly longer transit times. We observed a decrease in stream velocity and discharge that coincided with an increase in the specific conductivity and τ over the course of the season. Dissolved CH_4 and CO_2 concentrations, however, did not significantly change with increasing transit time and were on average 0.80 ± 0.72 (1SD, n=102) μM and (150 ± 68) μM respectively. We examined the sources of variability to discharge to better explain the physical parameters involved in the downstream export of dissolved gas and found that variability in depth, site, and velocity best explained variability in the overall discharge. These factors are dynamic over space and time, and as we observed changes in discharge and stream chemistry over the sampling period as we approached baseflow these factors co-varied.

SPATIAL AND TEMPORAL PATTERNS

Within-reach variability in dissolved gases and chemistry offers insight into the spatial distribution of gas production and consumption. We consistently observed a decreasing trend in dissolved CH_4 within sample reaches (Figure 4), but not for dissolved CO_2 or specific conductivity. When aggregated to the watershed level there was a mean decrease in dissolved CH_4 of around 17% (linear regression, $R_{adj}^2=0.81$, Figure 4b) over the ca. 20m reaches where

we made our observations. We observed a log-linear relationship between CH_4 supersaturation and O_2 subsaturation in these streams (Figure 3b) such that as O_2 concentrations rose toward saturation, the degree of CH_4 supersaturation decreases and the residuals for the linear model fit increased (Figure 3d), suggesting O_2 sensitivity as a factor in CH_4 abundance.

DISCUSSION

The emissions of CH_4 and CO_2 observed in this study were smaller than other Arctic and sub-Arctic studies in Alaska and Canada despite having similar dissolved gas concentrations. In their 2012 survey of the Nome creek catchment in Alaska [*Crawford et al.*, 2013] observed mean CO_2 flux rates of 0.45 mol m^2 d^{-1} and CH_4 flux rates of 0.63 mmol m^{-2} d^{-1}, however, additional work in sub-Arctic Quebec done by [*Campeau and Del Giorgio*, 2013] found even high median rates of CH_4 and CO_2 flux to the atmosphere (804 mmol CH_4 m^{-2} d^{-1} and 22 mol CO_2 m^{-2} d^{-1}). The disparity in emission rates across the Arctic is, like the emission rate itself, a function of the physical features of the stream and the concentration gradient between the stream and the atmosphere.

The majority of dissolved gases in Siberian streams were exported downstream as opposed to emitted to the atmosphere. The fate of these dissolved gases is unknown, but potential fates include later emission, consumption, or continued export. The consumption or storage of dissolved trace gases has been demonstrated in a number of systems worldwide [*Shelley et al.*, 2015; *Trimmer et al.*, 2015] and is thought to be a major, yet poorly understood process. We occasionally observed a decrease of dissolved CH_4 concentration over short distances where specific conductivity measures showed no sign of dilution, but never any net decrease in CO_2 in the same setting (Figure 4). The apparent decrease in dissolved CH_4 cannot be explained solely by emission to the atmosphere, so this suggests that these gases are being selectively consumed within the stream as opposed to being stored. We did not observe a

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relationship between stream landscape position and dissolved gas load (accumulation in higher order streams) for either CO_2 or CH_4, suggesting that CH_4 consumption is a spatially isolated process in these streams. Consumption of dissolved CH_4 by microbes in stream networks is an important but not easily observed feature of these stream systems since headwater streams tend to be disproportionately strong emitters of gas to the atmosphere and any reduction in the magnitude of gas emission lessens the effects of the positive feedback between trace gas emissions and a warming Arctic [*Shelley et al.*, 2014].

One possible explanation for this series of variability relationships is that CH_4 oxidation, an aerobic process that produces CO_2 as a byproduct, is a sufficiently common process to impact watershed scale variability in dissolved CH_4 and CO_2. Processes affecting these factors, in particular physical processes involving discharge, have the ability to contribute to increased CH_4 production and/or decreased CH_4 consumption in addition to modifying the ratio of downstream to atmospheric fluxes. Increased precipitation and rates of spring warming will significantly modify the flow regime of these streams and will multiply their relative importance for the cycling of C [*Holmes et al.*, 2008; *Lique et al.*, 2015]. In addition to the physical changes predicted, the release of permafrost C in the form of CDOM (colored dissolved organic matter) will likely increase stream water temperatures directly through increased absorption of solar radiation by the stream water itself. Warmer stream temperatures, in combination with increased substrate availability due to increased permafrost thawing rates, will allow for greater overall metabolic activity and a shift to more anaerobic metabolism if dissolved O_2 is sufficiently depleted in sediment pore waters. Recent work by Lee *et al* found that warming permafrost would likely increase metabolic rates for *in situ* methanogenic microbes [*Lee et al.*, 2012] which in turn allows for dissolved CH_4 to be imported into streams at a greater rate [*Campeau and Del Giorgio*, 2013], thereby increasing the overall net flux of CH_4 downstream while not increasing the magnitude of emissions to the atmosphere. The contribution of specific conductivity to the

overall variability of dissolved CH_4, which we interpret here as a measure of how much the stream water has been chemically and biogeochemically influenced by the sediments and riparian zone, suggests that CH_4 but not CO_2 is originating in the terrestrial ecosystem. This assertion lends further support to the idea that stream CH_4 excess is at least in part being driven by the degradation of permafrost DOC recently leached from the terrestrial zone or that stream CH_4 is actually riparian and sediment CH_4 that was lost to stream flow.

The patterns we observe in specific conductivity, CO_2 and CH_4 concentrations support a conceptual model where parcels of CH_4-rich water reach the stream because the water from permafrost thawing flows through hotspots of microbial activity where CO_2 is produced, O_2 is depleted and CH_4 is formed. Thaw water that merely flows over ice or frozen soil picks up neither the dissolved gases nor solids that contribute to elevated specific conductivity. In support of this notion, we found a positive relationship between CO_2 supersaturation and specific conductivity and there was a positive trend between specific conductivity and Julian day for all sites as the system approached its baseflow for the season, suggesting that C rich and O_2 poor waters from sediments and riparian zones were increasingly present in the stream as the open water season proceeded. Interestingly, the temporal change in specific conductivity overshadowed any spatial patterns in the specific conductivity, suggesting that the patterns of meltwater leaching were spatially homogeneous.

As the season progressed and stream velocity decreased, the reaeration coefficients for both gases also decreased. However, increased residence time of stream water within an observation reach allowed for a greater exposure of the water column to influxes of CH_4 rich riparian water. Eventually, we observed the pool features of these streams become nearly cut off from flow and effectively form a chain of small ponds along a flow path. Dissolved CH_4 concentrations rose during this time, suggesting that this change in stream function was likely enhancing gas flux to the atmosphere by stimulating the production or import of $CH_4.$These

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patterns, along with the greater importance of dissolved CH_4 for the overall flux (Figure 1a) suggest that CH_4 production in these streams is spatially heterogeneous. Further, the importance of variability in dissolved CH_4 for explaining the variability in dissolved CO_2 export (Figure 2f) suggests that there is likely CH_4 oxidation occurring in the stream water column or nearby sediments that is influencing the CH_4, CO_2, and O_2 dynamics.

The ratio of CH_4 flux to CO_2 flux has previously been used infer the relative proportion of ecosystem respiration that is anaerobic [*Segers and Kengen*, 1998; *Stanley et al.*, 2015]. Streams in our study tend to have lower ratios than most studies included in *Stanley 2015* which suggests that these streams are dominated by aerobic metabolism despite the positive CH_4 emission rate observed. This follows early work by Kling *et al* that terrestrial C in the Arctic is commonly respired as CO_2 in streams [*Kling et al.*, 1991]. Our observed dissolved O_2 values (Table 1), while slightly diminished from saturation, are still sufficiently high to allow for extensive aerobic metabolism which appears to be driving the very large fluxes of CO_2 we observed.
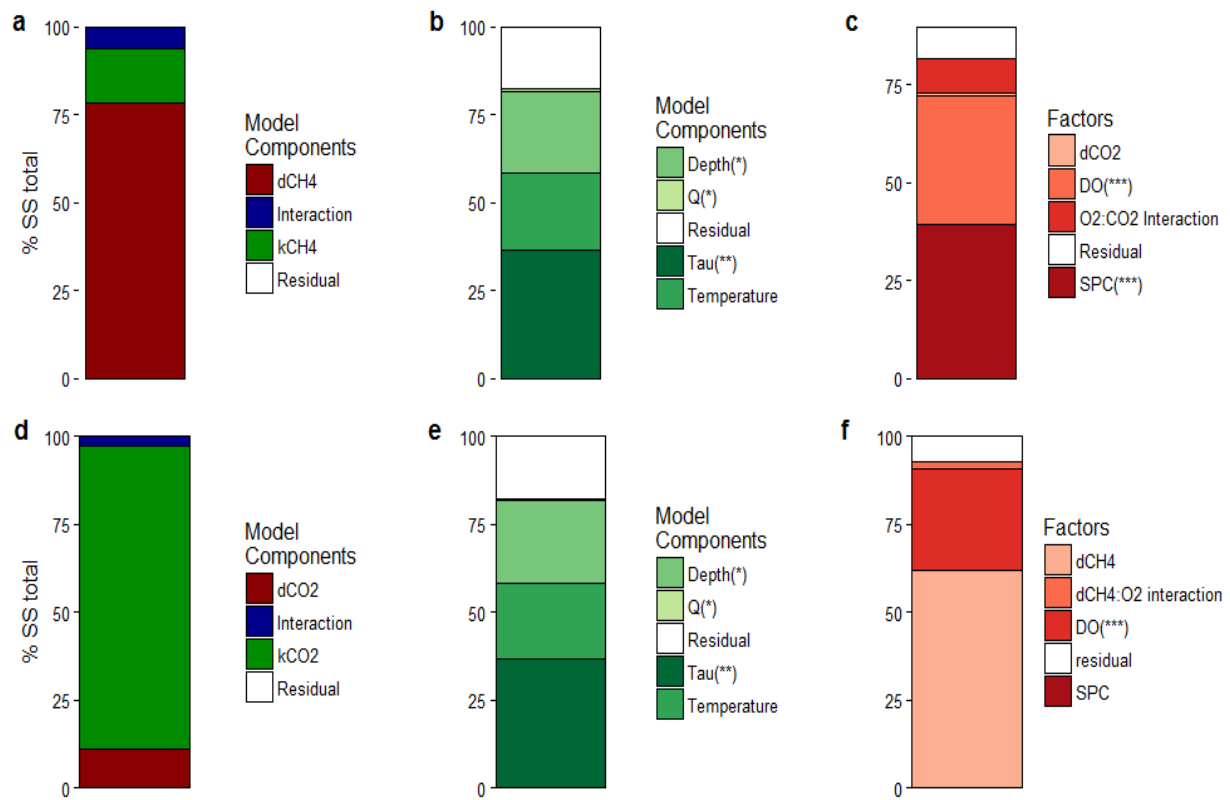
CONCLUSIONS

We observed significant and variable fluxes of CH_4 and CO_2 from streams surfaces to the atmosphere. Stream velocity decreased substantially over the course of the season as the streams approached and entered base flow. The transit time of water in a reach correspondingly increased and lead to higher observed rates of flux to the atmosphere relative to flux downstream. Our observations later in the season show increasing dissolved CO_2 and CH_4, decreasing concentrations of O_2, and higher specific conductivity. The combination of these changes resulted in an increase in fluxes to the atmosphere from lower order streams. Given the beaded morphology of these streams, this decrease in flow velocity and increase in transit time suggests that the pool features are likely net sources of dissolved gas (CO_2 and

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CH$_4$). Beaded streams, despite being ubiquitous landscape features of the Arctic are unique environments for methanogenesis and decomposition and are disproportionately strong emitters of CH$_4$ and CO$_2$ to the atmosphere.

Table 1.1 Mean and (standard deviation) of stream reach properties

Reach	Q (m³ s⁻¹)	Water Temp. (K)	DO (%)	k600 (m d⁻¹)	dCO₂ (mol m⁻³)	dCH4 (mol m⁻³)	Emission CO₂ (mol m⁻² d⁻¹)	Emission CH₄ (mol m⁻² d⁻¹)	Export CH₄ (mol d⁻¹)	Export CO₂ (mol d⁻¹)
y3r1	0.010 (0.006)	287.48 (2.55)	63.98 (8.9)	0.040 (0.047)	0.152 (0.03)	0.0005 (0.0002)	0.0033 (0.003)	9.98E-06 (7.64E-06)	0.415 (0.2)	118.57 (51.5)
y3r2	0.013 (0.016)	286.98 (2.05)	53.03 (11.78)	0.048 (0.06)	0.194 (0.07)	0.0008 (0.0004)	0.0038 (0.003)	1.20E-05 (1.00E-05)	0.541 (0.41)	156.81 (144.0)
y3r4	0.016 (0.016)	285.02 (2.14)	40.87 (21.91)	0.031 (0.02)	0.217 (0.08)	0.0017 (0.001)	0.0038 (0.001)	2.86E-05 (1.63E-05)	1.346 (0.43)	234.50 (151.1)
y3r5	0.034 (0.004)	287.15 (2.55)	83.83 (5.06)	0.015 (0.006)	0.078 (0.01)	0.0004 (0.0001)	0.00084 (0.0005)	4.07E-06 (2.02E-06)	1.163 (NA)	198.33 (NA)
y3r6	0.004 (0.003)	288.70 (3.61)	80.65 (4.03)	0.009 (0.002)	0.081 0.005)	0.0002 (0.00001)	0.00048 (0.0001)	5.15E-07 (4.88E-08)	0.067 (0.05)	27.70 (17.7)
y3r7	0.003 (NA)	286.05 (NA)	47.55 (NA)	NA	0.183 (NA)	0.0004 (NA)	NA	NA	0.095 (NA)	40.30 (NA)
y3r8	0.001 (NA)	288.25 (NA)	65.85 (NA)	NA	0.095 (NA)	0.0009 (NA)	NA	NA	0.059 (NA)	6.48 (NA)
y3r9	0.003 (NA)	284.95 (NA)	34.70 (NA)	NA	0.198 (NA)	0.0014 (NA)	NA	NA	0.378 (NA)	51.91 (NA)

Figure 1.1 Sum of squares error partitioned to model components for gas flux (a,d) the reaeration coefficient (b,e), and the dissolved gas concentration (c,f) for CH_4 and CO_2 respectively.
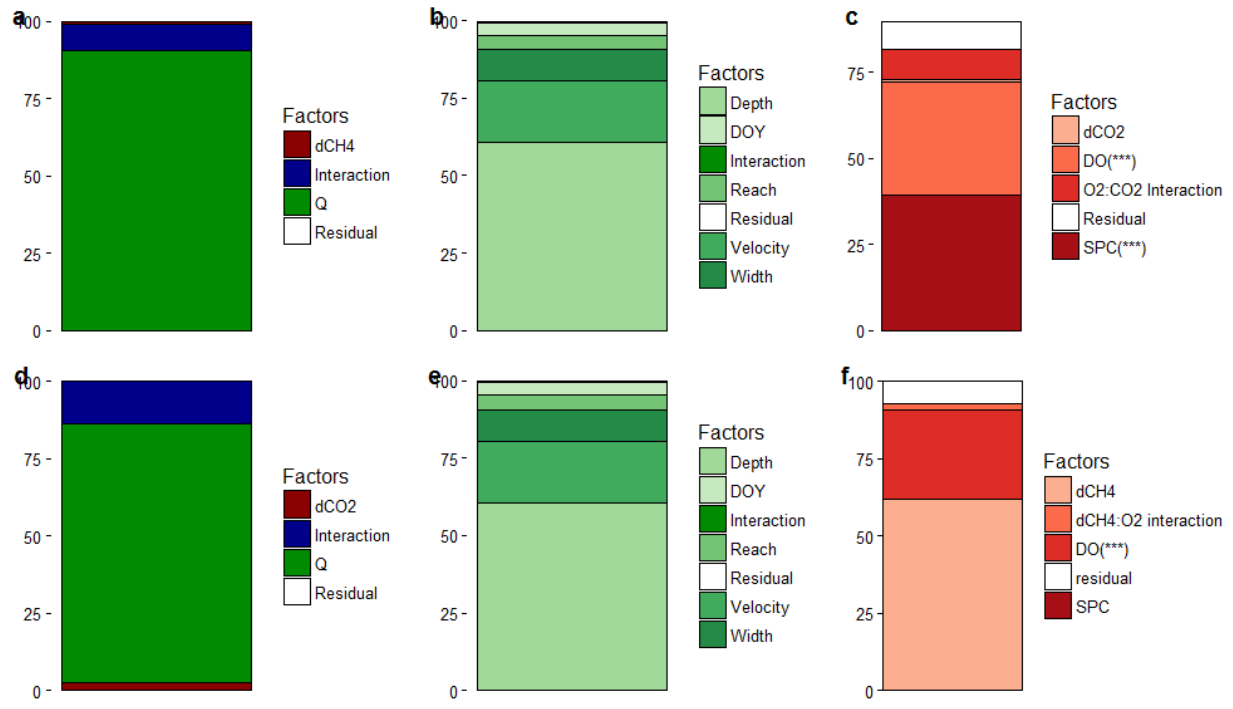
Figure 1.2 Sources of variability to downstream export flux for CH$_4$ (a) and CO$_2$(d), discharge(b,e) and the dissolved concentration of CH$_4$ (c) and CO$_2$(f)
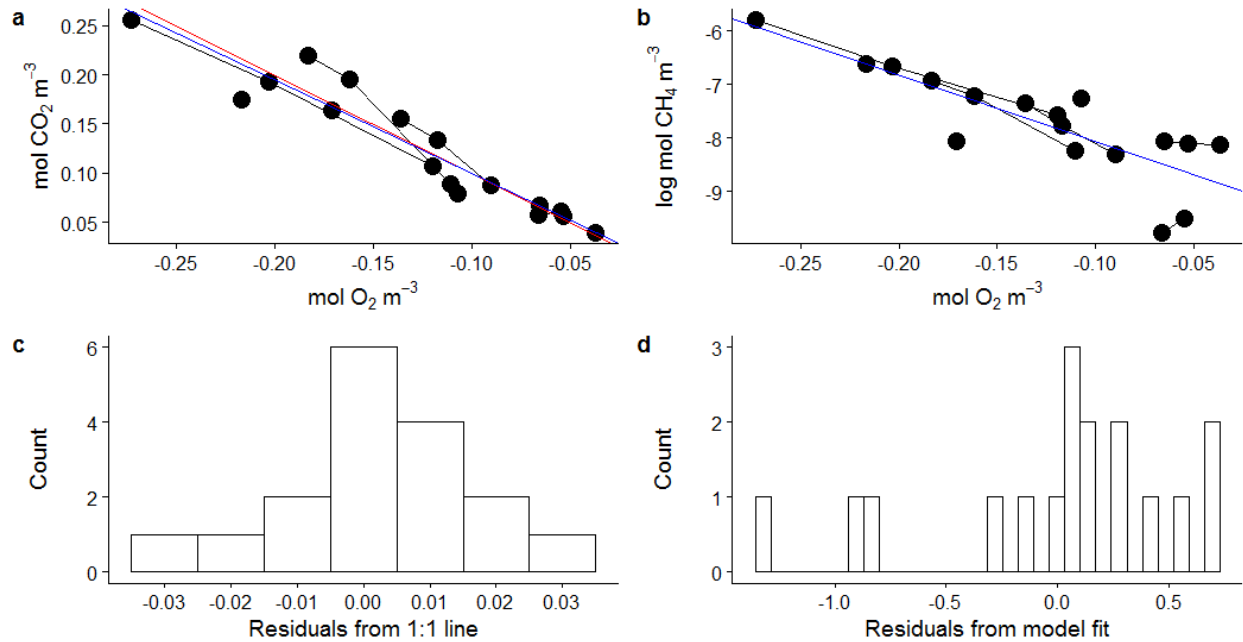
Figure 1.3 CO_2 excess concentration is inversely related to the O_2 deficit in the stream; the red line is the -1:1 line (a). For CH_4, however, this relationship is more closely when CH_4 concentrations are log transformed (b). Blue lines are the line of best fit for the linear model and have very similar slopes to the -1:1 for CO_2. Black lines connecting data points represent changes within a site over the course of the season. Panels c and d show the residuals of the linear models for CO_2 with O_2 and the log-linear fit between CH_4 and O_2, respectively
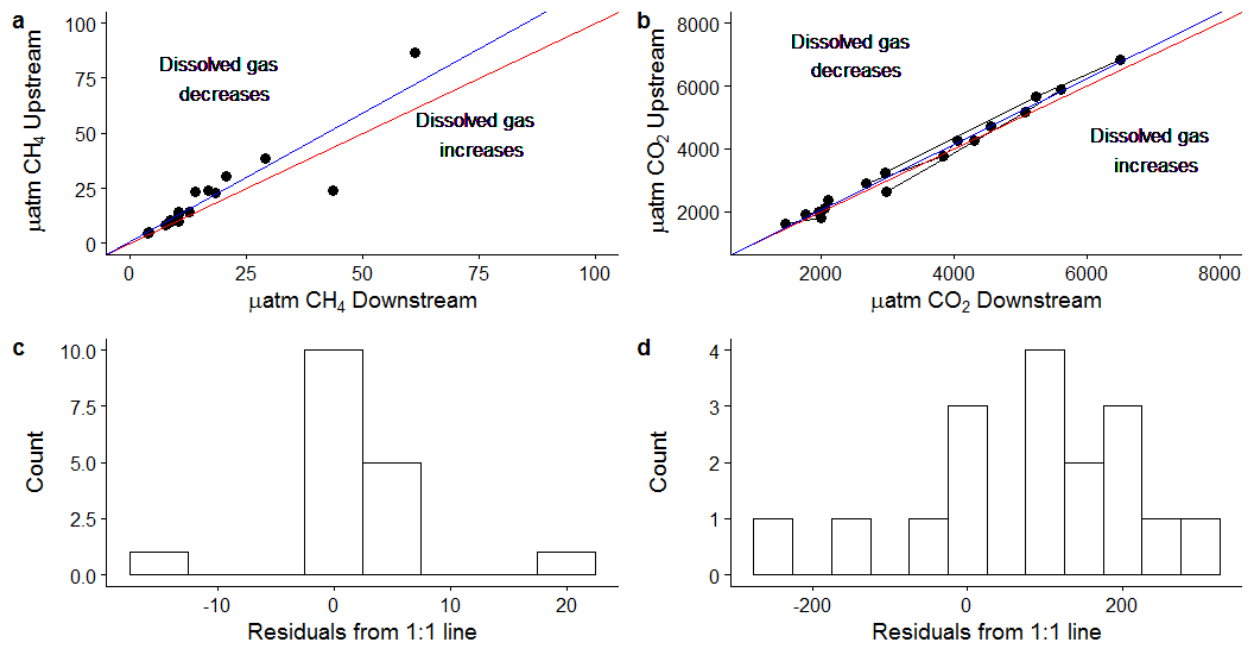
Figure 1.4. CH$_4$, but not CO$_2$ was observed to decrease within stream reach observations. Red lines represent a 1:1 relationship. Blue lines represent linear model fits used to generate residuals for sub plots c and d.

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CHAPTER 2

INTRODUCTION

Streams and lakes are integrators of terrestrial, aquatic, and atmospheric processes that occur in the landscapes they drain as well as valuable sentinels of global change [*Vannote et al.*, 1980; *Williamson et al.*, 2008]. Both overland and groundwater flow contribute the products of terrestrial biogeochemistry to streams [*Cole and Caraco*, 2001] and consequently the degree of connectivity between streams and their landscapes is partially a function of the hydrological cycle, which will continue to change as the climate warms in the coming century [*Jencso et al.*, 2010; *Covino*, 2016]. However, streams that drain other aquatic landscape features, such as lakes and wetlands, are additionally influenced by the products of the internal processes of those systems and any responses to warming occurring therein *[Lottig et al*, 2013a]. Mountainous regions are particularly sensitive to changes in temperature and precipitation due to their landscape position, inherent landscape complexity (e.g., topography, slope, aspect and exposure), and mechanisms responsible for elevation dependent warming [*Mountain Research Initiative EDW Working Group*, 2015]. The lakes and streams that drain mountainous areas are sentinels of changes that will occur as these ecosystems respond to climate and global change stressors.

Ecosystems with complex terrain, such as mountainous watersheds, can include a variety of sub-ecosystems within a small geographical area as a result of the change in elevation. These pockets, often lakes, meadows, or wetlands, are hotspots for biogeochemical cycling and have a high degree of connectivity and influence on stream chemistry [*Wickland et al.*, 1999b, 2001; *Millar et al.*, 2016]. As a result of proximity, stream chemistry downstream from these hotspots is altered and contributes to the overall variability of stream biogeochemistry in a watershed. However, the effect of these hotspots is eventually lost with increasing distance

[*Lottig et al.*, 2013b; *Crawford and Lottig*, 2014]. The effect strength of a biogeochemical hotspot on downstream chemistry varies greatly based on a number of factors such as the hydrological regime, the scale of the two systems, and the type of influence the hotspot exerts. Some studies seeking to determine the effect of lakes on downstream chemistry found that lakes tended to moderate downstream chemistry by delaying and processing the flow of solutes and that wetlands acted more like a direct subsidy [*Goodman et al.*, 2011; *Lottig et al.*, 2013b; *Crawford and Lottig*, 2014]. However, the direction and magnitude of the relationship is heavily influenced by the hydrological regime and most studies of this relationship occur in flat, temperate, peat-forming regions, not high gradient alpine and sub alpine systems.

Dissolved gas dynamics, especially exchange with the atmosphere, are a function of the overall biogeochemistry of the stream and the landscape it drains [*Hall et al.*, 2015]. Mountainous ecosystems are not thought to be major sources of trace gases to the atmosphere due to limitations on the production of these gases in the system [*Crawford et al.*, 2015], however changes occurring in high elevation landscapes will result in changes within the stream systems that drain them that may ease the deficit of dissolved gases preventing significant emission today. Internal cycling of dissolved gases is likely an important process for local microbial communities [*Shelley et al.*, 2015a; *Trimmer et al.*, 2015], despite the net effect being near zero as is commonly observed in studies of alpine and sub-alpine streams [*Crawford et al.*, 2015].

Landscape-scale patterns in dissolved gas dynamics in aquatic systems are increasingly acknowledged to be important sources of greenhouse gases to the atmosphere [*Stanley et al.*, 2015]. Emissions from streams in mountainous regions have largely been ignored to date due to low concentrations of dissolved gases [*Crawford et al.*, 2015]. However, certain mountainous regions are able to support higher emission rates [*Schelker et al.*, 2016] and continued warming will likely shift these systems from their historic ultra-oligotrophic state. The role of

autochthonous production in the generation of dissolved gases is of particular interest as key

metabolic processes, such as carbon cycling and primary production, are likely to change in

high latitude and alpine ecosystems in response to rapid rates of warming in high latitude and

elevation ecosystems [*Yvon-Durocher et al.*, 2010; *Kraemer et al.*, 2016]. Increases in algal

biomass, and the associated increase of DOC, has been shown to enhance CH_4 production

rates [*Liang et al.*, 2015]. However, studies on gas flux-productivity relationships overwhelmingly

come from productive wetlands and man-made unnatural aquatic ecosystems, such as

reservoirs, and there is a paucity of information on the potential implications of increased

autochthonous production on gas flux out of natural, oligotrophic systems.

In this study we set out to explore the relationship between streams and landscape

features common in high elevation systems by comparing trace gas emissions and chemistry

from different landscape units over time and by following up with incubations to determine the

responses of sediment microbes to alterations of their chemical environment. We employed

both field observations of gas emissions rates and seasonal patterns in water chemistry in

addition to lab incubations under altered chemical environments to determine the influence of

sediment microbe communities and loading from landscape features in producing trace gas

emissions.

METHODS

SITE DESCRIPTION

The Loch Vale watershed (LVWS) in Rocky Mountain National Park (ROMO) is an

instrumented catchment that has the focus of long-term ecosystem research since 1982 [*Baron

et al.*, 1991; *Baron and Arthur*, 1992; *Williams et al.*, 1996; *Baron and Campbell*, 1997]. LVWS

is a northeast-facing 6.6 km^2 catchment east of the continental divide in north central Colorado.

It ranges in elevation from 4000 masl at the continental divide down to 3100 masl; land cover is

82% granitic rock or talus. Surface water comprises 1% of the catchment. Rock and ice glaciers are present in both subcatchments of LVWS and contribute, along with snowpack, to stream flow during the open water months. Six percent of LVWS land cover is subalpine coniferous forest and 1% is wet meadows, the remainder is alpine [*Baron and Arthur*, 1992].

We selected five stream sampling reaches and one lake across the LVWS based on existing sample sites and accessibility (Icy Brook, Andrew's Creek, Sky Pond). These sites represent a range of elevations, stream discharges, and surrounding landscapes common in alpine ecosystems. Stream sites were sampled every two weeks in 2015 from June 28 to August 28. Sky Pond was sampled weekly in 2015 from June 25 through August 13.

FIELD COLLECTIONS

Discharge was quantified using a hand held flow meter and weighting rod at 20cm intervals across the two ends of the sample reach at each visit. Reach lengths ranged between 18 and 90m and were re-sampled at each visit (n=5). Weekly water chemical samples were collected in brown borosilicate glass bottles that had been baked at 550 C in a muffle furnace, immediately refrigerated upon return to the laboratory, and processed within 24 hours. Dissolved oxygen (DO) and stream temperature were collected at multiple points along the sample reach using a hand held Hach probe (Model HQ 40d) attached to the weighting rod and flow meter. We report the average of the values across a stream cross section. We observed minimal variation in either of these parameters across stream cross sections.

We used propane (C_3H_8) as a tracer gas to determine the gas exchange coefficient (K_{tracer}) for each of our stream reach-visits. Propane gas was bubbled into the stream approximately 4m above the upstream end of the reach and continuously added until all tracer gas collections were complete. Dissolved gas samples, both tracer and environmental, were collected using a headspace equilibration method at the center of flow downstream of the propane addition point at both the up and downstream ends of the reach. We used floats to

determine the approximate transit time of water and solutes through the stream reach prior to releasing the propane and timed our sampling to coincide with the mean transit time of these floats (tau). Dissolved gases (CH_4, N_2O, and CO_2) were collected using the headspace equilibration method and stored in field-evacuated 20ml vials before being transported to Colorado State University for analysis. Gas standards of known concentration were prepared in the field following the same protocol to determine the magnitude of any gas loss during transport.

Weekly Sky Pond phytoplankton chlorophyll a samples were collected from an inflatable boat with a peristaltic pump at the deepest part of the lake as well as at the lake outlet. Surface (0.5 m depth) and hypolimnion (6.5 m depth) were collected with acid-washed tubing through a peristaltic pump into 1-L brown HDPE bottles to minimize exposure to light and immediately held on ice. All phytoplankton samples were filtered in the shade at our field site and immediately frozen upon return to the laboratory, within 6 hours of collection. Additionally, water samples for chemical analyses were collected weekly in baked borosilicate glass bottles and stored on ice upon collection. Periphyton samples were collected at 5 different sample sites spatially distributed around the lake shore using the rock scraping method described elsewhere [*Richardson et al.*, 2014]. Briefly, at each sample site, we collected 3 rocks at random from the littoral zone and scraped, and pooled the biofilm in one 250mL brown HDPE bottles composite sample. Periphyton samples were immediately held on ice upon collection. All water samples and periphyton samples were filtered and stored at 4C within 24 hours of collection.

Stream sediments were collected on August 27, 2015 from five locations throughout the Loch vale Watershed. Samples were collected by hand from the top 5 cm of sediments underneath the main area of flow within the stream and stored with pore water in Whirlpak bags until processing within 24 hours.

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LABORATORY ANALYSES

Aliquots for nitrate (NO_3^-) and ammonium (NH_4^+) were filtered through baked Whatman GF/F glass-fiber filters and refrigerated until analysis, which was performed on an Alpkem Auto Sampler using standard methods at the EcoCore facility at Colorado State University. Subsamples for dissolved organic carbon (DOC) from stream sites were filtered, acidified, and refrigerated until shipment to St. Olaf College in Northfield MN for analysis. Subsamples for DOC from lake samples were filtered, acidified, and refrigerated until analysis on a Shimadzu TOC-L using standard methods at the EcoCore facility at Colorado State University. Within 24 hours of collection, we subsampled (n=3) aliquots of homogenized periphyton slurry and concentrated them onto baked GF/F filters in order to measure areal biofilm chlorophyll a (chl a). Chlorophyll a for phytoplankton and periphyton were determined using the standard EPA method [Arar and Collin, 1997]. Samples were extracted for 12-24 h in 90% acetone prior to analysis on a Turner AU-10 fluorometer.

Upon return to the laboratory, sediments were passed through a 2mm sieve to remove any large gravel and coarse woody debris. Subsamples of sediment were dried overnight at 60° C to determine sediment water content by mass loss. Subsamples from these dried sediments were packaged for Elemental Analysis (C and N) on a Costech Elemental Analyzer at St. Olaf College in MN. Additional sediment samples were analyzed for texture (Sand, Silt, and Clay fraction) at the Natural Resource Ecology Laboratory in Fort Collins, CO.

Samples for CO_2 and CH_4 were analyzed on a LGR DLT-100 greenhouse gas analyzer modified to receive injected samples. Nitrous oxide (N_2O) was quantified on a Shimadzu GC-14B with electron capture detector. All gas samples were analyzed within 2 weeks of collection by an autosampler and run with standard curves and repeat check standards to assure no instrument drift.

INCUBATION SETUP

A grab sample of the filamentous green algae *Zygnema spp.* was collected from Sky Pond and stored in a dark HDPE bottle at 4C for three weeks prior to filtration through a 0.2 um filter and addition to the incubations. During this time the algae were partially decomposed resulting in an algal "cocktail." Due to the absence of conjugating stages, it was not possible to identify the alga to the species level *[Wehr et al.*, 2015].

At the onset of the experiment, 10g of sediment from each site were added into 20, 60mL serum vials. Serum vials were then amended and sealed. Control treatments (each site, n=5) received 10mL of stream water, algal additions (+A, each site, n=5) received 5mL of stream water and 5mL of an algal solution. Nitrate additions (+N, each site, n=5) received 5mL of stream water and 5 mL of 20 µmol NO^-_3 solution. Combination treatments (+AN, each site, n=5) received 5mL each of stream water, the algal solution and the nitrate solution. Incubations were then sealed and their headspaces sampled every 48 hours over the course of 8 days for a total of four observations each. Between observations, incubations were kept at room temperature on an orbital shaker at 120rpm.

Incubation vials were sampled directly by an autosampler and analyzed at Colorado State University by a Los Gatos Research DLT-100 greenhouse gas analyzer modified to receive injection samples. Nitrous oxide samples were injected by the same autosampler into a Shimadzu GC-14B using N_2 as a carrier gas and quantified on an electron capture detector (ECD). Vials were sampled every 48 hours and were kept on an orbital shaker table at 120rpm when not being sampled. Headspace volume was determined gravimetrically by adding deionized water.

ANALYSES

Data were collated and basic calculations were performed in MS excel before being exported to R (version 3.3.1) for analysis and figure creation. We quantified the sources of

variability within the flux equation using a partial r^2 method. For each equation (flux equation and K_{Gas}), we set up a multiple linear regression between the equation output and its components. We quantified the partial r^2 of each model component by determining the total model sum of squares and dividing by each component sum of squares to determine a sum of squares percentage. For the dissolved gas, we used an all-subsets regression and selected the best model explaining the dissolved gas concentration by comparing BIC values and model r^2. We used this method to examine the relative contribution of model component variability to overall model variability (Figure 3).

We quantified gas fluxes from field samples following Raymond *et al* where the gas flux (F_{gas}) is a function of the concentration gradient between the stream surface and atmosphere (G) and the gas exchange velocity (K_{gas}) (Equation 1). The concentration gradient is difference between the dissolved gas concentration and the atmospheric concentration above the stream surface (mol m^{-3}).

1: $F(gas) = G * K(gas)$

2: $k_{Tracer} = \frac{1}{\tau} * \left(\frac{[Propane]_{Up} * Q_{Up}}{[Propane]_{Down} * Q_{Down}} \right)$

3: $K_{Gas}(m\ d^{-1}) = K_{Tracer} * \left(\frac{Sc_{Gas}}{Sc_{Tracer}} \right)^{-0.5}$

The reaeration coefficient for each trace gas was calculated by first calculating the reaeration coefficient for our tracer gas following Equation 2 [*Wallin et al.*, 2011]. We then converted the tracer reaeration coefficient to K_{600} and K_{CH4}, K_{CO2}, and K_{N2O} (Equation 3) using the Schmidt numbers (Sc) for each gas at the temperature of observation. We report K_{600}

values here unless noted otherwise. Gas flux calculations were made using the appropriate gas-specific K value.

We modeled a total of 23 fluxes from 5 sites over the course of an open water season for N_2O, CO_2, and CH_4 (Figure 1) using equation 1. Two fluxes from one of our sites (AG) were omitted due to insufficient recapture of our tracer gas, which prevented an accurate calculation. We still report values for the dissolved N_2O, CH_4 and CO_2 concentrations at these two visits.

Incubation time series data were analyzed using the ideal gas law. Observations of non-linear changes in headspace were discarded.

RESULTS

Streams in the LVWS were, on average, net sources to the atmosphere of all gases measured over the course of the season with mean emissions of (0.77±0.5 µmol N_2O, 1.24±1.75 mmol CO_2, and 0.29±0.22 µmol CH_4) m^{-2} d^{-1} (mean ± 95% CI). However, many sites shifted from being sinks to sources as the season progressed (Figure 1). Concentration gradient strength was highly variable by site and over the course of the study period with occasional spikes and slumps (Figure 2). Gas gradient strength (excess of atmosphere) was on average 1.4±0.7 µmol N_2O ,1.1±0.5 µmol CH_4, and 3.7±4 mmol CO_2 m^{-2} respectively. Reaeration coefficients (K_{Gas}) averaged 0.81±0.26 m d^{-1} across all sites over the whole season.

Sources of variability to emission rates are a function of the variability in the concentration gradient and the reaeration coefficient, respectively. We found that variation in the concentration gradient was the major source of variability to observed emissions for all gases quantified (Figure 3 a,c,e). Potential explanatory variables for the variability within the concentration gradient strength were selected for each gas using all subsets regression and model selection to determine which combination of covariates best explained the overall

variability in the concentration gradient strength. Variability in each gas concentration gradient was driven by different physical and biological components that either contributed to, or detracted from, the overall magnitude of the concentration gradient (Figure 3 b,d,f). Variability in the N_2O concentration gradient was best explained by the elevation (m ASL) for the sites where it was quantified, but the majority of the variability in the N_2O gradient could not be explained by covariates collected (Figure 3b). The variability of the CO_2 concentration gradient was primarily due to the variability in stream dissolved organic carbon (DOC) and to lesser extents stream and sediment N. Most notably, increases in stream DOC corresponded to increases in the CO_2 gradient strength (Figure 3d). Variability within the gradient strength of CH_4 was predominantly driven by the variability in the abundance of silt-sized particles in the stream sediments and to lesser extents the stream chemistry itself (Figure 3f).

The stream draining a lake (SP), but not a wetland (AG), had higher emissions of both CH_4 and N_2O averaged over the season than sites not influenced by a wetland or lake, but these were not significantly different (Figure 4). Emissions of CH_4 were consistently low across all sites, but net uptake from the atmosphere was only observed in SP at the beginning of the observation period. In the AG stream, which drains a wetland feature known to have positive net emissions to the atmosphere, stream CH_4 emissions were lower on average, but not statistically so, than all other sites despite the potential influence of the upstream wetland. All streams observed displayed net CO_2 uptake at some point during the sampling period but net positive emissions on average.

Episodic increases in N_2O and CO_2 were observed in the Sky Pond outlet stream that coincided with a late summer algal bloom in the lake upstream of the sample site (Figure 5). Benthic algal chlorophyll began to increase around Julian day 195 and peaked around day 220 (Figure 5a). This increase in algal chlorophyll coincided with a sudden increase in the concentration gradient strength for N_2O and consequently emissions. Water column algal

chlorophyll-a increased shortly after the increase in benthic algal chlorophyll a, around Julian day 205, and was much greater in magnitude at its peak on Julian day 220 (Figure 5b). This increase in water column chlorophyll coincided with increases in DOC in lake and stream water and the continued peak in the N_2O concentration gradient and emissions (Figure 5 c,e,f). CO_2 emissions appear to increase concurrent with the increase in water column algae chlorophyll and both stream and lake DOC (Figure 5 b,c,d).

Incubated sediments from all sites that are adjacent to landscape features (Sky Pond and Andrew's Meadow) showed a range of contrasting potential responses that varied by gas and site (Figure 6). Unamended controls showed significant differences between sites for each gas with AG being a net source of CH_4 and SP being a net sink (Figure 6c). Methane production was suppressed by any addition of NO_3^- in the sediments from AG, even in the combined algal cocktail and nitrate amendment. But, the addition of the algal cocktail did significantly increase CH_4 production. No amendments had any effect on the ability of SP sediments to produce or consume CH_4; in all treatments there was net uptake of CH_4 from the incubation headspace. Sediments from Sky Pond significantly increased N_2O production with the addition of algal solution both with and without additional NO_3^-. AG sediments were a net sink for N_2O across all treatments, however only the +AN treatment was significantly different from the control (Figure 6). Both sites responded positively with regards to CO_2 production with the addition of the algal cocktail (Figure 6).

We can approximate the redox status of a stream sediment by examining the proportion of total C emissions that are in the form of CH_4 as opposed to CO_2 (Figure 7. Within incubated sediments, significant responses with respect to N_2O were only possible when there were virtually no C emissions as CH_4 or when CH_4 uptake was observed.

DISCUSSION

Streams in the LVWS were, on average, net sources of N_2O, CO_2, and CH_4 to the atmosphere in 2015. Fluxes ranged from net uptake earlier in the season to net emission later on and varied within and between stream reaches in agreement with previous work done in the area by [*Crawford et al.*, 2015]. Upscaling these emissions to a larger scale is difficult given the degree of network variability and the importance of landscape features for driving emissions, but in general these emissions are lower than most temperate streams not in mountainous regions and virtually all high latitude streams quantified to date [*Butman and Raymond*, 2011; *Campeau et al.*, 2014] and in some cases were net sinks of gases, CO_2 and N_2O, from the atmosphere. Streams influenced by landscape features such as wetlands or lakes represented local extremes in terms of dissolved gas uptake and emission magnitude and variability and contributed significantly to the overall system average.

Variability in stream gas emissions from LVWS is driven by variability in the concentration gradient strength and not variability in the reaeration coefficient. Mountainous streams have an inherently high potential for emissions to the atmosphere given their turbulent flow conditions and high reaeration coefficients. However, low temperatures and low productivity in streams and landscapes commonly found at high elevations prevents the build up excess dissolved gas, which ultimately results in low emissions rates or even uptake of trace gases from the atmosphere. Due to the well-mixed nature of steep gradient streams, any increase in the concentration of dissolved gas has the potential to result in increased emission of gas. Additionally, alterations of the hydrological cycle, namely the timing, form, and magnitude of precipitation, will alter the timing and magnitude of changes in the reaeration coefficient and the potential for emissions in addition to potentially increasing the loading of dissolved gas or the required substrates into the stream. In similarly low productivity boreal ecosystems there has been a marked increase in stream DOC over the last several decades.

Pumpanen *et al* found that this increased DOC in the streams was due to increased flushing of the terrestrial C pool into the streams and was correlated with precipitation [*Pumpanen and Lindén*, 2014]. Increased DOC in stream waters has the potential to subsidize and stimulate microbial activity in sediments as we observed in this study.

Site landscape context appears to be related to the observed and potential microbial activity in streams sediments and emissions of N_2O, CO_2, and CH_4 to the atmosphere. At Andrew's Meadow, where consistently positive CH_4 emissions were observed in the field there is likely dissolved CH_4 being imported from the adjacent wetland, where quantifiable CH_4 emissions have been recorded [*Wickland et al.*, 1999a]. When we incubated these stream sediments under different biogeochemical conditions, they showed a relatively strong potential for the production of CH_4 and were sensitive to the addition of terminal electron acceptors (NO_3^-) that inhibited CH_4 production. However, in sites not influenced by wetlands the addition of an algal cocktail and NO_3^- had mixed or little effect on the net production of CH_4. At the stream site near the Sky Pond outlet, sediments experienced increases in DOC concurrent with the sharp increases in benthic and phytoplankton biomass in the lake Stream water. Stream sediment microbes have been shown to be able to process a significant portion of a stream DOC load flowing through the hyporheic zone *[Sobczak and Findla*y, 2002; *Briggs et al*, 2015] and we expect that this occurred here as well, especially considering the observed increase in dissolved CO_2.

We acknowledge that dissolved gas dynamics involve both the production and consumption of gas by sediment microbes which are difficult to disentangle. We were only able to observe either net consumption of dissolved gases during incubations and periods of net uptake of gas by the stream. However, the role of sediments in the uptake of dissolved gases is acknowledged to be important, but remains poorly understood beyond site-specific case studies. *[Shelley et al.* (2015)] found that primary productivity in an English chalk stream was

being heavily subsidized by the CO_2 from CH_4 oxidation, suggesting that relatively C poor

systems, such as LVWS, could be receiving allochthonous C in the form of atmospheric DIC.

Following this observation for CH_4, N_2O consumption is an acknowledged phenomenon in soils,

particularly agricultural systems, but has not received any attention in aquatic systems [*Jones et*

al., 2013]. Our observation of net N_2O uptake at the beginning of the season and then again in

the following year (Jochum et al., unpublished data) highlights the importance of this sink for

oligotrophic systems. Since N_2O is an intermediate product in both nitrification and

denitrification, its net uptake or production rate offers insight into the state of the local N cycle.

The Loch Vale watershed has been saturated with NO_3^- for decades as a result of direct N

deposition in addition to enhanced terrestrial nitrification [*Williams et al.*, 1996; *Osborne et al.*,

2016], so not NO_3 limitation, but rather C limitation of denitrification or inefficient nitrification is

occurring. It should be noted that while LVWS is considered to be saturated with NO_3, these

values are still considered to be low compared to agricultural systems where tens of mg per liter

NO_3 is not unreasonable [*Beaulieu et al.*, 2011].

Stream sediments from different locations within LVWS exhibited a range of potential

microbial activity both under control and amended conditions. We observed N_2O emissions in

the field increase when DOC and NH_4 increased and NO_3 decreased. This gas can be

produced from either the aerobic oxidation of NH_4 or the anaerobic reduction of NO_3. Our

incubations revealed that N_2O production is only possible when virtually none of the C-gas

production is in the form of CH_4 or when CH_4 is being consumed, an aerobic process (Figure 7).

From this we conclude that it is likely that inefficiencies in nitrification, not enhanced

denitrification, contributed to the production of N_2O in LVWS stream sediments.

Across all sites, the redox state of the sediments is a critical factor governing the types

of dissolved gases being produced. The rate of settling and types of settled materials in a

stream bed influence the redox state of those sediments by enhancing or diminishing the rate of

O$_2$ diffusion and consumption by microbes within the sediments.   Most sediments were highly

(>95%) sandy with the exception of the Sky Pond outlet stream where silt made up a more

significant portion of the total sediment. Our all subsets regression for CH$_4$ concentration

gradients revealed that the silt fraction is a significant predictor of the CH$_4$ concentration

gradient strength. This is likely due to the aforementioned effect of particle size on O$_2$

discussion into the sediment and rates of hyporheic flow [*Briggs et al.*, 2015]. We observed that

the bulk C:N ratio of stream sediments varied roughly by elevation with higher elevations site

having relatively less total C present. Additionally, the sites under the influence of major aquatic

landscape features represented the local extremes of sediment C:N and had strongly diverging

trace gas dynamics both in the field and in lab incubations.

CONCLUSIONS

Mountainous streams are places where dissolved gas dynamics are highly variable over

very short distances. The influence of landscape features, namely other aquatic systems, on

streams in high elevation ecosystems is significant, and the combined effects of expected

warming and hydrological changes within those features and the streams have the potential to

result in new dissolved gas and chemical dynamics. While these streams are not currently

significant sources of gases to the atmosphere, or significant sinks, their internal processing of
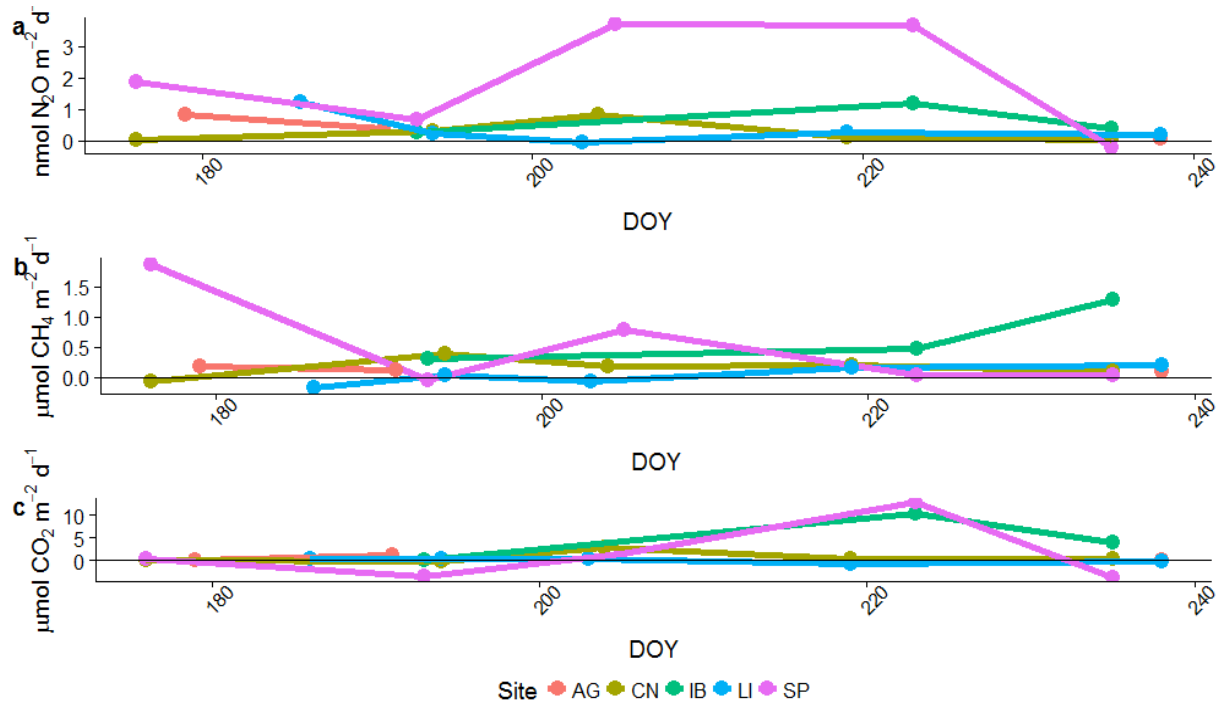
dissolved materials.

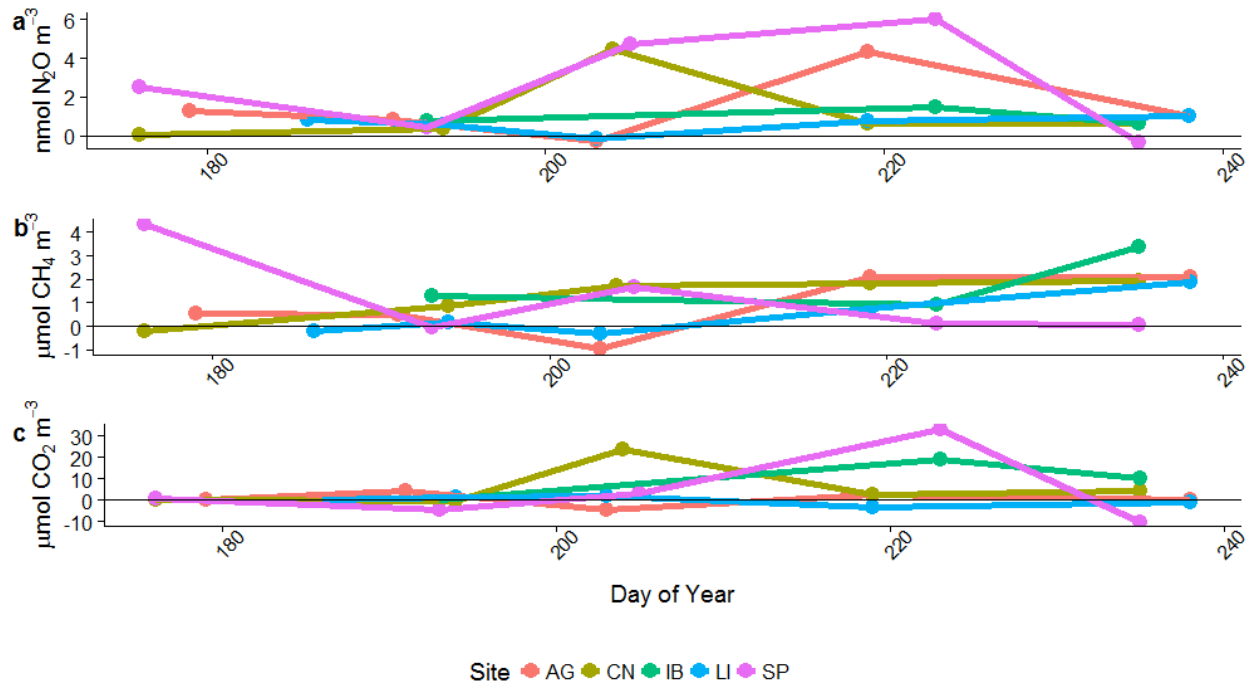Figure 2.1 Emissions of N_2O, CH_4, and N_2O by site over the season.

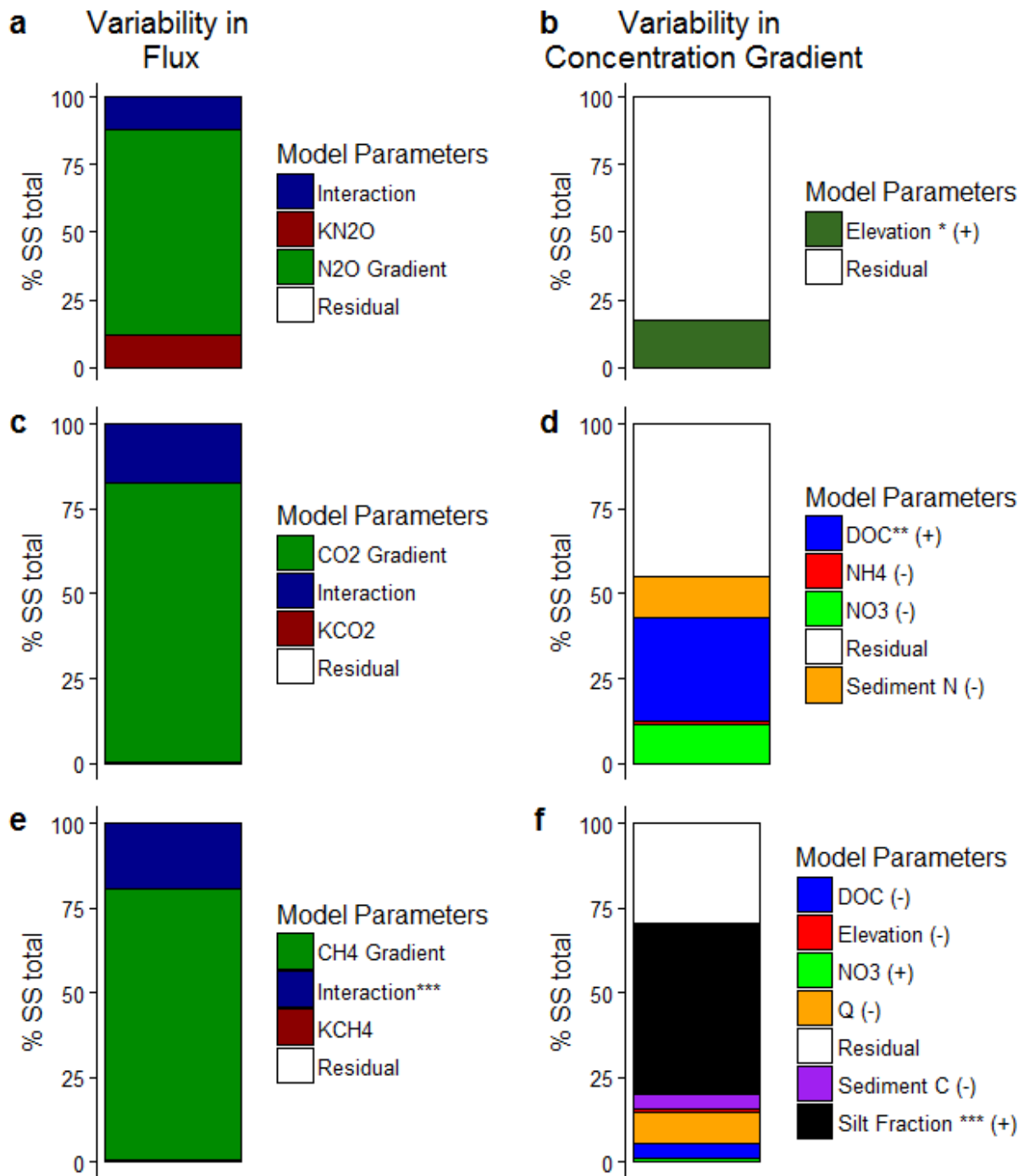Figure 2.2 Concentration gradient for N_2O, CH_4, and CO_2 for all sites over the season.

Figure 2.3 Sources of variability to emissions and the concentration gradient for N_2O, CO_2, and CH_4.
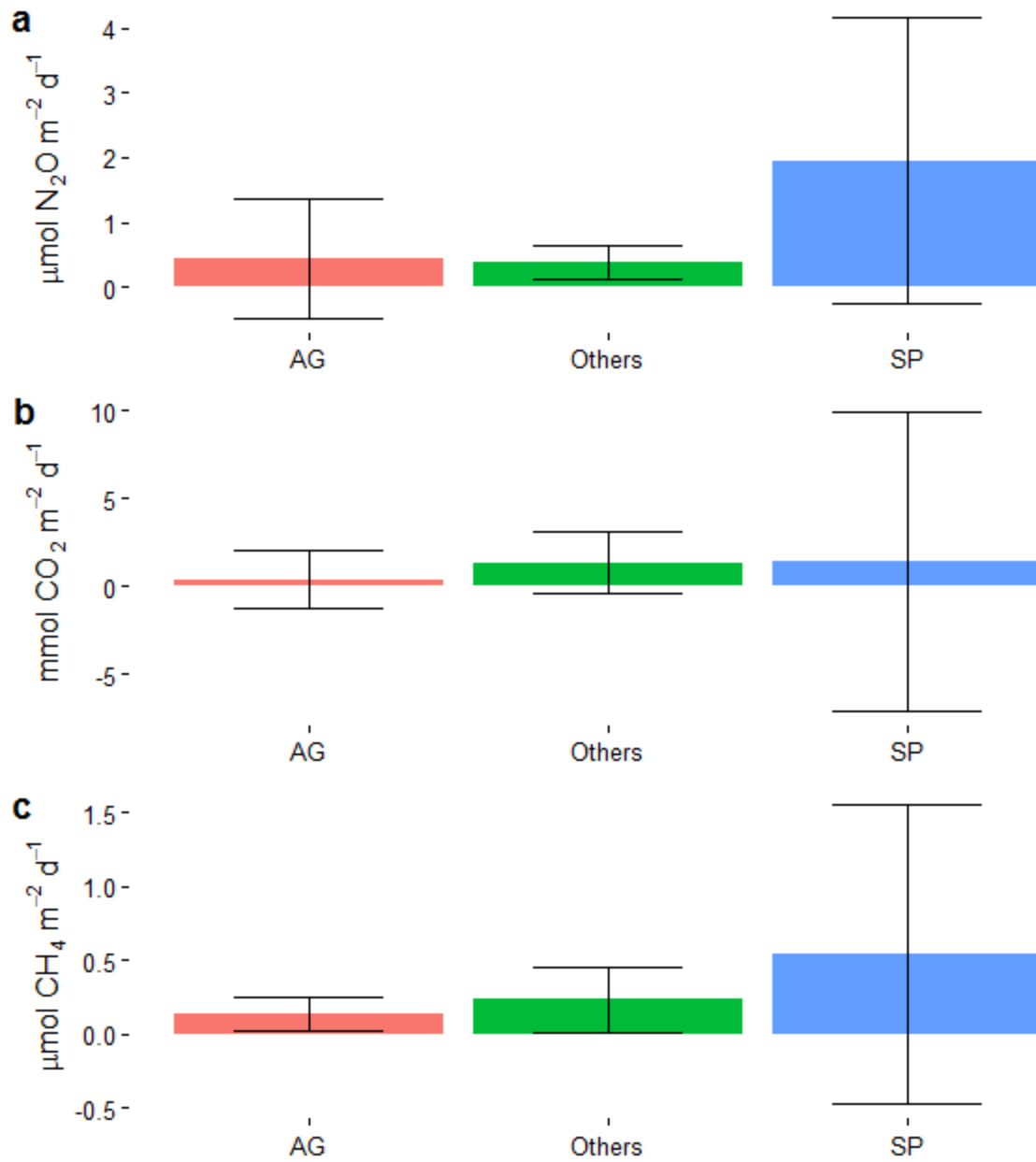
Figure 2.4. Mean emissions from streams influenced by aquatic features and those not. Error bars are plus or minus one SE from the mean.
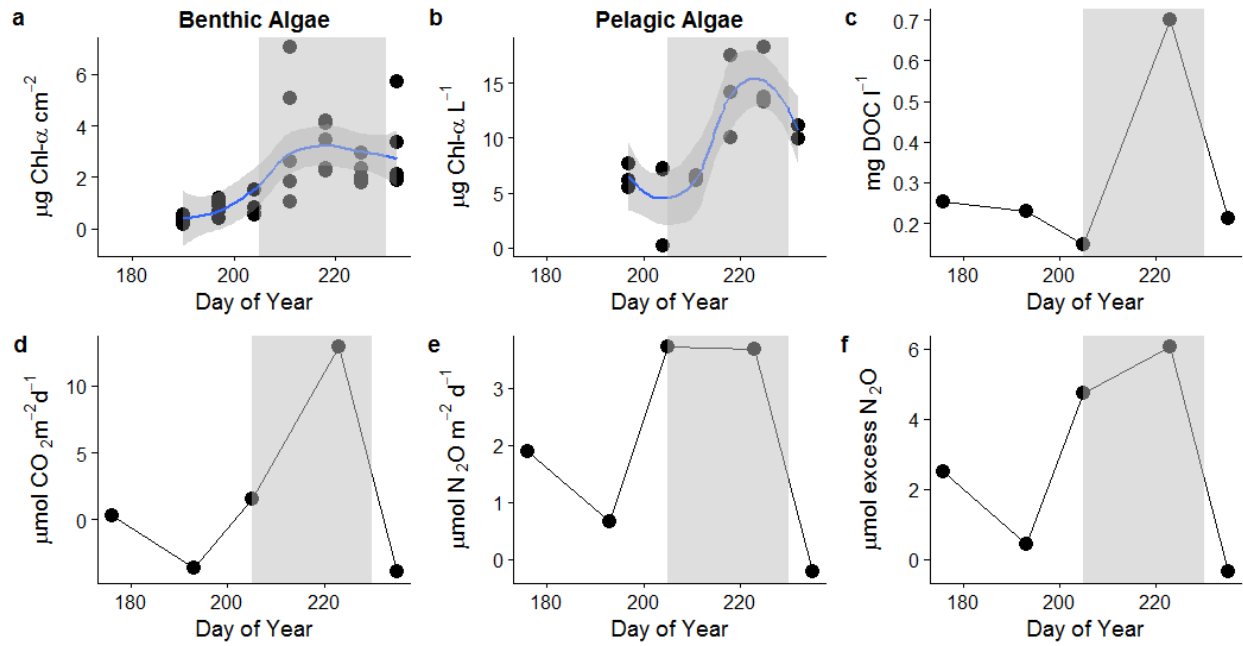
Figure 2.5. Changes in water chemistry and dissolved gas chemistry at the stream reach below sky pond and chlorophyll in sky pond during an algal bloom.
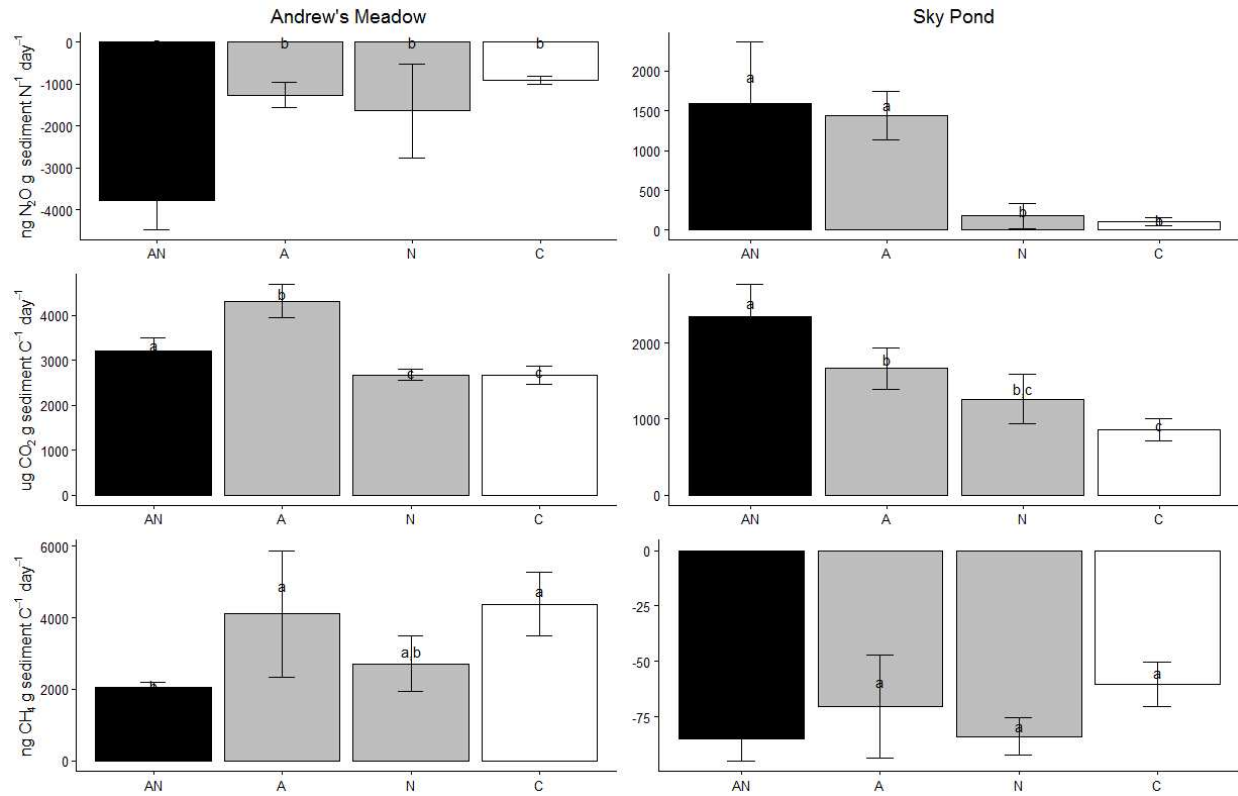
Figure 2.6. Responses to incubation amendments for stream sediments in Andrew's Meadow (AG) and Sky Pond (SP). "C" is the unamended control, "N" is $+NO_3^-$, and "A" is the algal cocktail.
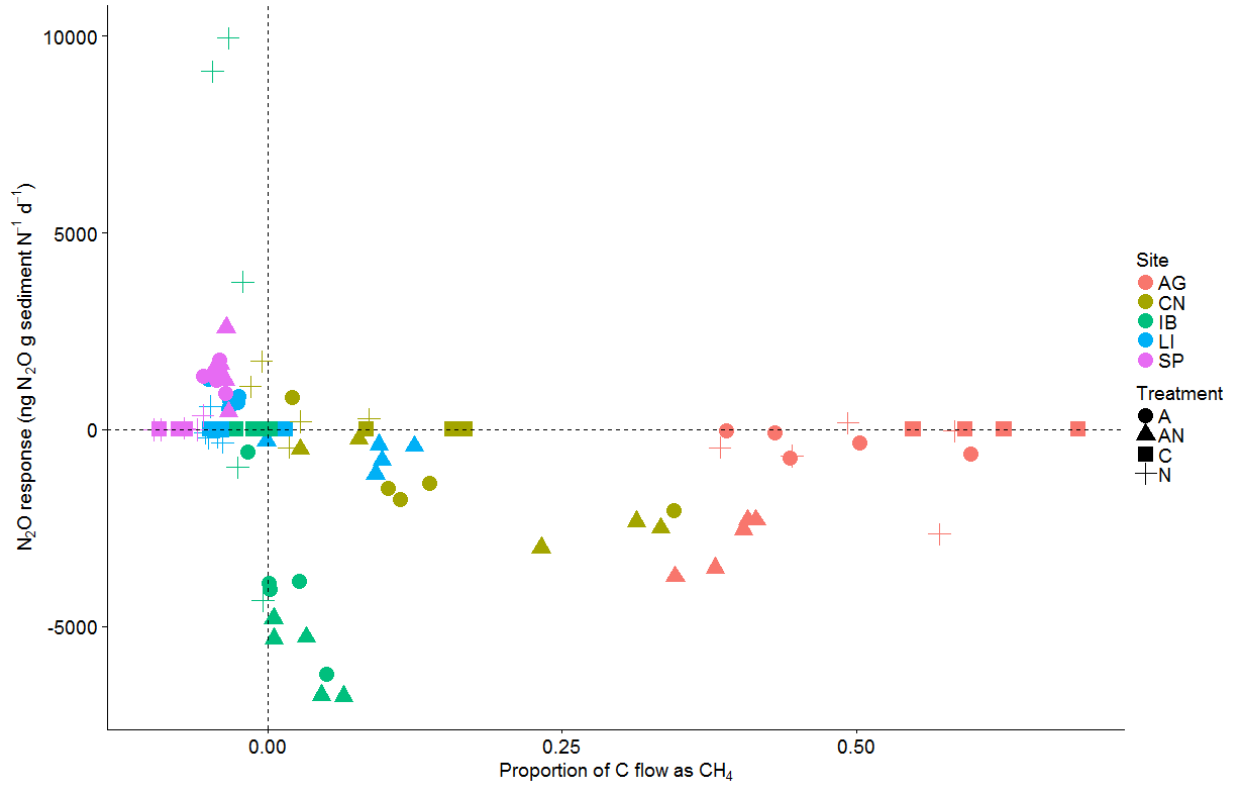
Figure 2.7. N_2O response to incubation treatments is only possible when virtually none of the total C converted to gas is converted to CH_4 or when there is CH_4 uptake by the sediments.

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CONCLUSIONS

In this dissertation I sought to address gaps in our understanding of trace gas emissions from streams in arctic and alpine environments, their magnitudes and sources of variability, and how stream sediment microbes could respond to hypothetical biogeochemical disturbances.

In my first chapter, I observed significant and variable fluxes of CH_4 and CO_2 from streams surfaces to the atmosphere in Siberia. Stream velocity decreased substantially over the course of the season as the streams approached and entered base flow. The transit time of water in a reach correspondingly increased and lead to higher observed rates of flux to the atmosphere relative to flux downstream. My observations later in the season show increasing dissolved CO_2 and CH_4, decreasing concentrations of O_2, and higher specific conductivity. The combination of these changes resulted in an increase in fluxes to the atmosphere from lower order streams. Given the beaded morphology of these streams, this decrease in flow velocity and increase in transit time suggests that the pool features are likely net sources of dissolved gas (CO_2 and CH_4). Beaded streams, despite being ubiquitous landscape features of the Arctic are unique environments for methanogenesis and decomposition and are disproportionately strong emitters of CH_4 and CO_2 to the atmosphere.

In my second chapter I found that high alpine streams are nearly neutral with respect to trace gas exchange under normal conditions due to a lack of resources needed to generate sufficient gas and high rates of exchange with the atmosphere. However, we found that, on average, these streams are net sources of N_2O to the atmosphere but can also switch rapidly between source and sink status. Supply limitation of gas emissions drives observed variability in gas flux at the network level and the emissions we do observe are likely driven by the activity of a few hotspots where conditions are better for microbial metabolism. Episodic releases of C and N from algae blooms triggered greater gas flux events that dominate seasonal flux patterns.

The effect of this added C was lost relatively quickly within the stream network, but larger and longer-lasting disturbances have the potential to affect a greater length of stream and contribute more greenhouse gases to the atmosphere.

Building upon my observation of microbial responses to algal C and N I conducted a series of incubations to determine the potential response of stream sediment microbes to biogeochemical disturbance. I found that stream sediment microbes are able to respond rapidly and significantly to biogeochemical disturbances. Disparities in the direction and magnitude of the response to disturbance can be partially explained by the C:N ratio of the sediments, but the existing microbial community and hydrological history of the site are also likely critical factors. Interacting acute (algal) and chronic (N deposition) disturbances have the potential to significantly induce a response from stream sediment microbes. In some cases, this interaction changed a sediment from being a net sink to a net source of gas or elicited a significantly stronger overall response.

BROADER/SYNTHETIC CONCLUSIONS

Alpine and arctic streams, both energy poor systems subject to warming, are going to change in the coming century. Gas emissions from arctic streams will be more influenced by changes to the hydrology of the system as opposed to microbial processes. These systems are already saturated with dissolved gas, but the current hydrological regime does little to release it to the atmosphere. Changes in the timing and intensity of the melt season, or increases in summer precipitation, have the potential to greatly enhance emissions by increasing the reaeration coefficient of the streams. In contrast, high elevation systems are well suited to emit gas to the atmosphere given the high degree of turbulence with which they flow, but lack the necessary materials to produce significant emissions. However, sediment microbes are poised to respond to any incoming substrate, and at some point a threshold will be passed where these

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microbes are able to efficiently recycle their material and shift the system to a higher level of overall productivity and emissions to the atmosphere.

FUTURE WORK AND LIMITATIONS

Spatial heterogeneity of both the biological and the physical drivers of gas emission within a stream is difficult to incorporate using current techniques. Hot spots and hot moments have the potential to, on aggregate, define the characteristics of a stream with regards to its biogeochemical behavior but often go unstudied in the limited scale field campaigns often employed. Future work focusing on the mechanics of the interaction between sediment microbes and their physical environment will be critical for developing an understanding of the biogeography of stream beds and the resulting potential for biogeochemical cycling. The advent of automated sensors has the potential to revolutionize the study of dissolved gases and other solutes in streams and capture the hot moments, if not the hot spots as well.

Within stream processes involving dissolved gas are often ignored when considering landscape scale responses to disturbance. Stream bed microbes have the potential to drive both the local and downstream stream foodwebs through their action, or inaction in the presence of these dissolved gases. Intermediate products of microbial activity are not part of our current understanding of streams and what little we do know of gas consumption instreams suggest that internal cycling may be critical in some landscapes, especially if there is generally a lack of material available as we see in the alpine and subalpine streams studied in this dissertation.