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Impact of changing hydrology on nutrient uptake in High Arctic rivers

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Abstract

Despite the importance of river nutrient retention in regulating downstream water quality, and the potential alterations to nutrient fluxes associated with climate-induced changes in Arctic hydrology, current understanding of nutrient cycling in Arctic river systems is limited. This study adopted an experimental approach to quantify conceptual water source contributions (meltwater, groundwater), environmental conditions and uptake of NO_3^-, NH_4^+, PO_4^{3-} and acetate at twelve headwater rivers in Svalbard and so determine the role of changing hydrology on nutrient uptake in these Arctic river systems. Most rivers exhibited low demand for NO_3^- and PO_4^{3-}, but demand for NH_4^+ and acetate was more variable and in several rivers comparable to that measured in sub-Arctic regions. The proportion of meltwater contributing to river flow was not significantly related to nutrient uptake. However, NH_4^+ uptake was associated positively with algal biomass, water temperature and transient storage area, while acetate uptake was associated positively with more stable river channels. Mean demand for NH_4^+ increased when added with acetate, suggesting NH_4^+ retention may be facilitated by labile DOC availability in these rivers. Consequently, nutrient export from Arctic river systems could be influenced in future by changes in hydrological and environmental process interactions associated with forecasted climate warming.

Introduction

Climate warming in Arctic regions throughout the 21st Century will be associated with reductions in glacier mass and alterations to the structure and extent of permafrost systems (Holland and Bitz, 2003; Anisimov *et al.*, 2007). In response, it is hypothesised that meltwater flow contributions to rivers will peak initially and then decline, while relative contributions of groundwater will increase in the long-term (Aðalgeirsdóttir *et al.*, 2006; Walvoord and Streigl, 2007). Although uncertainty remains, there is evidence to suggest these changes in high-latitude hydrology may increase the fraction of labile dissolved organic carbon (DOC) delivered to some Arctic rivers (Frey and McClelland, 2009; O'Donnell *et al.*, 2010). Warming is also likely to stimulate mineralization of nitrogen in soils (Jones *et al.*, 2005) and deeper seasonal active layers will increase the pool of nutrients that could be flushed potentially into rivers (Petrone *et al.*, 2006; Frey and McClelland, 2009).

Increased riverine nutrient fluxes are likely to be associated with higher biological activity in Arctic rivers (Lock *et al.*, 1990; Hershey *et al.*, 1997). This could be enhanced further by a shift towards groundwater-dominated rivers, characterised by less variable hydrological regimes, warm water temperature and stable channel morphologies (Walvoord and Striegl, 2007; Parker and Huryn, 2011;

Blaen *et al.*, 2012), which represent more suitable habitat conditions for biological growth and development than meltwater-dominated systems. Furthermore, warming may enlarge thaw bulbs and transient storage zones below river channels, thought to be important hotspots of biogeochemical processing (Zarnetske *et al.*, 2007; Merck *et al.*, 2012).

Climate-induced alterations to hydrology, nutrient availability and habitat conditions may impact particular ecosystem processes associated with autotrophic and heterotrophic activity in high-latitude rivers (Lecerf and Richardson, 2010). Notably, variation in nutrient uptake has important management implications for reducing nutrient loading and so regulating water quality downstream (Alexander *et al.*, 2007). While there are few studies on nutrient uptake in headwater Arctic rivers (but see Wollheim *et al.*, 2001), the environmental conditions that characterise many meltwater-dominated high-latitude rivers suggest that rates of nutrient uptake may be low in these environments (Scott *et al.*, 2010). In the context of future warming in at high latitudes, increased biological activity may lead to an increase in nutrient uptake in Arctic rivers relative to contemporary conditions (Rasmussen *et al.*, 2011). However, there is currently a paucity of information regarding controls on nutrient cycling in these systems and thus the evidence base for projection of future changes in nutrient uptake remains uncertain.

This paper addresses this major research gap by reporting on a study conducted in Svalbard. The aim was to characterise environmental conditions and rates of nutrient retention across a gradient of meltwater to groundwater influence as an analogue to understand how changing hydrology and environmental conditions may alter nutrient cycling in high-latitude regions. We hypothesised that:

1. decreased meltwater flow contributions associated with warmer and more stable channels and higher transient storage will support higher autotrophic and heterotrophic activity (Zarnetske *et al.*, 2007; Parker and Huryn, 2011);
2. decreased meltwater flow contributions and associated changes in environmental conditions will increase nutrient uptake velocities and rates of retention (Rasmussen *et al.*, 2011); and
3. the addition of labile DOC will stimulate N uptake by releasing N assimilation from C limitation (Johnson *et al.*, 2009).

Methodology

Study sites

The research was undertaken near Ny-Ålesund (79º N, 12º E) in north-west Svalbard. Twelve first-order rivers were chosen to represent a gradient of water source inputs from meltwater and shallow hillslope groundwater reservoirs (Figure 1). Sites A1-A6 were studied in 2011 and sites B1-B6 were studied in 2012. Canopy cover and associated shading were absent at all sites. Study reaches in each river were 60-70 m long, confined to a single channel with no tributary inputs, and selected to minimise longitudinal variation in gradient and river discharge.

Sampling framework

Conceptual water source contributions to river flow, transient storage metrics and environmental habitat conditions were quantified at each study site. These data were combined with data from short-term nutrient uptake experiments to understand the major controls on nutrient cycling in these Arctic river systems.

Water source quantification

A two-component end-member mixing model was used to separate river discharge into two conceptual water source components: (i) meltwater derived from snow and glacial ice melt, and (ii) shallow hillslope groundwater transmitted to the river channel primarily via subsurface flow through the active layer (Christophersen and Hooper, 1992). River water samples for each sampling reach were filtered through Whatman GF/F 0.7 µm papers and frozen within 6 h of collection. Snow, ice and hillslope groundwater samples were collected in the basin above each selected study reach and processed in the same manner. Dissolved Si concentrations were determined by the molybdosilic acid method (APHA, 1995). Si concentrations were used to proportion river discharge into meltwater and groundwater components, with meltwater characterised by low Si concentration (<0.01 mg l^{-1}) and groundwater by high Si concentration (0.4-2.4 mg l^{-1}). For more details on water source quantification see Blaen *et al.* (2013).

Nutrient uptake experiments

Nutrient uptake was measured in each river during July / early August 2011 or July 2012. River levels were stable on each sampling day. Water samples were collected at 10 m intervals along each study reach prior to experimentation to characterise ambient solute concentrations. Short-term additions of nitrogen (as NH_4^+ and NO_3^-), phosphate (PO_4^{3-}) and acetate, plus a conservative tracer (NaCl) were used to measure gross nutrient retention rates resulting from the interaction of physical and biological processes following standard methods (Tank *et al.*, 2006). Target enrichment levels above ambient concentrations were 15 µg l^{-1} NH_4^+, 20 µg l^{-1} NO_3^-, 30 µg l^{-1} PO_4^{3-} and 100 µg l^{-1} acetate. The target increase in electrical conductivity (EC) was 5-20 µS cm^{-1}. It is recognised that raising nutrient levels above ambient conditions can result in overestimation of uptake lengths (Mulholland *et al.*, 2002). However, the modest enrichment factors employed in this study suggest that measured uptake lengths are unlikely to deviate substantially from ambient lengths (Payn *et al.*, 2005; Rasmussen *et al.*, 2011).

Five nutrient additions were performed at each site: NO_3^-, NH_4^+, PO_4^{3-} and acetate were initially added separately prior to a further addition of NH_4^+ and acetate in unison. A solution containing either NH_4Cl, $NaNO_3$, Na_2HPO_4, CH_3COONa, or NH_4Cl and CH_3COONa, plus NaCl as a conservative tracer, was pumped continuously into a well-mixed area at the upper end of each reach using a Watson-Marlow peristaltic pump with a flow rate of 0.12 l min^{-1}. EC values were used to calculate river discharge during nutrient release and assess the time for nutrient concentrations to stabilise. Water samples were collected at 10 m intervals along each study reach once EC had reached asymptote. Samples were filtered in the field using Whatman GF/F 0.7 µm filter papers and frozen within 6 h.

NO_3^- and NH_4^+ were determined using an AutoAnalyzer 3 (Bran + Luebbe) with a 1 µg l^{-1} detection limit. Acetate and Cl^- were determined using a Dionex ICS-2000 with detection limits of 2 and 5 µg l^{-1}, respectively. PO_4^{3-} was determined by the ascorbic acid method (APHA, 1995) using a Helios Gamma spectrophotometer (Thermo Fisher Scientific) with a detection limit of 5 µg l^{-1}. Analytical precision was <5% for all determinands and deionised water blanks showed no detectable contamination from filter papers.

Uptake parameters were based on the longitudinal decrease in nutrient concentration through each study reach. Nutrient concentrations were divided by Cl^- to correct for minor changes in river discharge throughout the study reach. The relationship between background- and discharge-corrected nutrient concentration to distance downstream of the injection point was calculated as:

$$\ln N_x = \ln N_0 - kx$$

where N_0 is nutrient concentration at the addition site, N_x is nutrient concentration at x meters downstream of the addition site, and k is the per-meter uptake rate. From k, nutrient uptake length (S_w, m), velocity (V_f, m min^{-1}) and areal uptake rate (U, mg m^{-2} min^{-1}) were calculated using standard protocols (Tank *et al.*, 2006).

Solute transport modelling

Transient storage parameters were estimated for rivers from EC data using a one-dimensional advection-dispersion model (OTIS-P) to provide an integrated measure of hydrological retention in each reach (Runkel, 1998). Given a suite of initial boundary conditions for the head of each reach, the model adjusts parameters iteratively to produce a least-squares best fit to the downstream conservative tracer breakthrough curve measured as EC in the field (Figure 2). OTIS-P models were assessed for reliability by calculating Damkohler I (*DaI*) numbers (Edwardson *et al.*, 2003). Model outputs were used to calculate the ratio of the storage zone cross-sectional area to the main channel cross-sectional area (A_s/A) and the mean hydraulic residence time in the storage zone (T_{stor}) (Edwardson *et al.*, 2003).

Environmental variables

Several key ancillary variables for each study reach were recorded to examine potential environmental controls driving nutrient demand. Mean water temperature was calculated from measurements at the lower end of each reach every 15 min using Tinytag Underwater dataloggers (Gemini Data Loggers UK Ltd.). Incoming short-wave radiation was measured using a Kipp & Zonen CMP11 pyranometer in Ny Ålesund every 15 min. Suspended sediment concentration, SSC, was calculated from manual samples (500 ml) collected after nutrient injections. Samples were filtered onto pre-weighed papers, dried at 60 ºC for 48 h, and reweighed. Channel stability was assessed using the bottom component of the Pfankuch Index (Pfankuch, 1975), where lower values represent greater stability.

Two measures of river ecosystem metabolism were used to assess benthic activity in the study reaches. Firstly, five replicate samples of periphyton were scrubbed from cobbles, filtered onto papers and frozen until laboratory analysis. Cobbles were photographed in the field and cobble area was quantified using ImageJ software (Rasband, 2012). Chlorophyll *a* (mg m^{-2}) was determined using following standard methods (Steinman *et al.*, 2006). Secondly, rates of sediment respiration by microbial communities were determined as the change in dissolved oxygen (DO) over time. Following removal of the upper 5 cm of bed sediment, five 1 L HDPE bottles were half-filled with sediment and then topped up with river water. Sediments were sieved to exclude particles > 8 mm. Bottles were inverted to remove trapped air and DO was measured using a YSI 95 meter calibrated in the field. Bottles were sealed and buried in the bed for approximately 24 hours before DO was remeasured. Sediments were subsequently dried at 60 ºC for 48 h and weighed. Sediment respiration rates were normalised by sediment weight and reported as μg O_2 h^{-1} kg^{-1} sediment (Logue *et al.*, 2004).

Data analysis

Differences in nutrient concentration between meltwater and groundwater samples for each study river were assessed using independent sample *t*-tests. Potential associations between water source contributions, environmental variables and uptake parameters (V_f and U) were assessed using Spearman's rank correlation analysis due to the relatively small size of the dataset and the potential for non-linear relationships. Differences in V_f between nutrient types were tested for by one-way ANOVA followed by Tukey's *post-hoc* comparisons test. To assess the influence of DOC on NH_4^+ uptake and *vice versa*, demand ratios were calculated as the ratio of V_f during the simultaneous release of NH_4^+ and acetate to the V_f of each nutrient during individual releases. A ratio >1 indicates that V_f during the simultaneous release was greater than during the individual release, a ratio=1 indicates no difference in V_f, and a ratio <1 indicates a decrease in V_f for the simultaneous release relative to the individual release (Johnson *et al.*, 2009). Differences in V_f between individual and simultaneous uptake were compared using paired *t*-tests for each nutrient separately and then in unison. All data analyses, including regressions for nutrient uptake length calculations, were performed using SPSS version 19.0 (SPSS Inc., Chicago IL).

Results

Hydrological and environmental data are used to assess the influence of water source on river habitat conditions. These data are combined with results from nutrient uptake experiments to characterise nutrient cycling parameters and understand drivers of nutrient uptake in rivers in north-west Svalbard.

River hydrology and environmental variables

River discharge ranged from 5 to 240 l s^{-1} (Table 1) and was representative of the small rivers found in this area of Svalbard during summer (Blaen *et al.*, 2013). There was no evidence of substantial hillslope groundwater inflow throughout the study reaches. Ambient concentrations of NH_4^+, PO_4^{3-} and acetate were very low at all sites. Ambient NO_3^- concentration was more variable, ranging from 7 to 85 μg l^{-1} (Table 1). Ambient nutrient concentrations were not correlated with any measured environmental variables. End-member mixing analysis indicated that meltwater accounted for between 0% and 74% of total river discharge in the selected study reaches (Table 1). Meltwater relative contribution was not associated significantly with environmental variables. Correlation analyses showed significant relationships between water temperature and incoming short wave radiation (r=0.61, p<0.05), chlorophyll *a* concentration (r=0.65, p<0.05) and river discharge (r=0.62, p<0.05), and between SSC and Pfankuch index (r=0.76, p<0.01; Table 2).

Concentrations of NO_3^- and NH_4^+ in meltwater and groundwater samples were <100 µg l^{-1} and there were no significant differences in nutrient concentrations between sample types for any river basins (p>0.05 by t-test). Acetate was normally below detectable limits in all samples. However, PO_4^{3-} concentration was significantly higher in groundwater samples (mean±SD: 88±15 µg l^{-1}) than meltwater samples (mean±SD: 46±13 µg l^{-1}) at all sites (t=2.82-9.15, p<0.05). Mean water temperature ranged from 2.1 to 11.4 ºC. Chlorophyll *a* concentration ranged from 0 to 9.01 mg m^{-2} and rates of sediment respiration ranged from 0 to 157.1 µg O_2 h^{-1} kg^{-1} (Table 1). Transient storage area (A_s/A) ranged from 0.14 at site A4 to 3.08 at site B2 (Table 3). *DaI* numbers were within a range acceptable for reliable parameter estimation (Edwardson *et al.*, 2003). Mean storage zone residence times were related closely to transient storage area (r=0.90, p<0.01) and ranged from <1 min to 22 min. The proportion of river discharge comprised of meltwater was not significantly correlated with ambient nutrient concentrations, environmental variables or transient storage parameters (Table 2; p>0.05).

Nutrient uptake

At many sites there was no statistically significant downstream change in nutrient concentration during each short-term release (p>0.05). In rivers where significant changes in concentration occurred, uptake length (S_w) for all nutrients was <130 m (Table 4). Only two sites (A3 and B2) exhibited significant NO_3^- uptake, although NO_3^- uptake velocity (V_f) was generally higher than for other nutrients (Figure 3). Significant NH_4^+ uptake occurred at three sites (A1, A3 and B2) when added singularly. However, when added in conjunction with acetate five sites displayed significant NH_4^+ uptake (Table 3). Mean S_w for NH_4^+ shortened by 47 m when added in conjunction with acetate and V_f and U both increased. Similarly, acetate uptake was significant at three sites during individual injections, but at five sites during the simultaneous injection with NH_4^+. Individual injection acetate S_w (41-47 m) was lower consistently than individual injection NH_4^+ S_w (64-123 m). The mean NH_4^+ demand ratio was 3.2±1.2 (Figure 4), indicating demand for NH_4^+ increased when added in conjunction with acetate. In contrast, the mean demand ratio for acetate was 1.1±0.4, indicating that simultaneous addition of NH_4^+ had little influence on acetate uptake. However, paired t-tests showed no significant difference in V_f between individual and dual additions for both NH_4^+ (t=1.14, p=0.37) and acetate (t=0.25, p=0.82).

Correlation analyses between NH_4^+ and acetate uptake parameters and environmental variables were conducted only for dual additions due to a limited number of cases for single nutrient injections. For

NH_4^+, significant positive relationships were observed between V_f and water temperature ($r=0.84$, $p<0.05$), V_f and transient storage area ($r=0.90$, $p<0.05$), and U and chlorophyll *a* concentration ($r=0.81$, $p<0.05$) (Table 5). For acetate, V_f was negatively related to discharge ($r=-0.90$, $p<0.05$) and Pfankuch Index ($r=-0.99$, $p<0.01$) and U was negatively related to water temperature ($r=-0.99$, $p<0.01$).

Discussion

This study offers new insights into potential changes in riverine nutrient cycling that may occur with future climatic warming in Arctic regions. Demand for NH_4^+ was greater in warmer rivers with larger transient storage areas, and those with more algal biomass were associated with higher NH_4^+ uptake. Furthermore, the addition of a labile form of DOC stimulated NH_4^+ demand, indicating labile DOC availability may limit some freshwater biotic process rates in this region of Svalbard. The following section discusses firstly the influence of changing hydrology on environmental conditions and nutrient uptake in Arctic river systems. The section then considers potential drivers of nutrient uptake and assesses the role of DOC availability in controlling NH_4^+ cycling.

Environmental habitat quality along a water source gradient

Our first hypothesis, that a decrease in meltwater contribution would be associated with warmer and more stable channels and higher transient storage that support higher autotrophic and heterotrophic activity, was rejected because no significant relationships were observed between meltwater contribution and any measured environmental variables. However, the significant relationship between water temperature and chlorophyll *a* concentration suggested warmer rivers were associated with greater algal growth, as observed previously in Icelandic rivers (Gíslason *et al.*, 2000). Low water temperatures observed in all study rivers (maximum: 11.4 ºC) reflected the reduced magnitude of atmospheric energy inputs at high latitudes, runoff interactions with cold permafrost, and glaciers and snowpacks as a primary source of river discharge, while strong associations between water temperature and incoming shortwave radiation suggested the latter was a principal driver of thermal variability in these Arctic rivers (Blaen *et al.*, 2012). Interestingly, solute modelling indicated that the relative size of transient storage areas were comparable to those in Alaskan Arctic tundra systems and headwater rivers in temperate regions (Edwardson *et al.*, 2003; Zarnetske *et al.*, 2007; Scordo and Moore, 2009), suggesting sub-channel permafrost had little effect on transient storage in these high-latitude river systems.

Nutrient uptake along a water source gradient

Most rivers showed no response to additions of NO_3^- and PO_4^{3-}, and for four rivers (A5, A6, B3 and B6) there were no significant downstream changes in concentration of any nutrients during the injection experiments. This was unlikely due to saturation of biotic demand because ambient nutrient concentrations were low in all study rivers (Hoellein *et al.*, 2007). Instead, low chlorophyll *a* concentrations relative to other Arctic and sub-Arctic rivers (Gudmundsdottir *et al.*, 2011; Parker and Huryn, 2011) suggested that algal capacity for nutrient uptake was almost nonexistent at many sites. Flashy river flow regimes associated with Arctic meltwater systems (Hodgkins *et al.*, 2009) can scour bed sediments, thus destabilising channels and eroding biofilms responsible for nutrient uptake (Aldridge *et al.*, 2010), while high sediment loads in glacier-fed channels (e.g. Hodson *et al.*, 1998) may limit light availability to biofilms. Interestingly, while P availability limits biological activity in some Arctic freshwater systems (Lock *et al.*, 1990; Säwström *et al.*, 2007), the lack of response to PO_4^{3-} injections indicates that this may not be the case for rivers in this region of Svalbard.

Where significant declines in nutrient concentration occurred, short uptake lengths (often <100 m) indicated high retention efficiency (Dodds *et al.*, 2004). In contrast to NO_3^-, significant NH_4^+ uptake was observed at three sites when added singularly and at six sites when added in conjunction with acetate. Due to the nature of the methodology employed, measured declines in nutrient concentration can only be quantified as gross retention and more detailed information on the specific mechanisms involved are absent (Ye *et al.*, 2012). However, we suggest that the difference in response between different forms of N may be due to lower energy costs associated with NH_4^+ uptake resulting in preferential assimilation of this nutrient (Newbold *et al.*, 2006). Hodson *et al.* (2005) noted that NH_4^+ in rivers on the Brøgger Peninsula was less conservative than other species of N and suggested significant retention of this nutrient is common in Svalbard.

Our second hypothesis, that decreased meltwater flow contributions will increase nutrient uptake, was rejected because no significant relationship was observed between meltwater flow contribution and nutrient uptake metrics, nor did meltwater contribution appear to influence environmental conditions (above). Previous studies have suggested that nutrient concentrations in Arctic rivers are enhanced by leaching of groundwater from proglacial soils, although this is often most evident towards the end of the ablation season when soil nitrification rates are highest (Gersper *et al.*, 1980; Hodson *et al.*, 2002) and senescence of tundra vegetation reduces demand for nutrients (Tye and Heaton, 2008). Our study was conducted primarily in mid-July when high demand for nutrients by plants may have resulted in rapid terrestrial uptake (Keuper *et al.*, 2012), thus reducing the flux of nutrients to river channels and explaining the lack of significant differences in most nutrient concentrations between meltwater and groundwater end-members. Given that Arctic tundra ecosystems are often N-limited (Madan *et al.*, 2007; Kelley and Epstein, 2009), this may explain the surplus of PO_4^{3-} observed in groundwater end-members relative to meltwater.

Drivers of nutrient uptake in Arctic river systems

Uptake velocity for NH_4^+ was positively related to water temperature, suggesting low water temperature may act as a driving factor of river ecosystem metabolism in this region of Svalbard (cf. Rasmussen *et al.*, 2011). River metabolism is considered to be highly temperature-dependent (Yvon-Durocher *et al.*, 2012) with warmer temperature associated with increased photosynthesis, enzymatic and microbial activity, and nutrient uptake (Rasmussen *et al.*, 2011). Demand (V_f) for NH_4^+ was comparable to demand in lower-latitude Arctic, sub-Arctic and temperate headwater rivers (Figure 5; Ensign and Doyle, 2006; Rasmussen *et al.*, 2011). In contrast, areal-based uptake rates (U) were extremely low, most likely because rivers in Svalbard contain no macrophytes and the surface area for nutrient uptake by algal communities is relatively small (cf. Rasmussen *et al.*, 2011). However, the positive relationship between NH_4^+ U and chlorophyll *a* concentration suggests that biotic assimilation by autotrophs played a role in NH_4^+ uptake (Hall and Tank, 2003). In contrast, demand for acetate was not related significantly to chlorophyll *a* concentration, although this was not altogether unexpected because aquatic autotrophs obtain carbon predominantly through CO_2 and HCO_3^- (Allen and Spence, 1981) whereas uptake of dissolved organic carbon is controlled to a large extent by heterotrophic activity (Marti *et al.*, 2009).

The positive relationship between NH_4^+ uptake velocity and transient storage zone area indicates that increased hydraulic retention was associated with greater nutrient uptake capacity in these rivers. Conclusions of previous studies relating transient storage to nutrient uptake have been equivocal (Mulholland *et al.*, 1997; Hall *et al.*, 2002; Gücker and Boechat, 2004), but these results suggest temporary detainment of waters increased residence times and the contact of solutes with sediment biofilms (Merck *et al.*, 2012), thus increasing the potential for biogeochemical transformation. Interestingly, the lack of significant association between acetate retention and sediment respiration suggests microbial communities in hyporheic zones may not play as important a role in DOC processing in these Arctic rivers as in lower-latitude areas (e.g. Newbold *et al.*, 2006; Johnson *et al.*, 2009). The negative relationship between acetate U and water temperature is unclear. However, the negative relationship between acetate demand and the Pfankuch Index may be explained by more stable river channels promoting the growth and activity of heterotrophic organisms. Given that the Pfankuch Index is a relatively coarse device, we suggest future studies may benefit from a more detailed examination of the role of channel morphology in determining rates of nutrient retention in these rivers.

Regulation of NH_4^+ uptake by DOC availability

Our third hypothesis was that the presence of a labile source of DOC would stimulate NH_4^+ uptake by releasing N assimilation from C limitation in heterotrophic microbial communities. Taken alone, significant acetate uptake at only three sites suggested low demand for labile DOC. However, the observed increase in demand for NH_4^+ when added in conjunction with acetate suggests labile DOC availability does facilitate N retention in these rivers. It was less clear whether DOC uptake was influenced by NH_4^+ availability because demand ratios showed no clear pattern in relation to those of NH_4^+. The limited number of cases meant that these differences in nutrient demand were not statistically significant between single and dual additions, although it should be noted that the test did not account for rivers where uptake only occurred during the simultaneous additions. A previous study from Svalbard concluded that DOC availability regulated heterotrophic bacterial activity in lentic freshwaters in the Kongsfjorden area (Säwström *et al.*, 2007). Other studies have also established close links between the supply of DOC and demand for nitrogen in aquatic systems (Dodds *et al.*, 2004; Johnson *et al.*, 2009). In light of these results we neither reject nor accept our third hypothesis, but suggest further work is now needed to substantiate these findings. In particular, the application of stable isotope tracers may assist in understanding the relative roles of physical and biological retention in controlling downstream nutrient export (Tank *et al.*, 2006).

Conclusions and implications for nutrient cycling in Arctic rivers under a warming climate

This study investigated rates of nutrient uptake and links to controlling factors across a gradient of Arctic river types. The proportion of river discharge derived from meltwater was not significantly related to measured environmental variables (Hypothesis 1). A lack of significant removal of nutrients from the water column at several sites was attributed to cold water temperature, very low ambient nutrient concentrations, and low channel stability which together limited biotic growth and thus the capacity for nutrient uptake. However, nutrient retention variability was high between study rivers. Where significant retention occurred, short uptake lengths and high uptake velocities indicated high demand for nutrients. Uptake velocities for NH_4^+ were comparable to those in lower-latitude rivers, although areal-based uptake rates were low and limited probably by low algal biomass. Uptake of NH_4^+ was associated with warmer water temperature, algal growth and larger transient storage zones, while acetate uptake was associated with more stable river channels. The proportion of river discharge comprised of meltwater was not related to nutrient uptake (Hypothesis 2). Some evidence suggested NH_4^+ assimilation by heterotrophic communities was mediated by labile DOC availability (Hypothesis 3), although further work is required to explore more fully this potential relationship.

In the context of future warming in Arctic regions, shrinking glaciers and increased permafrost wasting are expected to result in an initial peak in meltwater generation followed by a shift towards groundwater-dominated river systems in the long term (Smith *et al.*, 2007; Walvoord and Streigl, 2007), which could increase nutrient loading in high-latitude rivers (Petrone *et al.*, 2006; Frey and McClelland, 2009). Moreover, there is growing concern over episodic atmospheric N deposition in the High Arctic (Kühnel *et al.*, 2011). Together, these factors could introduce substantial variation in nutrient fluxes and availability into historically sensitive and nutrient-limited environments (Shaver and Chapin, 1980). A combination of warmer water temperature, more stable river channels and increased nutrient availability is likely to increase freshwater biotic activity. The results of this study suggest that this may enhance retention of nutrients in some Arctic rivers. A concurrent increase in C supply linked to permafrost degradation (O’Donnell *et al.*, 2010) may enhance the capacity of these systems to process nutrients. Ultimately, future nutrient yields from high-latitude river systems will be determined by changes in nutrient loading versus the degree to which aquatic autotrophs and heterotrophs can assimilate and process these nutrients in a changed riverine environment.

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Figures

Figure 1 – Map of study area showing sampling sites, approximate river courses, relief (shaded), spot height measurements in meters asl, and glacier cover (dashed areas).

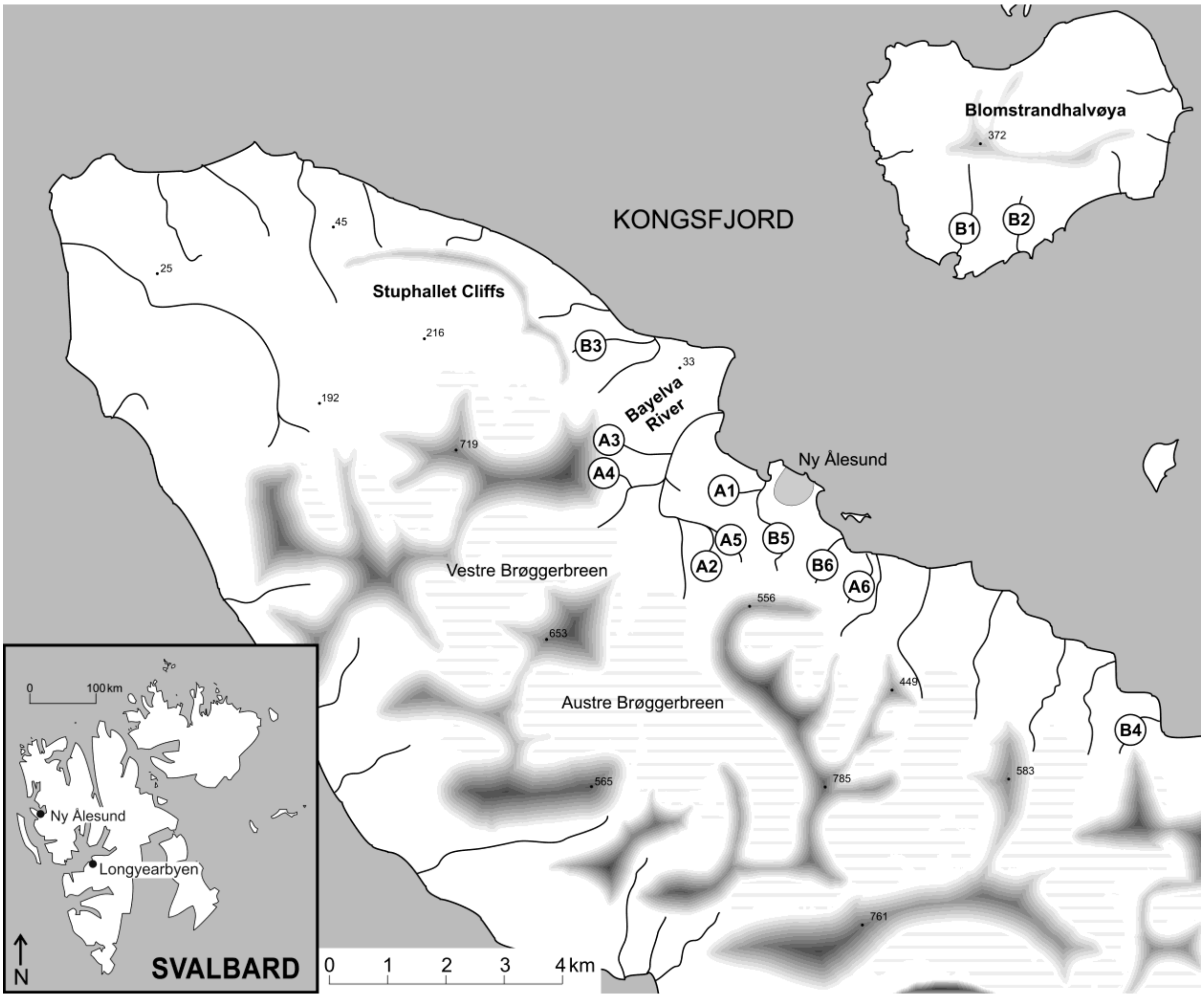


Figure 2 – Solute concentration curves as measured by electrical conductivity and OTIS-P model outputs for the main channel and transient storage zone for site B4

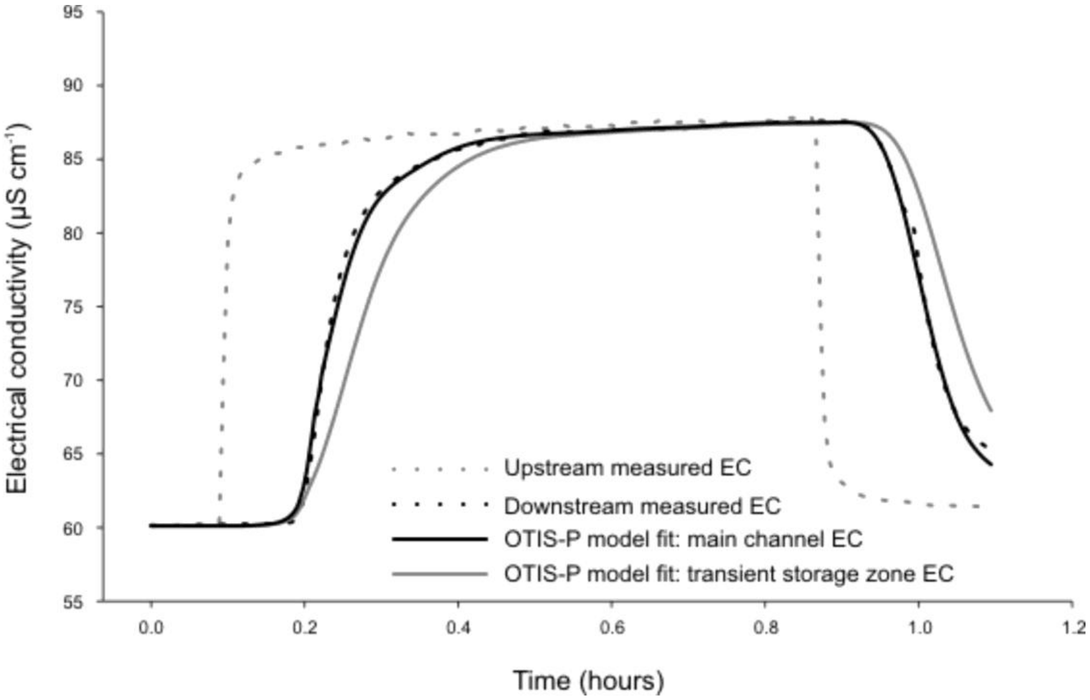


Figure 3 – Nutrient uptake velocity (V_f) for nitrate, ammonium, acetate and phosphate for single nutrient releases in the study rivers.

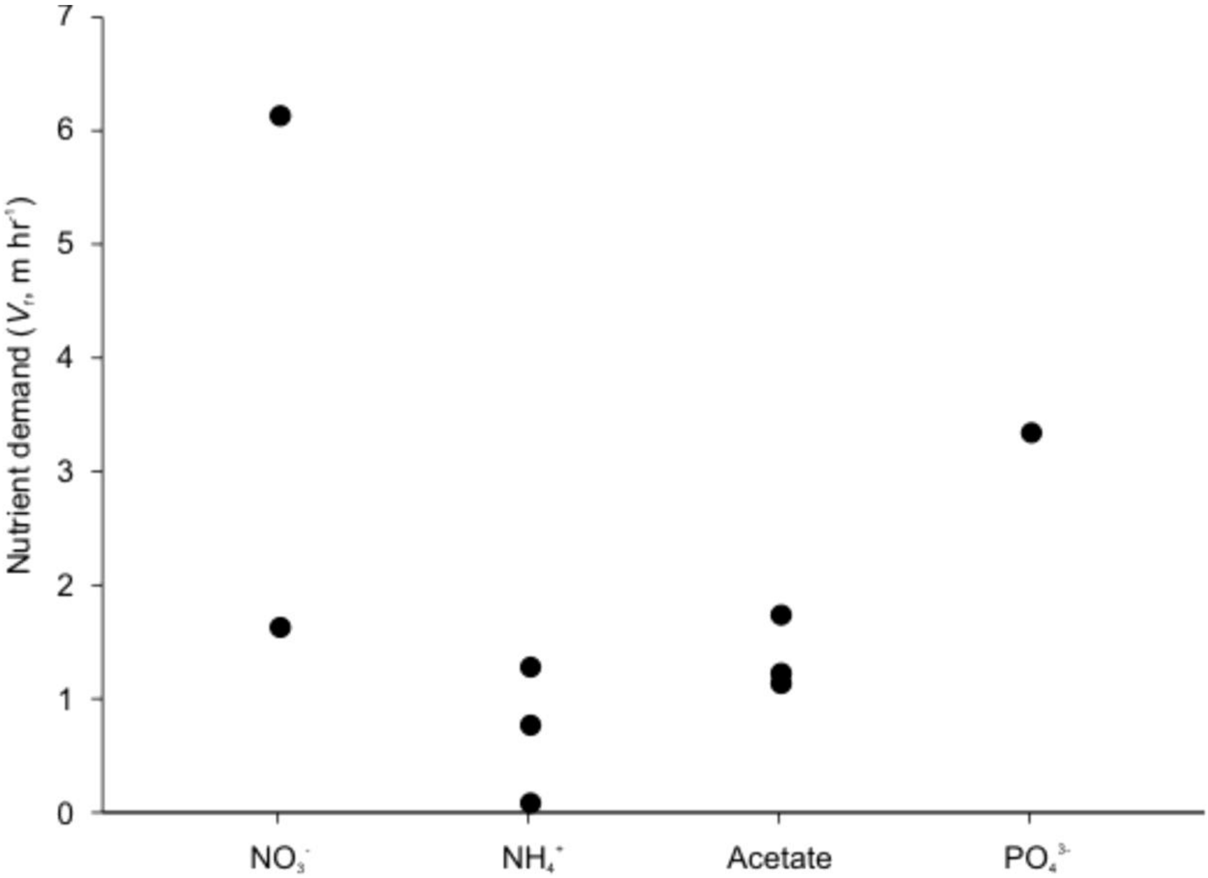


Figure 4 – Mean (±SE) ratios of simultaneous to individual nutrient uptake velocity (V_f) for ammonium and acetate. Nutrient uptake velocity was measured individually and then compared to when solutes were released together (i.e. NH_4^+ $_{+acetate}$ V_f : NH_4^+ V_f)

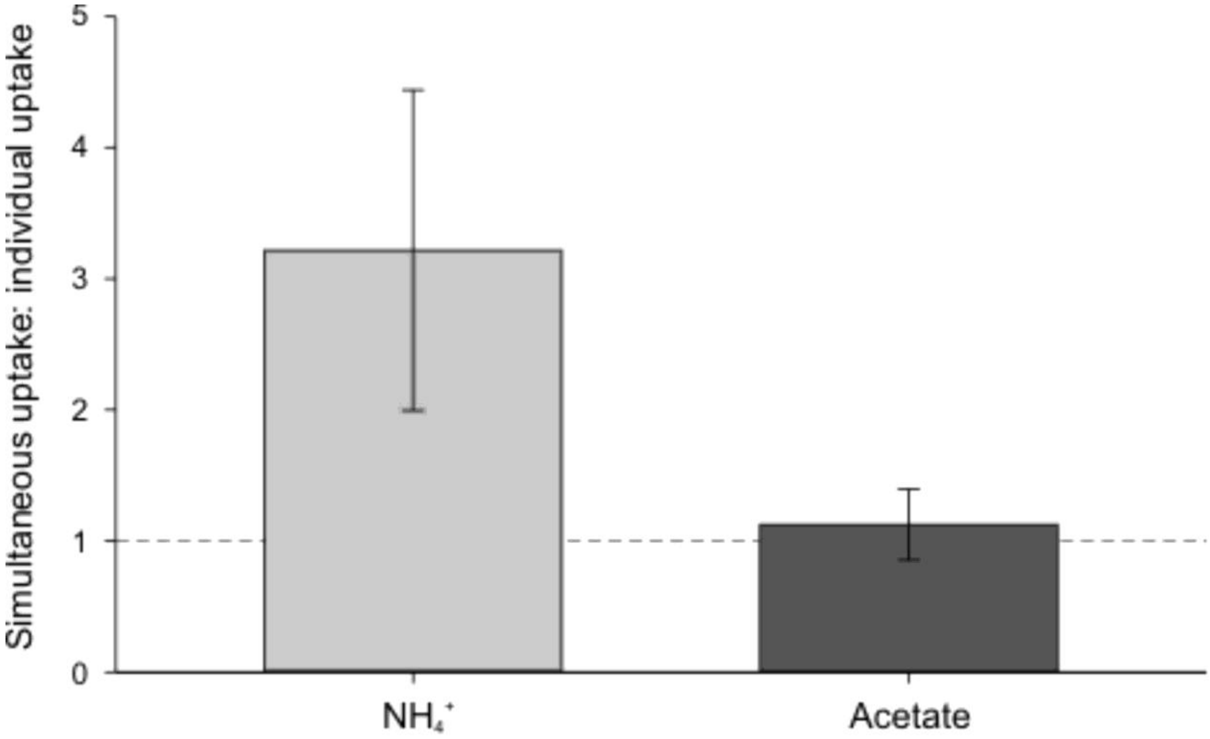
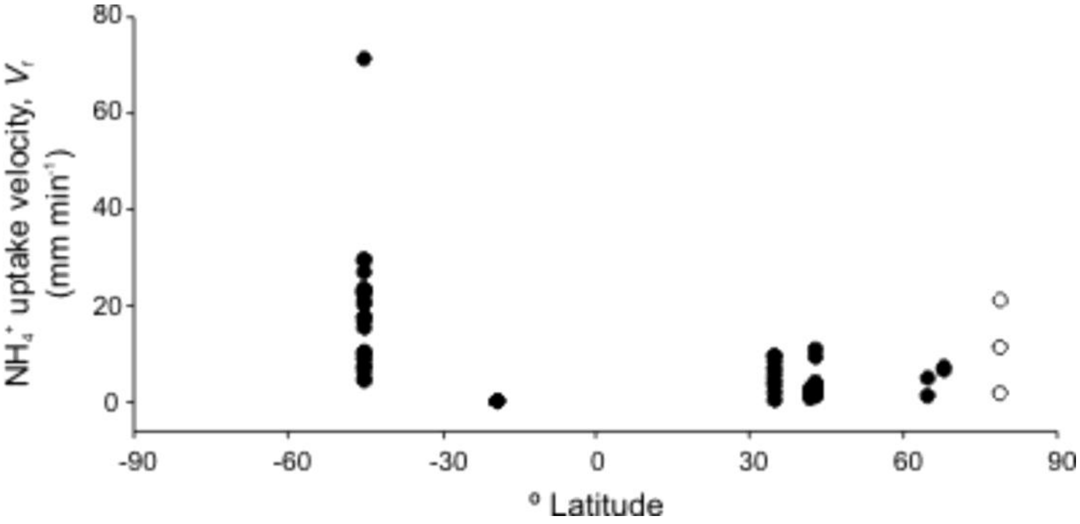


Figure 5 – Global nutrient uptake velocity (V_f) for ammonium using data from the present study (single additions only), Ensign and Doyle (2006) and Rasmussen *et al.* (2011). Rivers employed in this study are highlighted by open symbols.



Tables

Table 1 – Descriptions, background nutrient concentrations and environmental characteristics of the study rivers

Year	*Site*	*Discharge*	*Meltwater*	*Width*	*pH*	*Temperature*	*Suspended sediment*	*Conductivity*	*Pfankuch*	NO_3^-	NH_4^+	*Acetate*	PO_4^{3-}	*Chl a*	*Sediment respiration*
		$l\ s^{-1}$	*%*	*m*		*ºC*	$mg\ l^{-1}$	$\mu S\ cm^{-1}$	Index	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$\mu g\ l^{-1}$	$mg\ m^{-2}$	$\mu g\ O_2\ hr^{-1}\ kg^{-1}$
2011	A1	5	56	2.3	8.4	4.6	1	179	24	9	-	-	-	0.89	157
	A2	17	59	1.2	8.7	3.4	5	129	29	85	8	-	5	0.89	4
	A3	53	65	2.3	8.7	6.9	8	140	24	14	14	-	-	1.13	130
	A4	6	64	1.0	8.6	4.9	0	207	19	62	17	-	-	1.07	77
	A5	9	42	1.5	8.7	4.9	0	124	17	78	12	-	-	0.53	90
	A6	19	74	1.4	8.6	2.1	140	66	57	7	16	-	-	0.00	0
2012	B1	240	45	2.6	7.8	11.4	1	143	34	21	5	-	-	2.69	40
	B2	46	33	2.1	8.8	6.9	0	138	20	80	10	5	5	0.89	59
	B3	187	15	2.8	8.9	5.8	0	66	20	20	10	-	-	2.97	86
	B4	16	72	1.2	8.4	6.8	0	60	17	69	4	28	-	9.01	130
	B5	14	52	1.0	9.0	5.1	0	78	15	70	16	20	-	7.95	94
	B6	37	0	1.0	8.7	8.8	0	181	27	22	10	-	5	4.45	120

Table 2 – Spearman correlation coefficients for relationships between meltwater flow contributions and environmental habitat variables

	% Meltwater	*Discharge*	*Pfankuch Index*	*EC*	*SW radiation*	*Water temperature*	*SSC*	*Chlorophyll a*	*A_s/A*
Discharge	-0.29								
Pfankuch Index	0.11	0.52							
EC	-0.27	-0.08	0.22						
SW radiation	-0.26	0.53	0.14	-0.02					
Water temperature	-0.42	0.62 *	-0.11	0.26	0.61 *				
SSC	0.57	0.27	0.76 **	-0.12	-0.20	-0.31			
Chlorophyll a	-0.21	0.25	0.23	-0.07	0.60	0.65 *	-0.51		
A_s/A	-0.12	-0.50	-0.28	-0.32	-0.38	-0.18	-.200	-0.22	
T_{stor}	-0.03	-0.20	-0.13	-0.67	-0.37	-0.14	.090	-0.42	0.90 **

** and ** denote $p<0.05$ and $p<0.01$, respectively.* *$n=12$ except for A_s/A and T_{stor} where $n=8$*

Table 3 – Optimised output parameters and Damkohler numbers from OTIS-P model simulations for the study rivers

Site	*Relative storage zone area, A_s/A*	*Storage zone exchange coefficient, α* *s^{-1}*	*Mean storage zone residence time, T_{stor}* *min*	*DaI*
A1	1.0	0.0026	6.3	1.7
A2	-	-	-	-
A3	1.3	0.0014	15.5	0.7
A4	0.1	0.0005	4.4	2.6
A5	-	-	-	-
A6	-	-	-	-
B1	-	-	-	-
B2	3.1	0.0023	22.4	1.1
B3	0.9	0.0036	4.3	1.1
B4	0.5	0.0034	2.3	4.4
B5	3.0	0.0034	14.8	2.3
B6	0.8	0.0024	5.7	1.5

Sites where storage exchange parameters could not be estimated reliably are indicated by -

Table 4 – Nutrient uptake parameters for the study rivers. S_w is reported in m, V_f in m hr^{-1}, and U in µg m^{-2} hr^{-1}

Addition		*Site*											
		A1	*A2*	*A3*	*A4*	*A5*	*A6*	*B1*	*B2*	*B3*	*B4*	*B5*	*B6*
NO_3^-	S_w	-	-	16.29	-	-	-	-	47.70	-	-	-	-
	V_f	-	-	6.12	-	-	-	-	1.62	-	-	-	-
	U	-	-	83.95	-	-	-	-	113.2	-	-	-	-
NH_4^+	S_w	123.5	-	64.94	-	-	-	-	102.3	-	-	-	-
	V_f	0.07		1.27	-	-	-	-	0.75	-	-	-	-
	U	0.02	-	17.18	-	-	-	-	7.54	-	-	-	-
NH_4^+ *(+ Acetate)*	S_w	80.65	90.39	51.40	50.51	-	-	-	19.13	-	-	13.35	-
	V_f	0.22	0.54	1.41	0.55	-	-	-	4.03	-	-	3.90	-
	U	0.07	4.11	19.20	9.15	-	-	-	72.02	-	-	175.7	-
Acetate	S_w	-	41.20	-	-	-	-	-	44.74	-	-	46.50	-
	V_f	-	1.21	-	-	-	-	-	1.72	-	-	1.12	-
	U	-	12.09	-	-	-	-	-	1.72	-	-	8.79	-
Acetate *(+NH4+)*	S_w	-	40.10	-	-	-	-	65.20	61.13	-	25.25	28.24	-
	V_f	-	1.23	-	-	-	-	1.07	1.26	-	1.81	1.84	-
	U	-	12.56	-	-	-	-	1.08	6.31	-	8.40	11.5	-
PO_4^{3-}	S_w	-	-	-	-	-	-	-	-	-	-	15.71	-
	V_f	-	-	-	-	-	-	-	-	-	-	3.32	-
	U	-	-	-	-	-	-	-	-	-	-	8.29	-

- denotes no significant change in nutrient concentration throughout the study reach

Table 5 – Significant (p<0.05) spearman correlation coefficients for nutrient uptake parameter relationships with environmental variables

		n	*Discharge*	*Water temperature*	*Pfankuch Index*	*Chlorophyll a*	A_s/A ^
NH_4^+ *(+ Acetate)*	V_f	6	0.49	0.84 *	-0.58	0.64	0.90 *
	U	6	0.37	0.75	-0.70	0.81 *	0.80
Acetate $(+ NH_4^+)$	V_f	5	-0.90 *	-0.40	-0.99 **	0.60	0.40
	U	5	-0.80	-0.99 **	-0.40	-0.20	0.20

** and ** denote p<0.05 and p<0.01, respectively*

^ indicates n=5