

The High Arctic glacial ecosystem: new insights from nutrient budgets

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Abstract. This paper describes detailed budgets of water, Cl^- , dissolved Si and both inorganic and organic forms of nitrogen and phosphorus for two small glacier basins in Arctic Svalbard (Midre Lovénbreen and AustreBrøggerbreen). Rates of nutrient deposition are modest, dominated by inorganic nitrogen and episodically enhanced by extreme events. Hence deposition rates are also variable, ranging from 20 to 72 kg $\text{NO}_3\text{-N km}^{-2} \text{ a}^{-1}$ and 10–37 kg $\text{NH}_4\text{-N km}^{-2} \text{ a}^{-1}$ over just two consecutive years. Deposition of dissolved organic and particulate forms of nitrogen (DON and PN respectively) also appears significant and therefore requires further investigation (3–8 kg DON-N km^{-2} and 7–26 kg PN-N km^{-2} during winter – no summer data are available). Evidence for microbially mediated nutrient cycling within the glacial system is clear in the nutrient budgets, as is the release of large phosphorus, Si and organic/particulate nitrogen fluxes by subglacial erosion. The latter is entirely dependent upon the presence of subglacial drainage, promoting silicate mineral dissolution and the erosion of largely unweathered apatite. The large DON and PN fluxes are surprising and may relate to young organic nitrogen associated with microbial life within the glaciers. This is because wide spread assimilation of NH_4^+ and perhaps even nitrification occurs on the glacier surface, most likely within abundant cryoconite holes. Further microbial activity also occurs at the glacier bed, where denitrification and sulphate reduction is now known to take place. Thus a two component ‘glacial ecosystem’ is proposed that is highly sensitive to climate change.

Introduction

In recent years, ecologists have given major emphasis to the quantification of nutrient sources, transformations, and sinks at the catchment scale (Tockner et al. 2002). However, little attention has been given to the biogeochemical processes operating in cold regions, despite their sensitivity to climate change. These include ice-marginal ecosystems, where the abundance of inorganic nutrients may be perturbed by changes in cryospheric processes related to the leaching of nutrients from glacial till and seasonal snow cover (e.g. Appollonio, 1973; Quayle et al. 2002; Hodson et al. 2002, in press).

In a glacial context, studies of nutrient dynamics are particularly sparse and tend to be fragmented. The exceptions are inorganic carbon and silica, which have received significant research attention due to their importance with respect to geochemical feedbacks in the coupled cryosphere – atmosphere system (e.g. Sharp et al. 1995; Hodson et al. 2000; Tranter et al. 2002). Similarly,

glacial meltwater P concentrations have been used to assess the importance of rock weathering and suspended sediments in catchment P dynamics (Chillrud et al. 1994; Tockner et al. 2002; Hodson et al. in press). Otherwise, the nitrate anion (NO_3^-) is best known due to its role as a major ion and because it is recognised as a tracer of snowmelt (e.g. Tranter et al. 1994). The importance of NO_3^- in promoting microbial activity in glacierised catchments is also emerging as an area of current research (Sharp et al. 1999). However, other forms of nitrogen (NH_4^+ , dissolved organic N – hereafter ‘DON’) and phosphorus levels in glacial meltwater have been greatly neglected. This might reflect the increasingly redundant assumption that glacierised terrain is a largely abiotic environment, although recent microbiological studies are clearly challenging this assumption (Sharp et al. 1999; Skidmore et al. 2000; S awstr om et al. 2002).

Since no studies have presented comprehensive nutrient budgets for representative glacial catchments, the locus, magnitude and timing of nutrient cycling and transport are largely unknown. This paper therefore produces such budgets for nitrogen, phosphorus and dissolved silica in two adjacent glacierised catchments on Svalbard (Midre Lov enbreen and Austre Br oggerbreen). The comparison of the two glaciers is an important theme in the paper because delayed flow through a subglacial drainage system is absent at Austre Br oggerbreen. Thus we are able to adopt a paired catchment type approach and isolate the importance of subglacial processes.

The field sites

Both glacial catchments are situated in the Kongsfjord region of North West Spitsbergen, Svalbard (Figure 1). Details are given in Hodson et al. (2000, 2002, in press). Briefly, Midre Lov enbreen and Austre Br oggerbreen occupy catchments that are 10 and 32 km² respectively and both have mass balance records that demonstrate significant declines since the records began in the late 1960s (Hagen and Liest ol 1990; Kohler, unpublished data). Although both glaciers have a polythermal temperature structure, Austre Br oggerbreen is almost entirely cold-based and so no prolonged interaction between meltwaters and the glacier bed occurs (Hodson et al. 2002). In contrast, subglacial drainage can emerge from underneath Midre Lov enbreen all year and in spite of a significant cold ice surface layer (Hodson et al. in press). The presence and persistence of sub-freezing ice temperatures in both glaciers is greatly facilitated by the low rates of snow accumulation.

The southern sections of both catchments include mountains composed of phyllites and mica schists with beds of quartzite and some marble (Orvin 1934). North of these basement rocks, beneath the glacier termini and in the proglacial sandurs are younger carbonates, chert and some sandstone. Additionally, Devonian red bed sandstones are present in the Austre Br oggerbreen catchment which, along with a greater presence of carbonate rocks in the

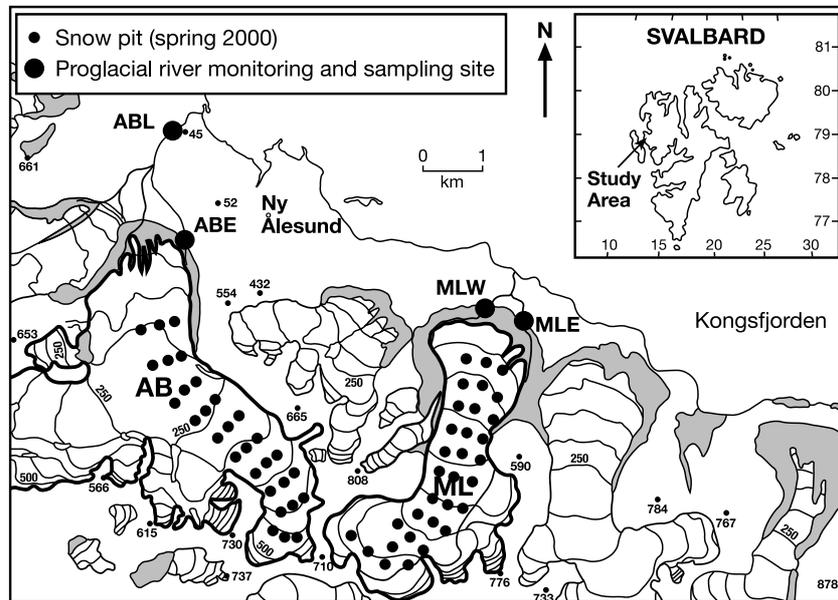


Figure 1. The field sites showing the two glaciers (outlined in bold) and their moraines (shaded area).

glacierised part of the Austre Brøggerbreen basin, represent the greatest differences in the geology of the two basins.

In both catchments, ground beyond the Little Ice Age moraines (which are ca. 1 km north of the contemporary ice margins) supports a sparse vegetation cover of *Dryas octopetala* and some polar willow (*Salix polaris*). Closer to the glaciers, higher plants are generally absent but mats of cyanobacteria (including *Nostoc* spp.) cover some areas and lichens are present upon moraine debris. Here significant populations of spiders and prey (chironimids) also exist at densities which indicate the potential to influence nutrient supply in these otherwise impoverished glacial tills (Hodgkinson et al. 2001). In addition, cryoconite melt holes on the glacier surface contain varied microbiological populations, including cyanobacteria (*Phormidium* and *Nostoc* spp.), chlorophytes (*Chlorella* and *Cylindromonas* spp.) and low numbers of ciliate organisms (Sävström et al. 2002; Laybourn-Parry, unpublished data).

Research methods

Hydrological monitoring

Ablation season field campaigns were carried out in 1999 (18 June–29 July; Day 169–210) and 2000 (17 June–10 August; Day 169–223) in the Midre Lovénbreen catchment. In the Austre Brøggerbreen catchment, field work was

carried out in 2000 only. Two principal monitoring locations were established on the main streams draining each catchment (Figure 1). At Midre Lovénbreen these consisted of two stations located at breaks in the end moraine believed to mark the maximum extent of glacial ice during the Little Ice Age (hereafter 'MLE' and 'MLW': see Figure 1). At Austre Brøggerbreen, the two sites were established at the ice margin in the vicinity of the eastern part of the end moraine (hereafter 'ABE') and some 3.5 km downstream from the ice front (hereafter 'ABL'). Like both MLE and MLW, ABE received runoff from the glacierised, mountainous and proglacial parts of the catchment. However, ABL received runoff from the entire ABE catchment as well as an additional glacier (Vestre Brøggerbreen) and an extensive, vegetated proglacial plain with sandur. These sites are all described in detail by Hodson et al. (2002).

Continuous records of discharge were estimated at all the principal sites. This involved using pressure transducers and Campbell Scientific data loggers logging at 30 s intervals and storing hourly averages for the MLE, MLW and ABE sites. Calibration of the transducer records was achieved using velocity area measurements every 1 or 2 days. Further details may be found in Mumford (2002). Errors in the discharge records were specified using the standard errors of the stage-discharge rating relationship, which varied between 16.6 and 10% at the MLW, MLE and ABE Sites. At ABL however, continuous records of runoff were provided from a crump weir maintained as part of the nation-wide monitoring undertaken by the NVE (Norwegian Water Resources and Energy Administration). Here errors of 3% have been specified by Pettersson (1991). Importantly, this year-round monitoring site was used to account for periods of unmonitored runoff at the other sites (see below).

In addition to runoff, summer precipitation amounts were logged as hourly totals using a Campbell Scientific 0.2 mm tipping bucket rain gauge installed in the proglacial region of Midre Lovénbreen. Additional weekly data were also used from the Norwegian Institute for Air Research (NILU) sampling site in Ny-Ålesund. Further details are available from Aas et al. (2001).

Runoff sampling

Sampling of meltwater was undertaken at the above principal runoff monitoring sites (see Figure 1) and also at a number of supraglacial streams, subglacial streams (Midre Lovénbreen only), and other proglacial streams where data loggers could not be installed. Single daily samples were collected from these sites between 14:00 and 20:00 h in 1999 and between 13:00 and 18:30 h in 2000. At Austre Brøggerbreen however, sampling was minimised to every 2 days after the initial snowmelt phase (i.e. after Day 203). All samples were taken from the stream with a clean 500 ml polyethylene flask, rinsed three times with meltwater and filtered immediately through 0.45 μm Whatman cellulose nitrate filter papers using a Nalgene polysulphone filter unit and hand pump. Deionised water blanks brought through the filtration procedure re-

vealed no detectable contamination from units or filter papers. All filtered samples were decanted into 60 ml Azlon polypropylene bottles for analyses (see below). In addition, one polypropylene bottle (125 ml in 1999, 60 ml in 2000) was held adjacent to the 500 ml sampling vessel, rinsed three times with stream water and then filled directly from the meltwater stream, unfiltered, for analysis of total P and N content.

Winter precipitation sampling

Sampling of the glacial snowpack took place at the beginning of the 1999 summer field campaign and in a much more detailed manner in the spring of 2000 (Days 118–121). Sampling conditions precluded the use of our 1999 data in the present paper due to an early onset of melt. In contrast, the snowpack survey of late April 2000 was conducted before the full development of the pre-melt season snowpack. These are typical problems in Svalbard and so our estimates of snowpack water equivalent were adjusted in accordance with data collected later on during the Norsk Polarinstitutts mass balance measurement programme (Hagen and Liestøl 1990; Kohler, unpublished data). Figure 1 shows the distribution of snow pits that we used during 2000. Three or more samples were collected across both glaciers in each of the 50 m elevation zones that are used by the Norsk Polarinstitutts mass balance monitoring.

The snow sampling protocol followed that described by Williams and Melack (1991) and Sickman et al. (2001). Thus an acid-washed PVC sampling tube was used to extract samples after rinsing with snow, all field personnel wore powder-free vinyl gloves and all samples were stored in double polyethylene bags that deionised water blanks showed not to be capable of releasing solute. Depth-integrated samples were taken down to the previous summer surface and included any icing formation within the pack. Firn samples were also taken separately. The density of all snow samples was determined gravimetrically using the contents of the tubes.

All snow samples were removed from the field as quickly as possible and stored in a freezer at $-18\text{ }^{\circ}\text{C}$ for less than 2 days in 1999 and 6 weeks in 2000. Samples were allowed to thaw completely at room temperature and then filtered, bottled and analysed following the protocol used for stream samples (see below).

Analytical protocols

Storage tests were used to develop a combination of Svalbard-based and UK-based analyses (see Mumford 2002). These showed that the major ions (except HCO_3^-), total phosphorus, total nitrogen, and even NH_4^+ remained unaltered for at least 3 months, provided that filtration was undertaken and the samples were refrigerated at $4\text{ }^{\circ}\text{C}$ in the dark. These species were therefore determined in the UK.

A FOSS-Tecator FIAstar 5000 was used to detect NH_4^+ following its liberation as NH_3 after the addition of NaOH. The gas was then detected photometrically at 590 nm (FOSS-Tecator, 2000a). In Svalbard, NO_3^- was determined photometrically at 543 nm following reduction to NO_2^- (after Mackereth et al. 1978; APHA, 1995). Analysis of sample without the reduction step allowed a correction to be made for any N present as nitrite. In this study, NO_2^- was not observed in measurable quantities. The detection limit for these tests was $3 \mu\text{g N/l}$. Precision errors were between 0 and 16% for NH_4^+ (mean 5.1%) and between 0 and 15% for NO_3^- (mean 2.6%). PO_4^{3-} was also measured in Svalbard following standard manual methods that include ascorbic acid reduction and spectrophotometric determination at 882 nm (Murphy and Riley 1962; Mackereth et al. 1978; APHA 1995). Dissolved phosphorus was often detected but was never quantifiable in any of the samples that were analysed (the detection limit was $5 \mu\text{gP/l}$).

Concentrations of total phosphorus in unfiltered samples and total dissolved phosphorus in filtered samples were determined following an acidic persulphate digestion method (FOSS-Tecator 2000b). For total nitrogen in filtered and unfiltered samples, an alkaline persulphate method was adopted (see Johnes and Heathwaite 1992) that enabled detection as NO_3^- in the sample using methods described above (FOSS-Tecator 2000c). Organic forms of nitrogen (hereafter 'DON') were then estimated as the difference between total dissolved N and the sum of the inorganic forms (NH_4^+ and NO_3^-) and reported above. The difference between total nitrogen and total dissolved nitrogen was then used to estimate particulate nitrogen (hereafter 'PN'). Here PN includes all organic as well as inorganic particles $>0.45 \mu\text{m}$. Dissolved organic and particulate forms of phosphorus were not estimated as no dissolved phosphorus was detected using our method (see above for detection limits).

SO_4^{2-} , Cl^- and NO_3^- levels in all filtered samples were determined using automated Dionex DX-100 ion chromatography upon return to the UK. Tests showed no significant difference with respect to the NO_3^- levels determined here and in Svalbard. Major base cation concentrations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by atomic absorption spectrometry in the UK laboratory after samples were acidified with 2% HNO_3 . Ca^{2+} and Mg^{2+} were measured in absorption mode, whilst Na^+ and K^+ were determined in emission mode. Caesium chloride was added to samples prior to Na^+ and K^+ analysis and lanthanum chloride was added prior to Ca^{2+} and Mg^{2+} analysis. Standard protocols were followed that are reported by Mumford (2002).

Sample pH was determined using a WPA portable pH meter and electrode with low ionic strength buffers (pH 4 and 7). The precision of pH measurements was ± 0.1 pH units. Total alkalinity (predominantly HCO_3^-) was determined by acidimetric titration. Lastly, dissolved silica was determined using a manual application of the molybdenum blue method reported by APHA (1995) and other standard texts. Duplicate pairs analysed throughout both seasons showed that mean precision errors for the above ion and dissolved Si tests were $<5.5\%$. The precision of the pH measurements was 0.1 pH units.

Estimation of nutrient budgets

In this paper, nutrient budgets are expressed in their most detailed form as:

$$\Downarrow^{\text{winter}} + \Downarrow^{\text{summer}} = Q^{\text{runoff}} \pm \Delta^{\text{bio}} \pm \Delta^{\text{ice}} \pm \Delta^{\text{crustal}} \quad (1)$$

where units are in $\text{kg m}^{-2} \text{a}^{-1}$, $\Downarrow^{\text{winter}}$ is the net winter bulk deposition measured at the onset of melt (positive for deposition, negative for net solute volatilisation or deflation), $\Downarrow^{\text{summer}}$ is bulk deposition during the summer, Q^{runoff} is the runoff nutrient yield and Δ^{bio} , Δ^{ice} and Δ^{crustal} are the net storage (negative)/release (positive) terms for biological (assimilation/mineralization), glacial (firn and glacier ice) and geochemical (dissolution/precipitation) processes in the catchment, respectively.

As we make use of mass balance data from the study sites, Δ^{ice} is further partitioned in the following manner:

$$\Delta^{\text{ice}} = S^{\text{firn}} - Q^{\text{ice}}, \quad (2)$$

where S^{firn} and Q^{ice} represent firn storage and glacier ice ablation, respectively. In the case of the water budgets, Δ^{ice} is therefore equivalent to the net mass balance of the glacier.

Since Δ^{bio} and Δ^{crustal} could not be measured directly, the sum [$\Delta^{\text{bio}} + \Delta^{\text{crustal}}$] was instead estimated from Eq. (1) once all other terms were known. Thus [$\Delta^{\text{bio}} + \Delta^{\text{crustal}}$] was highly sensitive to errors in the other budget terms, which necessitated the error estimation procedure, detailed later. We also used the degree of closure in the water and Cl^- budgets to look for further errors as in both cases they represent the simplified case where [$\Delta^{\text{bio}} + \Delta^{\text{crustal}}$] = 0.

Further details about the terms in Eqs. (1) and (2) that were estimated directly are given below.

Runoff yields (Q^{runoff})

Nutrient yields in runoff were estimated from the sum of daily discharge–concentration pairs (in g d^{-1}). The fluxes of the individual species were then estimated for the observation period following Eq. (3).

$$F_{\text{tot}} = \sum_{i=1}^n (Q_{\text{dtot}} C_i), \quad (3)$$

where F_{tot} , total flux of species of interest during observation period (g); Q_{dtot} = total discharge for individual days during period of interest ($\text{m}^3 \text{day}^{-1}$); C_i , concentration of single daily sample (mg/l).

Linear interpolation between values of C_i was employed to estimate a daily concentration series at the ABE and ABL sites after the sampling frequency was dropped to every other day (Day 203). Since diurnal variations in C_i were found to be muted in all streams (e.g. Hodson et al. 1998 and Mumford 2002),

the sampling frequency adopted in the present study was believed to be more than adequate for defining seasonal nutrient export.

In order to account for the full ablation season we used the total annual runoff records collected by the NVE at the ABL site to estimate the proportion encompassed by our observation period. The same distribution of runoff was therefore assumed at all sites, suggesting that 55 and 64% of annual runoff were measured in 1999 and 2000, respectively. Since water and solute fluxes were only missed at the end of the seasons, when variations in solute concentrations are usually muted, missing river fluxes were calculated from the product of the outstanding runoff flux and the volume weighted mean (hereafter 'VWM') concentration estimated from the last 10 days of the observation periods. The VWM concentrations were calculated using Eq. (4)

$$VWM = \frac{\sum_{i=1}^n (Q_i C_i)}{\sum_{i=1}^n Q_i}, \quad (4)$$

where VWM concentration of species of interest (mg l^{-1}) Q_i , instantaneous discharge at time of sampling ($\text{m}^3 \text{s}^{-1}$) C_i , instantaneous concentration at time of sampling (mg l^{-1}) n , number of samples.

Winter loading (\downarrow^{winter})

In a similar manner to other snow studies (e.g. Williams and Melack 1991; Sickman et al. 2001), estimation of chemical loading via snowpack development incorporated a VWM concentration and an estimate of SWE (snow water equivalent) across the glacier surface. VWM concentrations were therefore calculated in each elevation zone using Eq. (4) after substituting SWE (m) for Q ($\text{m}^3 \text{s}^{-1}$). Zone loadings were then estimated as the product of the zonal SWE-weighted mean concentration (VWM) and its SWE. Total loadings were then calculated as the sum of the area-weighted zonal loadings (Eq. 5).

$$L = \sum_{i=1}^{nz} \left(\left[\left(\frac{\sum_{i=1}^{ns} SWE_i C_i}{\sum_{i=1}^{ns} SWE_i} \right)_{Z_i} \times \overline{SWE}_{Z_i}^{NP} \right] \times Z \right), \quad (5)$$

where L , Solute loading of species of interest (g); SWE_i , SWE for individual pit (m); C_i , solute concentration for individual pit (mg l^{-1}); $\overline{SWE}_{Z_i}^{NP}$, Norsk Polarinstittut mean SWE for particular elevation zone (m); Z , zone area (km^2); nz and ns are number of zones and number of snow pits, respectively; Z_i indicates that data from each zone are treated separately.

In this paper, values of VWM for precipitation were based upon 1999/2000 data only and data were extrapolated to areas beyond the glacier mass balance

zones using simple quadratic regression relationships between SWE and altitude. The composition of the 1998/1999 snowpack was estimated from 1999/2000 data by using a scaling factor calculated using NILU data. These data report concentrations of Cl^- , NO_3^- and NH_4^+ (as well as other major ions) at Ny Ålesund. Ratios between the VWM concentrations of winter 1998/1999 and winter 1999/2000 derived from these NILU data were therefore used to transform our own concentration data for winter 1999/2000. In this way problems associated with the representativeness of the Ny Ålesund sampling site for the two local glaciers were reduced. However, since the NILU data lack DON and PN estimates, we instead assumed that the winter 1999/2000 $\text{DON}/[\text{NO}_3^- + \text{NH}_4^+]$ and $\text{PN}/[\text{NO}_3^- + \text{NH}_4^+]$ ratios were the same in 1998/1999.

Summer loading ($\downarrow^{\text{summer}}$)

The summer loading period was defined as the interval following the winter mass balance measurements (usually in April/May) and lasting until the end of the observation periods. The same scaling procedure defined above was also used to estimate the composition of bulk deposition during these intervals. However, in this case, uncertainty precluded the estimation of rainfall DON and PN data from just our own snowpit data. The concentration estimates for Cl^- , NO_3^- and NH_4^+ were therefore combined with precipitation data to estimate solute loading in the proglacial regions of the two glaciers. For this we used the most local precipitation gauges for each region namely our own gauge for Midre Lovénbreen (located at MLE; see Figure 1) and the NILU gauge for Austre Brøggerbreen (located at Ny Ålesund). The solute loading estimates were then distributed over each catchment using a precipitation gradient defined by average winter mass balance data. In both cases this was $26\% \text{ } 100 \text{ m}^{-1}$, which compares well with other studies of rainfall distribution across the Brøggerbreen catchment ($20\text{--}25\%/100 \text{ m}^{-1}$ according to Førland et al. (1997) and Hagen and Lefeauconnier (1995)). The use of a wet deposition gradient was not considered problematic because dry deposition represents a negligible proportion of bulk deposition for most solutes (Aas et al. 2001).

Ice melt (Q^{ice}) and firn storage (S^{firn})

The simplest means of assessing glacier ice and firn as nutrient sources/sinks was to incorporate the mass balance data and the chemistry of old snow and supraglacial streams sampled late in the 2000 observation period (1999 data were excluded for reasons that are discussed later). The mass balance data revealed that the negative balance of the two glaciers was responsible for 8 and 16% of proglacial runoff during the years under study. These runoff fluxes were then multiplied by the mean concentrations of solutes in four major supraglacial streams sampled on Day 220, 2000 to estimate “ Q^{ice} ”. The assumption

that late season (Day 220) supraglacial melt was representative of the composition of glacier ice was accepted because snowpack solute elution occurs in both catchments (Hodson et al. 2002; Mumford, 2002) and ensures that the composition of glacier ice, old snow and firn are similar with respect to the solutes of interest. Further, these dilute fluxes are likely to be insignificant terms in the budgets under consideration (see below).

The concentration of solutes remaining in the residual snow pack at the end of the ablation period was estimated from late season snow samples collected during September 2000. The product of the mean residual snowpack concentration data and its water equivalent (assessed as part of the mass balance monitoring) was therefore used to estimate firn storage at the end of each ablation season.

Error estimation

Errors were calculated using simple probabilistic approaches (Eq. 6: after Topping et al. 1972) on either a zonal basis (winter deposition), a daily basis (rivers) or across the entire glacier (firn storage and ice melt) and its basin (summer deposition). Where necessary, aggregation of errors was also undertaken using standard error theory.

$$E_F = \sqrt{(E_Q^2 + E_C^2)}, \quad (6)$$

where E_F , flux error (%); E_Q , error associated with water balance term (%); E_C , concentration error (%).

E_Q was derived from the standard errors of the stage-discharge rating relationships (rivers) and from Jansson's (1999) discussion of absolute glacier mass balance measurement errors (firn storage and glacier ice melt), which suggests a value of ca. 0.1 m/a for Δ^{ice} . The concentration error in all these cases was then specified using either analytical uncertainties for the study, or, where appropriate, standard errors associated with the calculation of a VWM concentration (after Mumford 2002). However, since neither E_Q nor E_C could be specified for summer bulk deposition, errors were assumed to be best represented by uncertainty calculations for snowfall (E_Q) and our own analytical errors for the same analytical protocols that NILU have adopted (E_C).

Results

Table 1 shows the nutrient budgets for the various sites together with the probable errors associated with their estimation. Figure 2 shows the most complete budgets available for the study sites, namely water, Cl^- , NO_3^- , and NH_4^+ (DON, PN, Si and TP lack estimates for summer deposition). In the

Table 1. Nutrient budgets for Midre Lovénbreen and Austre Brøggerbreen

	Water (m/a)	Cl (kg/km ² /a)	NO ₃ -N (kg/km ² /a)	NH ₄ -N (kg/km ² /a)	DON (kg/km ² /a)	PN (kg/km ² /a)	Si (kg/km ² /a)	TP (kg/km ² /a)
<i>1. Midre Lovénbreen, 1998/1999</i>								
Snow	0.520 ± 0.071	1150 ± 117	17.5 ± 1.26	9.11 ± 1.28	3.07 ± 0.799	25.8 ± 6.79	Tr	Tr
Rain	0.400 ± 0.071	451 ± 80.4	54.3 ± 11.4	28.2 ± 5.03	n.d.	n.d.	n.d.	n.d.
Firn	-0.06 ± 0.071	-47.6 ± 55.5	-0.39 ± 0.453	-0.10 ± 0.120	-0.62 ± 0.734	Tr	Tr	Tr
Ice	0.16 ± 0.100	25.1 ± 25.1	0.10 ± 0.062	0.20 ± 0.127	Tr	Tr	Tr	Tr
Runoff	-1.14 ± 0.0315	-1590 ± 61.7	-61.1 ± 3.90	-39.5 ± 2.85	-22.8 ± 3.08	-36.9 ± 4.38	-267 ± 21.0	-1060 ± 82.0
Residual	-0.120 ± 0.232	-16.3 ± 388	10.48 ± 17.5	-2.10 ± 10.4	-20.4 ± 5.90	11.14 ± 10.5	-267 ± 56.7	-1060 ± 229
<i>2. Midre Lovénbreen, 1999/2000</i>								
Snow	0.50 ± 0.071	1850 ± 188	9.57 ± 0.688	6.26 ± 0.881	2.81 ± 0.732	7.16 ± 1.89	Tr	Tr
Rain	0.35 ± 0.071	386 ± 78.6	10.7 ± 2.18	3.57 ± 0.727	n.d.	n.d.	n.d.	n.d.
Firn	-0.09 ± 0.071	-67.7 ± 52.7	-0.550 ± 0.430	-0.15 ± 0.116	-0.89 ± 0.703	Tr	Tr	Tr
Ice	0.07 ± 0.100	10.8 ± 15.5	0.040 ± 0.061	0.09 ± 0.125	0.00	Tr	Tr	Tr
Runoff	-0.83 ± 0.0275	-1960 ± 97.1	-21.6 ± 1.19	-3.01 ± 0.0943	-11.52 ± 1.02	-28.0 ± 1.57	-222 ± 13.3	-350 ± 32.6
Residual	-0.01 ± 0.268	217 ± 634	-1.80 ± 6.33	6.76 ± 1.42	-9.60 ± 3.76	-20.8 ± 2.46	-222 ± 61.5	-350 ± 105
<i>3. Austre Brøggerbreen and the Bayelva station (ABL), 1999/2000</i>								
Snow	0.43 ± 0.071	1940 ± 176	10.5 ± 0.776	6.32 ± 0.717	7.56 ± 1.84	11.5 ± 2.98	Tr	Tr
Rain	0.27 ± 0.071	292 ± 77.1	8.12 ± 2.14	2.70 ± 0.710	n.d.	n.d.	n.d.	n.d.
Firn	-0.04 ± 0.071	-32.9 ± 58.4	-0.27 ± 0.477	0.07 ± 0.130	-0.58 ± 1.03	Tr	Tr	Tr
Ice	0.29 ± 0.100	45.0 ± 15.5	0.18 ± 0.0610	0.36 ± 0.125	0.00	Tr	Tr	Tr
Runoff	-0.89 ± 0.0166	-2370 ± 45.9	-26.7 ± 0.478	-5.84 ± 0.112	-4.89 ± 0.186	-11.1 ± 0.427	-83.4 ± 1.58	-64.3 ± 2.02
Residual	0.05 ± 0.180	-126 ± 413	-8.14 ± 3.90	3.61 ± 1.41	2.09 ± 2.10	0.36 ± 2.75	-83.4 ± 8.35	-64.3 ± 6.60
ABL runoff	-0.85 ± 0.00791	-2190 ± 18.8	-24.3 ± 0.227	-3.33 ± 0.0334	-2.97 ± 0.0730	-23.4 ± 0.639	-123 ± 1.18	-51.3 ± 0.837

'Tr' denotes that trace quantities (below reliable detection) were present (and therefore negligible budget terms), whilst 'n.d.' means 'not determined.' 'DON', 'PN' and 'TP' represent operational definitions of 'dissolved organic nitrogen', 'particulate nitrogen' and 'total phosphorus', respectively. Inputs to the catchments are positive, whilst outputs (rivers) and sinks (firn) are negative. 'Residual' refers to any outstanding nutrient balance and so positive values indicate an excess of inputs.

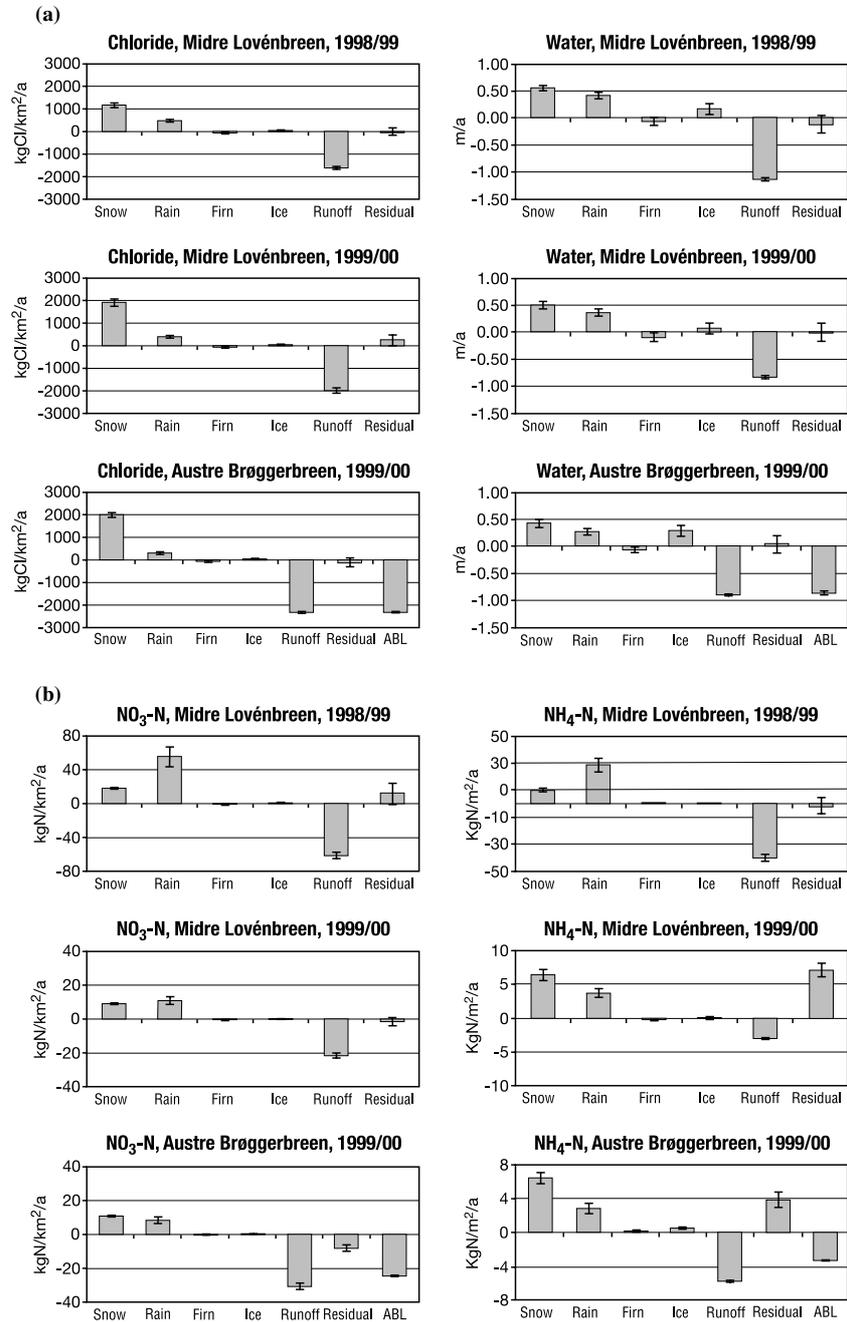


Figure 2. Budgets of water, Cl⁻ (Figure 2a), NO₃⁻ and NH₄⁺ (Figure 2b) and their probable errors for the various sites. 'ABL' denotes the runoff yields for the ABL site.

case of the water and Cl^- data (Figure 2a), budget closure occurs well within reasonable error limits and insignificant residual terms ('residual' in Table 1) suggest that all major components of these budgets are accounted for. This supports the assertion that Cl^- behaviour is conservative in the study basins (Hodson et al. 2002). However, the other solutes in Figure 2b do not indicate such behaviour on a consistent basis. For example, during 1999/2000 the NO_3^- budgets appear to balance at Midre Lovénbreen, whilst they indicate significant excesses in runoff at Austre Brøggerbreen.

Perhaps the least conservative nitrogen species in Figure 2 is NH_4^+ during 1999/2000. Both Midre Lovénbreen and Austre Brøggerbreen indicate significant retention of this N species during this particular year. This has also been observed in Midre Lovénbreen basin during 2001/2002 and 2002/2003 (Wynn, unpublished data) and we therefore suggest that this is a common occurrence in Svalbard glacier basins.

A striking feature of the data set is the important inter-annual variability in all of the major nitrogen fluxes. Figure 3a, b combine NILU data (Aas et al. 2001) with our own rainfall observations to show why. The monthly data clearly indicate major deposition over the catchments during June 1999 (Figure 3a). When weekly data are considered, a very significant episode of deposition is apparent between Day 178 and Day 180 in 1999 (Figure 3b). This had an immediate impact upon stream NO_3^- and NH_4^+ concentrations that persisted for the entire observation period due to storage in the subglacial system (see Mumford, 2002). It is therefore clear that the nitrogen budgets for 1998/1999 were greatly influenced by this particular wet deposition event.

The other nutrient budgets in Table 1 reveal important internal sources of Si and TP due to chemical and physical erosion (see Hodson et al. 2000, in press). Thus riverine yields are the dominant feature of these budgets. The relative magnitude of the yields also testifies to the importance of subglacial processes because for Si they are ca. 3× greater at Midre Lovénbreen when compared to Austre Brøggerbreen, whilst for TP yields they are in excess of one order of magnitude greater. Interestingly, there are also much larger riverine yields of DON and PN at Midre Lovénbreen relative to Austre Brøggerbreen. These are only partly accounted for by DON and PN loading via winter snowpack and, although data are missing, are unlikely to be accounted for by summer deposition (which should be broadly similar in the two glacier basins). Further examination of the data show that the large DON and PN surpluses are entirely derived from the subglacial river that drains through the MLE Site.

Discussion

Bulk deposition and variability in nutrient export

In all cases except NH_4^+ , the largest single term in the budgets for each nutrient was runoff. Runoff N was dominated by NO_3^- , which accounted for the majority

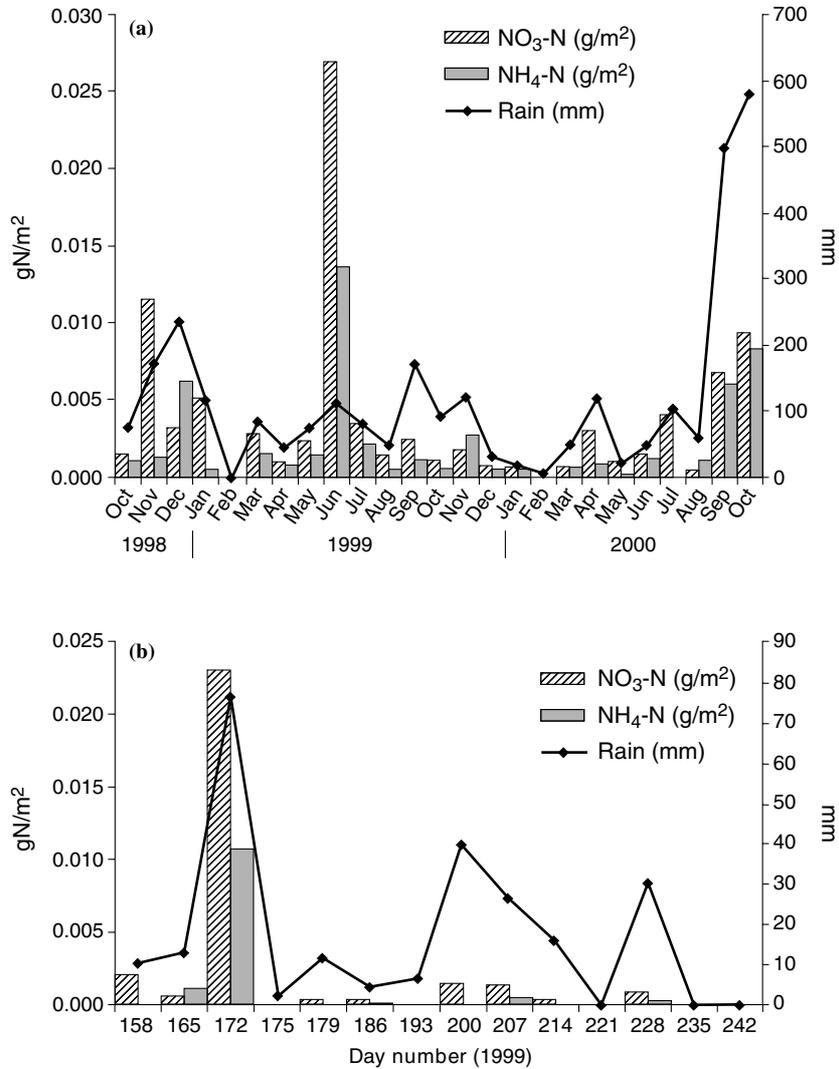


Figure 3. Deposition of inorganic nitrogen (NO_3^- and NH_4^+) in the Midre Lovénbreen basin on a monthly basis during the entire study period (Figure 3a) and on a weekly basis during the summer 1999 observation period only (Figure 3b).

of inorganic N at all sites during the years monitored. However, the composition of dissolved inorganic N (DIN) differed between the two years, being 61% NO_3^- in 1998/1999 and 82–88% NO_3^- in 1999/2000. DIN export also differed in magnitude between the 2 years: NH_4^+ yields in runoff during 1998/1999 were an order of magnitude greater than during 1999/2000. The difference was less significant for NO_3^- , being 2.5× greater in 1998/1999. A striking feature of the

nutrient yields is therefore the potential inter-annual variability due to the episodic deposition of nitrogen (Figure 3). In this study, such an event was witnessed during the early stages of the ablation season, when runoff infiltration into frozen ground was minimal. This enabled a greater impact upon the magnitude of the nutrient yields transported by the rivers and shows that summer wet deposition can dominate both the inputs and outputs of nitrogen from the Arctic glacial cryosphere. In contrast, large runoff fluxes that are caused by glacier ice ablation do not appear capable of enhancing the runoff yield of nitrogen, largely because glacier ice is dilute and therefore a poor source of this nutrient (Table 1).

It is unfortunate that a lack of data precludes full assessment of DON and PN deposition. However, the winter snowpack data clearly indicate that DON and PN deposition are significant and since most Arctic monitoring programmes only consider N in the form of NO_3^- and NH_4^+ , we argue that urgent attention be given to potentially labile inputs of DON and even PN (especially in the context of particulate organic matter).

A glacial ecosystem?

Several artefacts of our data set suggest that nutrients display distinctly non-conservative behaviour in the glacier basins under study, particularly during 1999/2000, when no large episodic events 'swamped' the summer data. Since non-conservative behaviour may indicate nutrient turnover by a viable microbial biomass, we argue that the following features may be diagnostic of the presence of a 'glacial ecosystem':

- (1) An additional source of NO_3^- means that runoff yields exceed deposition by a significant margin at Austre Brøggerbreen, but not at Midre Lovénbreen (where a small excess is less than probable error);
- (2) Large scale NH_4^+ retention occurs at all sites during 1999/2000;
- (3) Major surpluses of DON and PN exist in runoff from Midre Lovénbreen (due to large subglacial river fluxes) which are absent at Austre Brøggerbreen.

In the discussion below it is suggested that these are clear signs that the glaciers themselves bear the characteristics of an ecosystem characterised by microbial utilisation of one or more nutrient pools. Therefore, in order to account for these characteristics, we argue that (1) is not significant at Midre Lovénbreen due to denitrification in a partially anoxic subglacial environment, where high flushing rates and erosion also cause (3). Further, (2) is believed to occur due to biological activity which we have observed on the surface of both glaciers, and may involve nitrification. The two contrasting environments of the glacier bed and the glacier surface are therefore discussed in this context below.

Subglacial nutrient transformations: evidence for denitrification

Drainage of subglacial water from beneath Midre Lovénbreen is often characteristically anoxic during the winter and the early stages of the summer ablation season (Wynn, unpublished data; Wadham pers. comm. 2001). When this runoff freezes during the winter period, an extensive icing often forms over ca. 0.2–0.7 km² of the proglacial region (Wynn 2001). Pockets of anoxic sediments characterised by sulphate reduction are abundant beneath this icing and may also be observed in tills recently exposed by glacial retreat. Further, the widespread occurrence of these bacteria has been inferred by Wynn (in prep.) following his analysis of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in the SO_4^{2-} of subglacial drainage. Earlier observations of sulphate reduction beneath glaciers also exist and suggest that this microbially mediated process may be common beneath both Arctic and Alpine glaciers (see Sharp et al. 1999; Skidmore et al. 2000; Bottrell and Tranter 2002; and Wadham et al. in review). We believe that denitrification may also be a feature of these environments because the NO_3^- content of winter icings and early subglacial drainage is often close to detection limits and extremely low relative to Cl^- and NH_4^+ (Wynn, in prep 2001). Second, Skidmore et al. (2000) has showed that significant depletion of NO_3^- occurs following the anaerobic incubation of basal glacier ice collected from other glaciers (Ellesmere Island, Canada). Third, there are periods when the NO_3^- content of subglacial drainage at Midre Lovénbreen drops below detection limits during the course of the ablation season. Figure 4 shows such a scenario: a period of declining NO_3^- is coincident with a decrease in the SO_4^{2-} content of subglacial drainage. This cannot be explained by dilution because all other snowpack-derived solutes (e.g. Cl^-) actually increase and because NO_3^- was present in all other streams draining the glacier at the time (Hodson, unpublished Data). The short-lived loss of NO_3^- (also observed in bulk meltwaters at MLE) and the decrease in the SO_4^{2-} during a period in which the ionic strength of subglacial meltwaters was generally increasing suggests that delayed runoff from the bed may be influenced by sulphate and nitrate reduction. Similar events of NO_3^- loss have also been observed at Haut Glacier D’Arolla prior to Bottrell and Tranter’s (2002) study of microbial sulphate reduction at this site (see Tranter et al. 1994). These observations suggest that denitrification is a detectable feature of nitrogen cycling in subglacial environments beneath Midre Lovénbreen and a number of other glaciers.

Although little can be said of the DON and PN nitrogen pools in the present study, there is clear evidence that the subglacial river generates an excess of these two species in runoff relative to riverine yields at Austre Brøggerbreen. Also, since summer deposition of PN and DON are likely to be broadly equivalent in the two glacier basins, some internal source(s) of DON and PN appears to be present at Midre Lovénbreen that is intimately linked to its subglacial drainage. Both of these artefacts could indicate the evacuation of subglacial microorganisms together with the dissolved by-products of their activity/decay. However, an entirely physical reason for the presence of DON

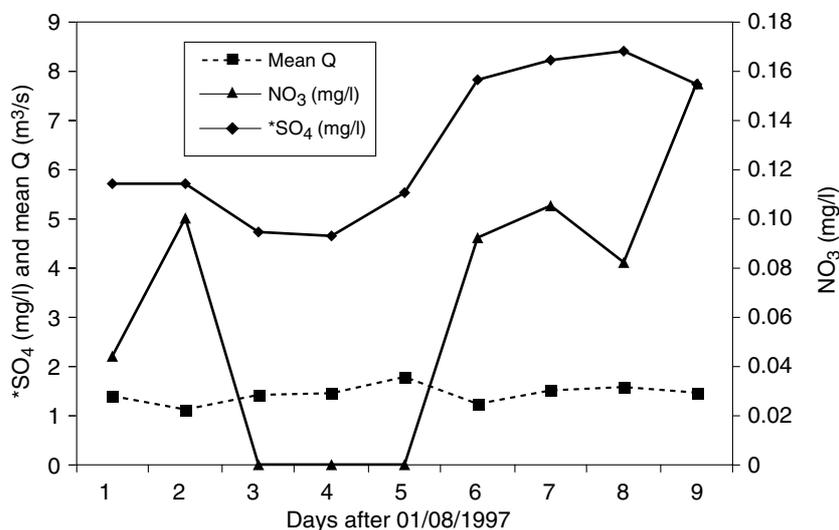
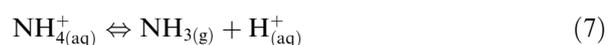


Figure 4. Periodic disappearance of NO_3^- and declining SO_4^{2-} concentrations in the subglacial stream emerging from beneath Midre Lovénbreen during 1997 (Hodson: unpublished data). Average total runoff recorded at the downstream MLE site is also shown.

and PN in the turbid subglacial meltwaters is also considered later in this manuscript.

Supraglacial nutrient transformations: NH_4 assimilation and nitrification?

Under current mass balance conditions, the surfaces of both glaciers are characterised by rapid snowline recession and high end-of-summer snowlines (Kohler, unpublished data). This suggests that any snowpack-related process responsible for the ‘loss’ of NH_4^+ in Table 1 is most important during the early stages of the ablation season. Such processes may involve volatilisation and/or assimilation by snowpack biota. However, the former (see equation 7) is unlikely because the pH of the snowpack is low (5.21–5.70: Mumford, 2002) and its snowmelt (even during elution) is relatively dilute. Both of these conditions greatly minimise NH_3 gas diffusion across the air–water interface (see Thibodeux 1996).



Our observations upon the bare glacier ice surfaces exposed following snowpack recession favour an alternative, biotic control upon the NH_4^+ ‘loss’ in the budgets specified in Table 1. This is because ca. 6% of the ablation areas were characterised by cryoconite holes: small oligotrophic melt pools that are formed by the solar heating of dark, organic matter on glacier ice (e.g. Wharton

et al. 1981; Takeuchi et al. 2001; Sävström et al. 2002; Tranter et al. 2004). These features rapidly form once such matter is deposited (either by wind or by water) upon the ice of these glaciers. Research in Arctic and Antarctic environments has found sufficient microbial life in these holes to suggest that they may be important loci for liquid water N utilisation and even atmospheric N fixation across the glacier (Wharton 1981; Sävström et al. 2002; Tranter et al. 2004). Importantly, free water in the snowpack (due to rain-on-snow or saturation by melting) bathes the microorganisms on these glaciers in nutrient-rich solutions that can promote nutrient uptake early in the ablation season (c.f. Jones and Deblois 1987). Further, our preceding discussion indicated that nutrient supplies may be supplemented after recession of the transient snowline by concentrated, episodic summer precipitation falling directly onto the glacier.

Studies of cryoconite biota therefore started upon Midre Lovénbreen during 2000 (see Sävström et al. 2002). The holes studied were typically up to 20 cm deep and 10 cm wide with a thin cover of organic matter at the base. Communities of organisms within the holes have been shown to include cyanobacteria, bacteria, nanoflagellates, ciliates and algae (Sävström et al. 2002). Samples of water and bottom material were abstracted from cryoconite holes on Midre Lovénbreen and analysed for biomass and photosynthetic capacity (see Sävström et al. 2002). Bacterial concentrations were generally higher in bottom material than in overlying water. Within this benthic material cyanobacteria were also common and included *Nostoc* spp. Photosynthetic rates ranged from 0.60–157 $\mu\text{g l}^{-1} \text{h}^{-1}$ and compared favourably to proglacial and extraglacial lakes in the study area (J. Laybourn-Parry, personal communication 2003). Nutrient analyses found low concentrations in the dissolved phase within the holes (largely because they were continuously bathed by dilute icemelt during the sampling period). However, N and P levels in the benthic organic matter and debris were very significant and so the PN and TP concentrations of entire holes ranged from 6.31 to 34.70 mg N l^{-1} and 1.80 to 4.05 mg P l^{-1} . These observations clearly show that primary productivity is detectable upon the glaciers following the retreat of the transient snowline and so it is reasonable to suggest that microorganisms present within cryoconite holes may have been responsible for the uptake of NH_4^+ from snowmelt. Further, given that ca. 6% of the ablation areas of the study glaciers are characterised by cryoconite material, the holes themselves might represent one of the largest potentially labile nutrient pools in the entire system.

Studies from other cold regions have also reported the utilisation of NH_4^+ and its conversion to NO_3^- (Campbell et al. 2000), a feature that might explain the surplus of NO_3^- in runoff from Austre Brøggerbreen and that may be masked in the Midre Lovénbreen data set by denitrification occurring at the glacier bed. For example, Baron et al. (1995) reported that although NH_4^+ and NO_3^- contributed to total inorganic N deposition in approximately equal amounts, NH_4^+ became rapidly consumed or oxidised to NO_3^- in the snowpack, in soils or in surface waters. Further, Sueker et al. (2001) observed identical artefacts in her study and suggested that either an unaccounted-for

source of NO_3^- was present, or that nitrification was occurring. The latter conclusion was also reached by Tockner et al. (2002) in their study of an Alpine glacier basin in Switzerland. However, studies of Alpine snowpacks in the U.S. have failed to observe nitrification (Williams et al. 1996), whilst other glacial studies have supported the notion that an additional source of NO_3^- might be present which is unrelated to microbiological processes, namely the oxidation of geologic N (Tranter, unpublished data; Mumford 2002). At present the importance of both young and old organic matter are therefore under close scrutiny in the Midre Lovénbreen and Austre Brøggerbreen glacier basins, and the presence of nitrifying bacteria in both the snowpack and cryoconite holes is being examined (e.g. Wynn in prep.).

Glacial erosion and nutrient provision

The efficacy of sediment evacuation by glacial meltwaters in Svalbard is reasonably well known (e.g. Hodson et al. 1997), as are the rates of chemical denudation that occur (Hodson et al. 2000). Thus it is already well known that subglacial drainage exerts a major influence upon the export of suspended sediment and crustally derived solute from the glacier basins present. Table 2 suggests that this also explains the large TP and Si fluxes from Midre Lovénbreen relative to Austre Brøggerbreen. This is because high rock–water contact ratios are restricted to areas at the margin of Austre Brøggerbreen where large, lateral and englacial drainage channels become deeply incised into till and moraine near the ice margin. The opportunity for rock–water interaction and erosion in such environments is greatly restricted when compared to those afforded by a distributed subglacial drainage network (e.g. Hodson and Ferguson 1999).

Since dissolved phosphorus was not detected in the present study, the great majority of the TP must be sediment-bound in some way. Hodson et al. (in press) and Mumford (2002) show that this is indeed the case and that nearly all the sediment-bound P is present as unweathered apatite, the principal form of P in the earth's crust. Thus glacial erosion favours potentially large TP yields (especially where subglacial drainage is present), but very little of this P is readily bioavailable. Hodson et al. (in press) argue that the effects of apatite disaggregation by glacial erosion may therefore be most important over longer time scales, following the development of soils with long residence time hydrologic flow paths through them. A similar argument has been developed for the impact of physical erosion upon silicate weathering (e.g. Millot et al. 2002). Thus the full impact of glacial erosion upon the bioavailability of P and perhaps also Si cannot be inferred from short data series and research upon the mobility of these key nutrients over longer time scales (c.f. Anderson et al. 2000) should be undertaken.

An unexpected feature of the nutrient budgets was the significant surplus of DON and PN in runoff at Midre Lovénbreen. Our data show that this is

entirely due to the subglacial river, giving further evidence that a major organic nitrogen pool and microbial community might exist beneath these glaciers. However, it is also possible that some organic nitrogen (particulate or dissolved) may be derived from either young organic matter associated with the cryoconite biota, or older organic matter associated with over-riden soils and bedrock. The latter might be particularly important in the context of PN because it might be released when the aggressive digest procedure is applied to the very turbid subglacial water samples. However, since cryoconite holes and (periodically) turbid runoff were also reported at Austre Brøggerbreen, neither of these sources of N appear to explain the large subglacial yields of DON and PN. A further possibility that the PN excess was due to nitrogen adsorption onto suspended sediments (e.g. as NH_4^+ and thus accounting for its 'loss' in the budgets) may also be discounted since standard sorption tests failed to indicate the occurrence of this process (Mumford 2002). Therefore, further studies are required to characterise the organic and particulate nitrogen pools that our nutrient budgets have revealed to be of significance.

Downstream changes in nutrient yields

Figure 5 shows the water, Cl^- and nutrient fluxes at the ABE site expressed as a ratio of that at the ABL site. Due to differences in the catchment areas, the ratio is ca. 0.31 when the yields (fluxes standardised with respect to catchment area) are identical. Thus ratios in excess of 0.31 identify the proglacial region as a sink for solute/nutrient (DON , NH_4^+ and, to a lesser extent TP), whilst

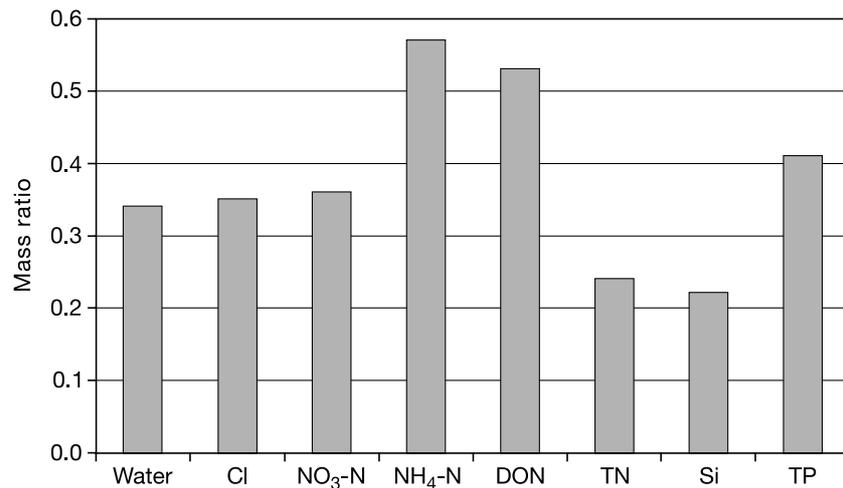


Figure 5. Ratios of ABE site fluxes to ABL site fluxes.

lower ratios identify it as a source (e.g. PN and Si). Major ion and suspended sediment transport data from these sites have also been analysed successfully in this manner by Hodson et al. (1998, 2002). Interestingly, the ratios are close to 0.31 for the water, Cl^- and even NO_3^- , indicating quasi-conservative behaviour throughout the entire basin. High ratios for NH_4^+ (0.57) and DON (0.53) however, clearly indicate that N retention is a major feature in the forefield downstream from the ABE Site. Importantly, the high ratio for DON might also indicate that labile organic N species are present in atmospheric deposition. The conservative behaviour of NO_3^- is surprising because Hodson et al. (2002) found evidence that nitrification in proglacial soils enhances the NO_3^- content of runoff during warm periods after snowpack recession. It is possible that this was suppressed by low air temperatures during the 2000 ablation season (the July average was only 3.5 °C at 100 m altitude: Hodson, unpublished data) caused by the return of freezing conditions in late July, a period when soil temperatures would normally be close to their annual maximum.

Hodson et al. (2002) examined geochemical data from the ABE and ABL Sites and concluded that the downstream sandur and forefield were geochemically significant in the context of carbonate and silicate weathering. This is also a major finding in the work undertaken at similar distances from an ice margin by Anderson et al. (2000) in Alaska. In our case, the downstream release of Si occurs on a sufficient scale to greatly reduce the ABE/ABL flux ratio for Si to 0.22. Thus, the low ratio for Si shows that even shallow permafrost soils and aquifers in the forefield may promote extended rock–water contact and result in significant enhancement of silicate denudation rates.

Conclusion

Glaciers in Svalbard, part of the European High Arctic, receive modest rates of nutrient deposition that may be highly variable from year to year due to extreme episodic events. This can have a marked effect on the magnitude of nutrient deposition and also nutrient yields transported by rivers into adjacent fjords. We find that organic forms of nitrogen are present alongside NH_4^+ and NO_3^- and therefore urge the role of former to be assessed in the context of Arctic ecosystem processes. This is because only inorganic forms of nitrogen have been typically considered in the past.

Construction of detailed nutrient budgets that make use of the above nutrient deposition estimates has now been undertaken for two high Arctic glacier basins in Svalbard. Water and Cl^- budgets were also constructed and their closure within reasonable error limits was used to provide support for the fact that, during ‘normal’ water years (not subject to extreme nutrient inputs associated with a large degree of uncertainty), nitrogen budgets are distinctly imbalanced, suggesting that additional microbially mediated processes may be

operative. Interestingly, comparison of a cold-based glacier with a polythermal one allowed both the supraglacial and subglacial environments to be assessed in this context. We found that the former probably impinges most significantly upon the nutrient budgets by promoting NH_4^+ assimilation and perhaps nitrification within cryoconite holes. Snowpack biota may also be responsible but there is a tendency for low rates of winter snow accumulation and rapid snowline recession during the ablation period on Svalbard. In contrast, the subglacial environment appears to promote denitrification because we have observed anoxic conditions in its runoff, sulphate reduction in tills exposed by recent ice retreat and also the periodic disappearance of NO_3^- in subglacial drainage.

Our study therefore shows that these glaciers cannot be regarded as abiotic environments and should instead be viewed as complex ecosystems where two quite contrasting environments (the surface and the bed) can significantly modify the flux of nutrients released during melt. Interestingly, the two contrasting environments, where present, are intricately linked by the penetration of surface water, nutrients and (presumably) biota into the glacier bed. Lastly, since the glacier thermal regime governs the presence/absence of subglacial drainage and itself is dependent upon glacier mass balance, this 'glacial ecosystem' may be regarded as extremely sensitive to climate change.

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