

Chemical and isotopic characteristics of weathering and nitrogen release in non-glacial drainage waters on Arctic tundra

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Abstract

Soil-water interactions in coastal tundra soils are a potential source of nutrients for surrounding fjordal and coastal ecosystems. Changes in water chemistry and stable isotope composition from 3 streams in west Spitsbergen were examined to assess the sources and losses of nitrogen, sulfur and carbon in thin organic tundra soils overlying sediments. Studies were undertaken from snowmelt (mid June) through to the end of the summer (September) in both 2001 and 2002. Drainage water chemistry was dominated by the solution of Ca-Mg carbonates with $\delta^{13}\text{C}$ values in the waters being uncharacteristically high (approx. -2‰ at the end of the season), reflecting a largely open system in which the CO_2 is derived equally from the atmosphere and plant/soil sources. Early melt waters had $\delta^{34}\text{S}$ values dominated by sea salt reflecting the close proximity to the ocean. However, as the season progressed the marine influence lessened. Extrapolation of the data suggests that the origin of non-sea salt $\delta^{34}\text{S}$ was the oxidation of reduced sulfur from coal particles in the subsoil. Concentrations of inorganic N in stream waters were generally very low. However, NO_3^- values were found to increase as the season progressed, possibly through increased microbial activity in the soil and the early senescence of tundra plants reducing demand. Dual isotope analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ suggested that the vast majority of snow-pack NO_3^- was assimilated by the soil microbial biomass before being released, recycled and lost to drainage waters. Organic N concentrations in drainage waters were generally equal to or greater than losses of inorganic N from tundra soils. The study demonstrated the effectiveness of stable isotope data for understanding biogeochemical cycling and soil-water interactions in tundra ecosystems. The implications of the results are discussed in relation to climate warming.

1. INTRODUCTION

Studies of chemical budgets and hydrochemistry in the European High Arctic have largely focused on glacial catchments (Tranter et al. 2002; Wadham et al. 2004; Hodson et al. 2005; Wynn et al. 2006). These systems have major roles in (i) regulating the biogeochemical cycling of nutrients that may impact both freshwater and marine ecosystems and (ii) in our understanding of cryosphere-atmosphere interactions and the potential feedbacks that contribute to climate regulation (Tranter et al. 2002). The evolution of snowmelt chemistry in these glacial catchments is largely influenced by the presence of meltwater derived from stored glacial ice and snow and the substantial contribution of solutes released during the weathering and leaching of underlying rock and glacial tills (Hodson et al. 2005). In contrast, relatively little published work exists regarding the chemistry of soil-water interactions in those parts of the polar tundra free of the complications of glacial systems in the European High Arctic. In Spitsbergen, Stutter & Billett (2003) undertook chemical analysis on a range of stream and drainage waters draining different tundra vegetation types from Dicksonland, whilst Pecher (1994) examined temporal changes in surface and soil pore waters in Liedefjorden. Hodson et al. (2002) and Cooper et al. (2002) both examined changes in the hydrochemistry of glacial meltwater streams that had major drainage contributions from tundra.

This paper reports work examining the hydrochemistry of drainage waters from low-lying coastal tundra. These areas are generally drained via small streamlets or drainage gulleys that often include an element of overland flow. Sources of water include melting snow, springs that are generated partially from melting soil moisture, and precipitation. These areas are often characterised by thin organic soils overlying sediments, and are a potential source of nutrient enrichment to fjords and the ocean. Changes in the major element hydrochemistry of the drainage waters in conjunction with their stable isotope composition were analysed from the onset of snowmelt and through the snow free period that occurs during the summer in the High Arctic.

It is anticipated that weathering processes of the sub-soil sediment, and biogeochemical cycling within the thin organic soil will determine the solute composition of the waters draining tundra soils. However, some nutrient enrichment of fjordal and coastal waters from tundra soils may also occur from the long-range transport of pollutants such as reactive nitrogen deposited and later released from the snowpack. A key aim of this study was to assess the relative contributions in the drainage waters of atmospheric (snowpack) and soil (microbially) derived NO_3^- . Increased deposition of atmospheric reactive N, emitted and transported from industrialised areas (Mosier et al. 2001), has been recorded and may impact delicate N-limited ecosystems. Evidence of this increased deposition has been found in firn ice cores from many parts of the Arctic, where a doubling of inorganic N concentrations has occurred since the industrial revolution (Laj et al. 1992; Fischer et al. 1998; Simoes and Zagorodnov, 2001). The inputs of reactive N have been found to vary with geographical position and proximity to anthropogenic sources (Jaffe and Zukowski, 1993). Consequently, yearly atmospheric N deposition is estimated to be $\sim 1.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Norwegian high Arctic, but $\sim 10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ on the Taymyr Peninsular in Russia and parts of northern Alaska (Woodin, 1997). Research has shown that during winter, reactive N is deposited in the snowpack and is released at snowmelt in the early summer. It then contributes to a pulse of N to terrestrial ecosystems that are effectively 'switching on' for the summer growing period (Russell, 1990). Initial research, largely on alpine tundra and high elevation catchments, suggested that this pulse of N was either a result of: (a) preferential elution of snowpack NO_3^- and/or; (b) the flushing of NO_3^- produced by microbial nitrification throughout the winter. However, recent research has suggested that atmospherically derived NO_3^- may enter a period of temporary storage in the soil microbial biomass (Sickman et al. 2003) or in plants (Billborough et al. 2002) before being re-released as organic forms of N, back into the terrestrial N cycle. Therefore, this work attempts to quantify the inputs of snowpack deposited N and its subsequent fate in a High Arctic location.

2. SITE DESCRIPTIONS AND METHODS

2.1 Streams

Sampling was undertaken at 3 streams on the shores of Kongsfjorden, close to the research settlement of Ny Ålesund, Svalbard (78°54'N, 11°53'E; Figure 1). Kongsfjorden is 20 km long and varies in width between 4 and 20 km. The landscape surrounding the fjord has been shaped by glacial activity with active glacial, hydro-glacial, periglacial and coastal processes still continuing (Svendsen et al. 2002). Mean annual precipitation is 412 mm. The prevailing wind direction is from the south east with a second mode from the north-west (Svendsen et al. 2002). Average air temperatures start to drop below freezing in early September, reaching a mean monthly temperature of -17°C in February, before rising above freezing in early June to reach a mean monthly temperature of +5°C in July (<http://isohis.iaea.org>). Snow starts to accumulate from December onwards, building to depths of ~ 0.5 m in flat, shoreline areas, and melting in June. Thawing of the soil during the summer extends to a permafrost depth of about 1m (Roth and Boike, 2001).

2.1.1. Stream 1.

The principal site, sampled in 2001 and 2002, was a small catchment draining into Kohamnlaguna, on the shore south of Brandalpynten, about 2 km north west of Ny Ålesund (Stream 1, Figure 1). The site has a maximum altitude of 25 m, covers about 2 ha, and in summer comprises a low gradient, boggy basin bounded on the north and south by drier, slightly raised gravelly areas, and on the west, at the head of the catchment, by the slopes of a series of rock and gravel terraces. These terraces represent raised beach sequences, which are a major geomorphological feature of the Bröggerhalvöya peninsula, and characterise the late Weichselian and Holocene history of sea level in this part of Spitsbergen. The Bröggerhalvöya peninsula emerged when glacial-isostatic rebound exceeded the sea level rise leaving three large beach ridges that are found at ~29, 37 and 45m altitude. The ridges are between 100 – 200 m wide with a relief of ~5m. Below 20m, as in this study site, a series of narrow (5-10m)

and low (< 2m) strandlines are found that reach to the present shoreline where a barrier beach ridge is actively forming (Forman et al. 1987). Radiocarbon dating of whalebones has been used to date relative sea level change on Bröggerhalvøya. Deglaciation is considered to have occurred in two steps. Initial unloading of the ice could have involved the break up of the marine-based ice sheet on the Spitsbergen bank in the Barents sea approximately 13000 yrs B.P., followed by the second step that resulted in the deglaciation of the major fjords by about 9000 B.P. (Forman et al. 1987). A thin (typically < 4 cm) organic soil horizon has developed on the better drained areas. Vegetation was similar to that of an adjacent study area described by Tye et al. (2005). Bryophytes and *Salix polaris* grow on the organic soil, with a thick moss carpet common in the basin along with a cryptogamic crust including species of the blue-green algae *Nostoc*. In summer several streams run east through the basin to the shore. The largest stream, Stream 1, was selected for sampling. As the total catchment drainage was over a broad area, and not on bedrock, it could not be accurately gauged.

2.1.2. Streams 2 and 3.

Two additional streams (Streams 2 and 3 in Figure 1) were sampled in 2002 to provide data supplementary to that obtained from Stream 1. Stream 2 was a small stream running to the shore to the west of Brandalpynten, and draining ground similar to that surrounding Stream 1 about 1 km away. Samples were also collected in 2002 from a gauging station of the Norwegian Polar Institute (Norsk Polarinstitutt) on a stream draining part of the island of Blomstrandhalvøya (Stream 3). This catchment is characterised by a higher altitude (369 m at the highest point), steeper gradient slopes, more visible bedrock consisting of the Generalfjella Formation Marbles (Harland, 1998) of Devonian age, and relatively little soil cover compared with the area drained by Streams 1 and 2.

2.2. Sampling and analysis

The snowpack in the catchment of Stream 1 was sampled in late April of 2001 and 2002. For chemical analysis, fifteen snow cores were collected over a 100 x 100 m area using a 4.9 cm diameter plastic tube inserted down to the base of the snowpack, and the snow transferred to a pre-conditioned plastic bag. Snow depth, volume and weight from each core were determined so snowpack density could be calculated. Estimates of NO_3^- and NH_4 inputs on a $\text{kg}\cdot\text{ha}^{-1}$ basis were derived by combining depth and density measurements from each core to estimate snow water equivalent (SWE). The concentrations of NO_3^- and NH_4 were multiplied by the SWE to obtain snowpack contents (Sickman et al. 2003). Samples for $^{15}\text{N}/^{14}\text{N}$, $^{34}\text{S}/^{32}\text{S}$ and $^{18}\text{O}/^{16}\text{O}$ isotope analysis, of up to 80 kg snow, were collected from a smaller number of pits in the same area (Heaton et al. 2004). In 2002, ice samples from the bottom of the snow pack were collected by chiselling ice out from known areas. The ice was weighed, allowing the calculation of density and SWE. Inputs of NO_3^- and NH_4 were calculated in a similar manner as for the snow.

Samples of drainage waters were collected from Stream 1, at approximately weekly intervals, during mid June to early September of 2001, and at Streams 1, 2 and 3 during mid June to early September of 2002. For Stream 1 [data for Stream 2 are not presented], estimates of flow rate (Figure 2) were determined by damming the drainage channel just above the collection point and diverting the flow via guttering pipe from which the volume of water per minute was determined. Samples for chemical analysis were collected in 1 L LDPE bottles. Samples of up to 100 L in jerry cans were collected for $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ and $^{34}\text{S}/^{32}\text{S}$ analysis, and 500 mL in polycarbonate bottles for inorganic $^{13}\text{C}/^{12}\text{C}$ analysis. The latter samples, which were free of any turbidity, were collected unfiltered to avoid potential loss of CO_2 , and the TDIC (total dissolved inorganic carbon) immediately precipitated as barium carbonate by addition of alkaline barium chloride. Two samples filtered before addition of barium chloride showed no difference from their unfiltered counterparts.

2.2.1. Post Sample Collection Procedures

On return to Ny Ålesund samples for chemical analysis were filtered through 0.45 µm nylon filters into LDPE bottles. Separate sub-samples were taken for major cation (Ca, Mg, K, Na), major anion (Cl, NO₃-N, SO₄-S, HCO₃⁻) and DOC/DON (dissolved organic carbon / dissolved organic nitrogen) analysis, and a further sub-sample was acidified with 10 % HCl for NH₄⁺ analysis. All samples were stored at <4°C. Barium carbonate was recovered by filtration and washing through 0.8 µm filter paper and dried at 50°C to constant weight.

Of the large samples for isotope analysis, a small unfiltered portion was retained for water ²H/¹H and ¹⁸O/¹⁶O analysis, and the remainder passed through ion exchange resins in the manner described elsewhere (Heaton et al. 2004). Ammonium recovered from the cation resin was converted to ammonium sulfate on quartz filter paper using a static alkaline diffusion method (Sigman et al. 1997; Heaton, 2001). Sulfate was eluted from the anion resin and converted to barium sulfate (by precipitation with barium chloride). NO₃⁻ was eluted from the anion resin using 3M HCl, neutralised with silver oxide (Ag₂O) and freeze dried to silver nitrate (AgNO₃) (Silva et al. 2000; Heaton et al. 2004).

2.2.2. Chemical Analysis

Alkalinity (predominately HCO₃⁻) was determined within 10 days of collection through colourimetric titration using a BDH pH 4.5 indicator. NO₃⁻ and NH₄ were determined immediately after collection. Nitrate was determined after reduction to nitrite using the colourimetric method of Mackereth et al. (1989) with 4 cm cells (no initial nitrite was detectable in any samples during this study). The detection limit was 0.21 µm L⁻¹ and the precision errors were calculated at 0.25 to 2 % at 2.85 µm L⁻¹ for different analytical runs. Ammonium was determined using salicylate and sodium dichloroisocyanurate solutions (HMSO, 1981). Detection limits were 0.21 µm L⁻¹ and analytical precision was < 5 % at 7.13 µm L⁻¹. In Nottingham, Ca, Mg, Na, K were determined using flame atomic absorption

spectrometry. Analytical precisions were calculated to be between 0.2 – 3.5 % for Ca at 125 $\mu\text{m L}^{-1}$, 1.2 to 8.3 % for Mg at 411 $\mu\text{m L}^{-1}$, 1.4 to 2.3 % for Na at 109 $\mu\text{m L}^{-1}$ and 0.4 to 2.3 % for K at 12.8 $\mu\text{m L}^{-1}$. Anions (Cl^- , SO_4^{2-}) were measured using ion chromatography. Analytical precision was between 5 to 8 % for Cl^- at 282 $\mu\text{m L}^{-1}$ and 3.7 to 5 % for SO_4^{2-} at 124 $\mu\text{m L}^{-1}$. Mean charge balance errors (CBE in %) were calculated as

$$CBE = \frac{(\sum^+ - \sum^-)}{(\sum^+ + \sum^-)}$$

where Σ^- and Σ^+ are the combined equivalents of the measured anions (HCO_3^- , SO_4^{2-} , Cl^- and NO_3^-) and the cations (Ca, Mg, K, Na) respectively. Analysis of DOC and DON was carried out using a Shimadzu Total Organic Carbon (TOC) / Total organic nitrogen (TON)-V analyzer. Analytical precision was 3.9% for DOC at 166 $\mu\text{m L}^{-1}$ C and 9.8 % for DON at 36 $\mu\text{m L}^{-1}$ N.

2.2.3. Stable Isotope Analysis

$^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ and $^{34}\text{S}/^{32}\text{S}$ ratios were determined in VG SIRA, VG Optima, and Finnigan Delta+ isotope ratio mass spectrometers, and are reported as δ values where:

$$\delta^2\text{H}, \delta^{13}\text{C}, \delta^{15}\text{N}, \delta^{18}\text{O}, \delta^{34}\text{S} \text{ (in per mille)} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

for $R = ^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ and $^{34}\text{S}/^{32}\text{S}$, respectively.

The standards are: VSMOW for $\delta^2\text{H}$, and for $\delta^{18}\text{O}$ of water, NO_3^- and SO_4^- ; VPDB for $\delta^{13}\text{C}$, and for $\delta^{18}\text{O}$ of carbonate; atmospheric N_2 for $\delta^{15}\text{N}$; and VCDT for $\delta^{34}\text{S}$. Corrections to these standards were undertaken by comparison of samples to within-run materials: waters calibrated against VSMOW and SLAP; a calcite calibrated against NBS-19 and NBS-18; IAEA-N-1 ammonium sulfate (assumed $\delta^{15}\text{N} = +0.4\text{‰}$); IAEA-NO3 potassium nitrate (assumed $\delta^{18}\text{O} = +25.6\text{‰}$); and a barium sulfate calibrated against NBS-127 (assumed $\delta^{18}\text{O} = +9.3\text{‰}$, $\delta^{34}\text{S} = +20.3\text{‰}$).

Precision of replicate analyses of samples was generally better than $\pm 1\text{‰}$ for $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\pm 0.3\text{‰}$ for $\delta^{13}\text{C}_{\text{TDIC}}$, $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\pm 0.3\text{‰}$ for $\delta^{18}\text{O}_{\text{SO}_4}$, $\pm 0.3\text{‰}$ for $\delta^{34}\text{S}_{\text{SO}_4}$, and $\pm 0.4\text{‰}$ for $\delta^{15}\text{N}_{\text{NH}_4}$. As discussed below, precision for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ was dependent on the degree to which the silver NO_3^- was contaminated by organics (Heaton et al. 2004); uncontaminated samples generally replicate better than $\pm 0.4\text{‰}$ for $\delta^{15}\text{N}_{\text{NO}_3}$, and $\pm 1\text{‰}$ for $\delta^{18}\text{O}_{\text{NO}_3}$.

3. RESULTS

3.1 Snow at Site 1

3.1.1. Chemistry

The average compositions of the snowpack at Site 1, based on several cores taken over an area of about 1 ha in April 2001 and April 2002, are shown in Table 1. Average snow depths and densities for the sampled cores were 37 cm (range: 25-60cm) at 0.33 gm.cm^{-3} in 2001, and 25 cm (range: 10-45 cm) at 0.31 gm.cm^{-3} in 2002. Frequent freeze-thaw cycles in the early winter commonly lead to the formation of an ice lens at the base of the snowpack (Gerland et al. 1999), and this was sampled at four core locations in 2002 (Table 1). Mean thickness of the basal ice layer sampled in 2002 was 14 cm (range 10-22 cm; SD = 5.5 cm). Basal icing across our study area was extensive. In 2001 a walk over survey carried out during snowmelt suggested the mean ice layer was approx. 10 cm thick ($n = 8$). Variations in the thickness of the basal ice reflected the undulations of the surface; ice depth being deeper in depressions where meltwater or precipitation could accumulate on frozen soil, and little ice appearing on the very highest parts on the surface. During the spring melt, much of the ice remained after the majority of the snow had melted. However, it was apparent that meltwater collected on top of the ice during snowmelt as well as infiltrating beneath it. In addition, single samples of fresh snow were collected within a few hours of falling on 23 April 2001, and 5 April 2002 (Table 1).

The major ion chemistry of the snowpack on Brandalspynten was dominated by Na and Cl⁻, with snowpack Na/Cl⁻, K/Cl⁻ and Mg/Cl⁻ ratios similar to those of seawater, and snowpack Ca/Cl⁻ and SO₄/Cl⁻ ratios slightly elevated relative to seawater (Table 1). There was less of a marine influence found in the chemical analyses of the ice layers and fresh snowfall. NO₃⁻ and NH₄ concentrations were similar to those reported from other parts of Svalbard (Caritat et al. 2005; Hodson et al. 2005; Wynn et al. 2006). Combining snowpack chemical and density data, inputs of NO₃-N and NH₄-N from the snow pack were estimated to be 59 and 30 g ha⁻¹ in 2001, and 18 and 12 g ha⁻¹ in 2002, respectively. Measurement of the 2002 basal ice-lens, however, indicated that it contributed an additional 33 g ha⁻¹ NO₃-N and 6 g ha⁻¹ NH₄-N.

3.1.2. Isotope data

The snowpack displayed large spatial variations in $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (e.g. up to 5‰ range in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ between cores). All samples, however, including the ice at the base of the 2002 snowpack, lay close to the Global Meteoric Water Line (Rosanski et al. 1993) collectively defining a relationship $\delta^2\text{H}_{\text{H}_2\text{O}} = 7.8 \cdot \delta^{18}\text{O}_{\text{H}_2\text{O}} + 12$. Weighted mean $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for the 2001 snowpack were -65‰ and -10.0‰, and for the 2002 snowpack plus ice layer were -73‰ and -10.4‰, and may be compared with the long-term weighted mean for October to April precipitation at Ny Alesund: $\delta^2\text{H}_{\text{H}_2\text{O}} = -78\%$; $\delta^{18}\text{O}_{\text{H}_2\text{O}} = -11.3\%$ (data for 1990-2001 at <http://isohis.iaea.org>).

The $\delta^{34}\text{S}_{\text{SO}_4}$ values and SO₄²⁻/Cl⁻ ratios of the snowpack were typical of precipitation in coastal areas, and suggest a dominant contribution of seawater sulfate with $\delta^{34}\text{S}_{\text{SO}_4} = +21\%$, together with a smaller amount of atmospheric sulfate which normally has lower $\delta^{34}\text{S}_{\text{SO}_4}$ values (Wadleigh et al., 1996, 2001). The $\delta^{18}\text{O}_{\text{SO}_4}$ values for the snowpack sulfate were also typical

for precipitation, but generally do not allow distinction between marine and non-marine sources (Wadleigh et al., 1996).

The $\delta^{15}\text{N}_{\text{NH}_4}$ values for snow (Table 1) were within the range of values typically reported for precipitation from a limited number of studies in other areas (c. -8 to +2‰), and $\delta^{18}\text{O}_{\text{NO}_3}$ for the snow were within the upper range of values reported for other parts of the globe (c. +20 to +80‰; Heaton et al. 1997; Kendall, 1998; Heaton et al. 2004). In contrast, $\delta^{15}\text{N}_{\text{NO}_3}$ values, particularly for the 2001 snow, were markedly lower than the typical c. -5 to +5‰ range for atmospheric NO_3^- from other parts of the globe. The Ny Alesund snow $\delta^{15}\text{N}_{\text{NO}_3}$ values bore similarities to atmospheric NO_3^- in Antarctica, and may reflect a component of stratospherically-derived NO_3^- (Heaton et al. 2004).

3.2. Stream 1

3.2.1. Flow

The earliest stages of snowmelt resulted in slumping of the snowpack, but with the initial liquid water still held within the remaining snow porosity. Stream flow, and the collection of stream water could therefore only begin towards the end of the snowmelt, when some bare ground or ice was apparent that allowed overland flow to begin. At this point the tundra consisted of semi-frozen soil with about 75% of the area covered with a patchwork of snow and ice. Figure 1 shows the flow rate of Stream 1 at each sampling time shown on the graphs as day number. In Tables 2 & 3 day numbers are presented with equivalent dates. In the earliest period of sampling, corresponding to the main snowmelt phase, high flow in the Stream 1 was augmented by wide-scale overland flow via several smaller streams. After snowmelt, flow rate rapidly declined and was linked to the melting of a snow bank on the gravel terrace escarpment slope at the head of the catchment (persisting to mid-July), thawing of frozen soil moisture (sometimes appearing as springs at the foot of the escarpment), and summer precipitation of

snow or rain (Figure 2). In the summer of 2002, flow completely dried up for 12 days between day 189 and 201.

3.2.2. Chemistry

Table 2 reports concentrations of major cations and anions in Stream 1. Mean charge balances for 2001 and 2002 were +3.09 and -0.28 % respectively. To compensate for possible dilution effects, and on the assumption that Cl^- is conservative, water chemistry is examined relative to chloride – i.e. as ion/ Cl^- ratios. Thus in Figure 3 we display the temporal changes in water chemistry of Stream 1 in terms of ion/ Cl^- ratios, and compare these with measured ion/ Cl^- ratios from the snowpack which are marked arbitrarily at day 150.

Ca/Cl^- and Mg/Cl^- ratios (Figure 3a & 3b) in the earliest stream samples rose rapidly above those of the snowpack, and continued to rise slightly throughout the latter part of the drainage period. These increases were closely matched by increases in HCO_3^- so that $2 \cdot (\text{Ca} + \text{Mg})/\text{HCO}_3^-$, on a molar basis, maintained a value close to 1. Na/Cl^- and K/Cl^- (Figure 3c & 3d) ratios in the streamwater showed little change over the 11 week sampling periods, with Na/Cl^- ratios remaining essentially similar to their seawater ratios in the initial snowpack, and K/Cl^- ratios being slightly higher than in the initial snowpack. The $\text{SO}_4^{2-}/\text{Cl}^-$ ratio (Figure 3f) started close to that of the snowpack before increasing progressively with time.

Concentrations of inorganic N are displayed as $\text{NO}_3^-/\text{Cl}^-$ ratios and NH_4/Cl^- ratios in Figures 3(g) and 3(h), respectively. During the early part of the summer, from the onset of snowmelt in mid-June to about mid-July (2002) or late July (2001), $\text{NO}_3^-/\text{Cl}^-$ ratios remained similar to those of the initial snowpack. Thereafter the ratios rose progressively to the end of sampling in early September. The rise in $\text{NO}_3^-/\text{Cl}^-$ ratios in July reflected an increase in NO_3^- concentrations (Table 2) whose timing did not appear to correspond to changes in any other chemical parameter, but was at a time when the tundra flora was tending towards senescence. In 2002,

two samples with particularly high NO_3^- concentrations and $\text{NO}_3^-/\text{Cl}^-$ ratios (days 201 and 231) corresponded to the occurrence of rainfall following prolonged dry periods.

NH_4/Cl^- ratios in Stream 1 started similar to those of the snowpack, and remained fairly constant (2001), or declined slightly (2002) during the summer. The exception was a high NH_4/Cl^- ratio in late June 2001 (day 173), associated with a day of 16 mm rainfall.

Concentrations of both DOC and DON in the stream water peaked during the middle of the study period in 2002. However, Figure 3(i) shows that the DON/Cl^- ratio remained fairly constant during the study period. The DOC/Cl^- ratio decreased slightly as the season progressed (Fig 3j). The DOC/DON ratio varied between 13-29, generally slightly lower than values obtained from high elevation catchment streams reported by Williams et al. (2001) and Hood et al. (2003) (Fig 3k). Concentrations of DON, measured in 2002, were almost always higher than the total inorganic nitrogen (Table 2). In common with NO_3^- , enhanced DON and DON/Cl^- ratios were associated with rainfall following prolonged dry periods (days 201 and 231).

3.2.3. Isotope data

$\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for Stream 1 waters started off similar to those of the initial snowpack, with a change to slightly higher values overall during the summer (Figure 4). The relationships between $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, defined by all the stream waters, were $\delta^2\text{H}_{\text{H}_2\text{O}} = 4.9 \cdot \delta^{18}\text{O}_{\text{H}_2\text{O}} - 22$ for 2001, and $\delta^2\text{H}_{\text{H}_2\text{O}} = 6.0 \cdot \delta^{18}\text{O}_{\text{H}_2\text{O}} - 16$ for 2002. In both cases these 'slopes' were lower than those of the snowpack (7.8, above).

Figure 5 displays the $\delta^{34}\text{S}$ values of sulfate in Stream 1 as a function of the percentage of non-sea-salt sulfate (NSSS). The latter was calculated on the assumption that sea-salt has a

$\text{SO}_4^{2-}/\text{Cl}^-$ ratio of 0.052 and was the source of all Cl in the stream water; thus $\% \text{NSSS} = [1 - (0.052 \times \text{Cl}/\text{SO}_4)] \cdot 100$ (Newman et al. 1991). The data for the 2001 and 2002 Stream 1 samples display very similar, clearly linear trends of decreasing $\delta^{34}\text{S}_{\text{SO}_4}$ with increasing NSSS, and collectively define a relationship: $\delta^{34}\text{S}_{\text{SO}_4} = -0.21 \cdot (\% \text{NSSS}) + 18.9$, $r^2 = 0.93$, with snowpack samples lying close to this line (Figure 4). Bearing in mind the simplified assumptions in calculating % NSSS, confidence is justified by the fact that the intercept at +18.9‰ is close to the $\delta^{34}\text{S}_{\text{SO}_4}$ value for modern seawater (+21‰). The pure, 100% NSSS end-member has a calculated $\delta^{34}\text{S}_{\text{SO}_4}$ value of -2.1‰.

The $\delta^{18}\text{O}$ values for sulfate in all but the first Stream 1 sample of 2001 were between -0.3 and +1.4‰, and significantly lower than the values for the snowpack (+9.5 and +9.7‰). Plotted on the same basis as above, a linear relationship for the sulfate oxygen: $\delta^{18}\text{O}_{\text{SO}_4} = -0.05 \cdot (\% \text{NSSS}) + 4.6$, $r^2 = 0.41$, is not as clear as that for sulfate sulfur, with the +4.6‰ intercept being lower than the $\delta^{18}\text{O}_{\text{SO}_4}$ value for seawater (+9.5‰). The calculated pure NSSS end-member $\delta^{18}\text{O}_{\text{SO}_4}$ value of -0.4‰ is within the large range reported for limited data from glacial catchments (Bottrell and Tranter, 2002; Wadham et al. 2004).

As pH values were close to neutral, the TDIC should be dominantly present as HCO_3^- . Changes in $\delta^{13}\text{C}_{\text{TDIC}}$ values are listed in Table 2, and displayed for 2002 in Figure 6. In 2002, the earliest drainage waters of Stream 1, occurring during the snowmelt period of high flow and low HCO_3^- , had $\delta^{13}\text{C}_{\text{TDIC}}$ of -7.5‰. With the higher HCO_3^- concentrations found throughout the remainder of the season the $\delta^{13}\text{C}_{\text{TDIC}}$ values were maintained between -4.4 and -1.5‰. These values are high: considerably higher than those typical of drainage waters in temperate regions (usually <-6‰), and at the upper end of ranges reported for water from glaciated catchments (Aucour et al. 1999; Telmer and Veizer, 1999; Wadham et al. 2004; Spence and Telmer, 2005).

Yields of inorganic N from the 2001 resins were only sufficient for $\delta^{15}\text{N}_{\text{NO}_3}$ analysis of two late season samples (Table 3a), and insufficient for $\delta^{15}\text{N}_{\text{NH}_4}$ analysis. For the 2002 samples (Table 3b) $\delta^{15}\text{N}_{\text{NO}_3}$ values exhibited a fairly narrow range, -1.9 to +1.9‰, higher than that of the initial snowpack (-6.9‰). Six stream water $\delta^{15}\text{N}_{\text{NH}_4}$ values displayed a broader range, -7.2 to -0.7‰, slightly lower than the snowpack (-0.3‰).

Difficulties associated with the preparation of pure silver nitrate, and the resulting consequences for $\delta^{18}\text{O}$ analysis of NO_3^- , have been discussed previously (Heaton et al. 2004). Table 3 displays the measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of silver nitrate samples together with their C/N (weight) and N/O (atomic) ratios. The C contents reflect contamination of the silver nitrate by organic matter, which should not substantially affect the measured $\delta^{15}\text{N}$ values but, through the presence of relatively large amounts of organic O, does affect the apparent $\delta^{18}\text{O}$ values (Heaton et al. 2004). The presence of contaminant O was evident from the N/O ratios, which should be 0.33 for pure nitrate, but were commonly much lower than this in the silver nitrate prepared from the Stream 1 samples (Table 3). The measured $\delta^{18}\text{O}$ values and N/O ratios are plotted in Figure 7 and compared with contamination-corrected values for snowpack NO_3^- . The stream NO_3^- samples displayed a well-defined linear trend of $\delta^{18}\text{O}$ values from -5 to 0‰ at N/O ratios of 0.33 (i.e. for pure NO_3^-), to an extrapolated value between +15 and +25‰ at N/O ratios near zero (i.e. for the contaminant end-member). None of the stream NO_3^- samples had $\delta^{18}\text{O}$ values deviating significantly from this trend. There is therefore no evidence for snowpack NO_3^- , with its characteristically high $\delta^{18}\text{O}$ values of +70 to +80‰, being present in the drainage waters of Stream 1.

3.3. Stream 2 and Stream 3

The 2002 chemistry of Stream 2 is shown in Table 4. Low rainfall meant that samples could not be collected during July to mid August. But for the early summer and late summer samples

the pattern of major ion concentrations, ion/Cl ratios and isotope compositions were generally very similar to those of the nearby Stream 1. Stream 3, on Blomstrandhalvøya, showed similarities to Stream 1 in the main weathering processes (Table 5): e.g. a marked increase in HCO_3^- matched by increased Ca + Mg (though with a lower proportion of Mg in Stream 3); very similar $\delta^{13}\text{C}$ values; and SO_4^{2-} displaying a progressive rise, with the proportions of NSSS approaching 90% towards the end of summer. In contrast, Stream 3 had considerably lower concentrations of Na and Cl, and quite different abundances of inorganic nitrogen: NO_3^- and NH_4 concentrations being significantly lower in Stream 3 compared with Stream 1. DON concentrations were found to be below detection limits whilst DOC concentrations appeared to be highest between Day 176 and 194 before declining towards the end of the season, a pattern replicated by the DOC/Cl⁻ ratio (results not shown).

4. DISCUSSION

4.1 General chemistry

The chemistry of the earliest stream waters, sampled during the period of high overland flow during the main snow-melt phase in mid-late June, clearly reflected the chemistry of the snowpack, which was dominated by salts of marine origin: high Na and Cl contents, with concentrations of Na, Cl, Mg and K, and the $\delta^{34}\text{S}_{\text{SO}_4}$ values, very similar to those of seawater. It is possible that much of this salt, sampled in the snowpack in April, resulted from wind transfer from the neighbouring Kongsfjorden, rather than by precipitation in snow. Transfer of sea salts could have been from sea spray blown from the unfrozen fjord. Alternatively, when the fjord is frozen high concentrations of sea salt can accumulate in the surface layers of snow covering sea ice, and this snow is readily swept on-shore by the common easterly winds (Domine et al. 2004). This mechanism would account for the concentration of marine salt at Streams 1 and 2 being higher than those at Stream 3. The latter site has a catchment elevation (up to 369 m) much higher than the former sites (up to 25 m), and is therefore less likely to intercept wind drift from the fjord.

During the remainder of the summer sampling season, July through August, the water sampled in Stream 1 represented drainage through the unfrozen ‘active layer’ of tundra over a catchment area of about 2 ha. The thermal development of the active layer at a site about 1 km away from Stream 1 has been described by Roth and Boike (2001). When air temperatures rise above freezing the downward transfer of heat is greatly increased by the infiltration of water and water vapour derived from snowmelt. Thus, for their 1999 season, this warming resulted in a temperature of 0°C being reached at the soil surface when the snowpack disappeared in mid-June, 0°C at 0.5 m depth after 20 days; and 0°C at 1 m depth after a further 20 days (late July). The depth of the active layer thereafter stabilised at about 1 m for a further 60 days before rapid freezing of the whole depth in late September (Roth and Boike, 2001).

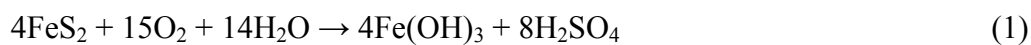
Although the flow of the stream clearly responded to occasional summer precipitation (rain or snow), this was a hydraulic response; no observations of overland flow after the mid-late June snow-melt were recorded. Instead, the relative constancy in the chemical concentrations and $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the stream suggests that the sampled waters always passed through the active layer. As the stream only represents the surface interception of the water table, the measured flow of the stream (Figure 1) will always be an underestimate of the total drainage rate from the catchment. The period of very low flow rates for Stream 1 during July to mid-August 2002, however, does correspond to a time when the waters had higher $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (Figure 3), and a relatively low $\delta^2\text{H}_{\text{H}_2\text{O}}/\delta^{18}\text{O}_{\text{H}_2\text{O}}$ slope of 6 (above). These features are probably a result of slight evaporation (Clark and Fritz, 1997).

The main changes in chemistry through July and August appear to reflect two types of water-mineral interaction: oxidation of reduced sulfur, leading to increases in the proportion of NSSS; and, more dominant, the solution of calcium-magnesium carbonates, leading to increases in Ca and Mg balanced by HCO_3^- . The dominance of Ca and HCO_3^- in tundra drainage and soil waters from NW Svalbard, as well as their general increase in concentration

through the summer has been noted previously (Pecher, 1994; Hodson et al 2002; Stutter & Billett, 2003). Weathering of feldspars by reaction with dissolved CO₂ is assumed to play only a minor role in production of HCO₃⁻ in this catchment, because the concentrations of K and Na, major components of feldspar, were essentially unchanged from snow pack values. From the results of the current study the mechanisms of these processes can be examined using isotope analysis.

4.2 Sulfur oxidation

Extrapolation of the data in Figure 5 suggests that the NSSS had a $\delta^{34}\text{S}_{\text{SO}_4}$ value of about -2.1‰. Results of analyses of different rock types collected as pebbles from the gravel terraces of the catchment are shown in Table 6. Fragments of the Tertiary coal formerly mined at Ny Alesund are common, and had by far the highest S content (1580 ppm) with a $\delta^{34}\text{S}$ value of -0.9‰. As oxidation of reduced S (e.g. pyrite) to SO₄:



usually involves very little change in $\delta^{34}\text{S}$ values (Canfield, 2001), we would expect coal-derived sulfate to also have $\delta^{34}\text{S}$ values close to -0.9‰. The isotopic fractionation associated with crystallization of sulfate salts is also small (Raab and Spiro, 1991), so episodes of precipitation and re-resolution of gypsum attending dry or wet periods in the active layer (Cooper et al., 2002) should also result in little change in $\delta^{34}\text{S}$ values. The $\delta^{34}\text{S}_{\text{SO}_4}$ data are therefore entirely consistent with the oxidation of reduced sulfur in coal particles in the subsoil being the ultimate source of NSSS.

The factors which can influence the $\delta^{18}\text{O}$ values for sulfate produced by Reaction 1 are more complex (van Everdingen and Krouse, 1985; Toran and Harris, 1989; Holt and Kumar, 1991; Bottrell and Tranter, 2002). The SO₄²⁻ oxygen atoms are derived from both atmospheric O₂ and from water. The former has a $\delta^{18}\text{O}$ value of about +23.5‰ (Kroopnick and Craig, 1977), and

the latter averaged about -9‰ for Stream 1 in both 2001 and 2002. This large difference means that the $\delta^{18}\text{O}_{\text{SO}_4}$ value is very sensitive to the proportions of atmospheric O_2 versus H_2O used in the oxidation reaction. Calculating these proportions is complicated by uncertainty in the magnitude of the oxygen isotope fractionations accompanying incorporation of O_2 oxygen or H_2O oxygen (Holt and Kumar, 1991). However, using the criteria of Bottrell and Tranter (2002) for an average Stream 1 $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of -9‰, the $\delta^{18}\text{O}_{\text{SO}_4}$ value of -0.4‰ we have calculated for the NSSS end-member sulfate would imply that atmospheric O_2 supplied about 40%, and water about 60% of the sulfate oxygen. This is consistent with the aerobic, oxidising conditions required for Reaction 1 (van Everdingen and Krouse, 1985; Bottrell and Tranter, 2002).

4.3 Carbonate solution

The sulfuric acid produced by the above oxidation of reduced sulfur has often been cited as having a significant influence on carbonate dissolution in glacial systems or other areas with high rates of water-rock interaction (Spence and Telmer, 2005):



The amount of NSSS in Stream 1 waters, however, was relatively small compared with the bicarbonate concentrations. NSSS/ HCO_3^- , on an equivalents basis, ranged from 0.02 to 0.12, and for the average stream water composition the HCO_3^- produced by Equation 2 would only account for 6% of the total HCO_3^- . Solution of CO_2 from the atmosphere or from soil respiration, and reaction with the resultant carbonic acid, must therefore represent the main mechanism for the solution of carbonate minerals.

Modelling the chemistry and $\delta^{13}\text{C}$ values of TDIC requires assumptions to be made as to whether the system is 'open' or 'closed' to the soil atmosphere. Since the active layer in the catchment of Stream 1 is thought to average only 1 m at its deepest, and the humus layer and plant rooting depths are only a few cm, an 'open' system is assumed in which the TDIC freely

exchanged with the soil atmosphere, and the soil atmosphere was a mixture of atmospheric CO₂ and plant/soil-respired CO₂. The partial pressure of the total gaseous CO₂, pCO_{2TOT}, was computed from the water chemistry using the PHREEQC programme (Parkhurst, 1995). On the basis that the partial pressure of atmospheric CO₂ is 360 ppm, the partial pressure due to soil-respired CO₂ was then calculated as: pCO_{2SOIL} = pCO_{2TOT} - 0.00036. For most of the drainage season soil-respired CO₂ was estimated to make up 40-60% of the total CO₂; i.e. soil-respired CO₂ and atmospheric CO₂ were present in roughly equal amounts.

The δ¹³C value of atmospheric CO₂ is about -8‰. For soil-respired CO₂ we assume a δ¹³C value of -23‰. This is based on the δ¹³C value for organic matter in the soil being -27‰ (Table 6), but increased by 4‰ to account for possible isotope fractionation due to diffusion (Cerling et al. 1991). From this the δ¹³C value of the total gaseous CO₂ is:

$$\delta^{13}\text{C}_{\text{CO}_2\text{TOT}} = [-23 \cdot (\text{pCO}_2\text{TOT} - 0.00036) - 8 \cdot (0.00036)] / \text{pCO}_2\text{TOT} \quad (3)$$

Using the carbon isotope fractionations between gaseous CO₂ and dissolved carbon species given by Zhang et al. (1995), and the proportions of dissolved carbon species computed using PHREEQC, the CO₂-TDIC isotope fractionation can be calculated and, therefore, the value for δ¹³C_{TDIC} (Figure 6). Skidmore et al. (2004) noted how kinetic, non-equilibrium isotope fractionation may have a marked effect on the δ¹³C_{TDIC} values of fast-flowing glacial streams during water-carbonate interaction over a few hours. However, as the slow flow rates of Stream 1 suggest that the residence time of water in the catchment was at least several days, our calculations assume isotope equilibrium.

Figure 6 shows the δ¹³C_{TDIC} values calculated for Stream 1 waters in 2002, compared with their measured values. Over much of the summer calculated and measured values were in qualitative agreement. However, there was a tendency for calculated values to be about 2‰ lower than

measured value in the earlier part of the summer. This discrepancy suggests that the system was not entirely open. Mineral carbonate in the gravels of Site 1 had a $\delta^{13}\text{C}$ value of +2 to +3‰ (Table 6). Solution of this carbonate, under semi-closed conditions where there is not complete exchange with soil CO_2 , would raise the calculated $\delta^{13}\text{C}_{\text{TDIC}}$ values above those shown in Figure 5, toward closer agreement with the measured values.

Similar calculations for Stream 2 and Stream 3, assuming an open model system, again yield calculated $\delta^{13}\text{C}_{\text{TDIC}}$ values similar to the measured values; typically agreeing to within $\pm 2\%$. In contrast to the three streams in 2002, however, calculations for Stream 1 in 2001 yield $\delta^{13}\text{C}_{\text{TDIC}}$ values of -16 to -13‰, which are much lower than the measured values. This is a consequence of the pH values measured for Stream 1 in 2001 being lower than those in 2002 (Table 2). This results in higher estimates for $\text{pCO}_{2\text{TOT}}$ using PHREEQC, and hence lower calculated $\delta^{13}\text{C}_{\text{CO}_{2\text{TOT}}}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ for 2001. An error in pH measurements in 2001 might explain this discrepancy, though we have no way of accounting for this error.

4.4 Nitrogen

4.4.1. Nitrate

$\delta^{15}\text{N}$ values for organic matter in soil near Stream 1 were +1 to +2‰ (Table 6). Since isotope fractionation during bacterial mineralisation and nitrification of organic matter in nutrient-poor soils is generally thought to be small (Heaton, 1986; Kendall, 1998), similar values might be expected for soil-derived NO_3^- . On this basis, the $\delta^{15}\text{N}$ values of NO_3^- in Stream 1 waters of 2002, typically -1 to +2‰ (Table 3), are what might be expected for soil-derived NO_3^- , but are quite different from the snowpack NO_3^- (c. -7‰) (Table 1).

A distinction between soil-derived and atmospherically-derived (i.e. snowpack) NO_3^- , however, is more easily based on $\delta^{18}\text{O}$ analysis (Amberger and Schmidt, 1987; Durka et al.

1994; Kendall, 1998). On the theoretical assumption that nitrification derives two thirds of its oxygen from H₂O (average for Stream 1 = -9‰), and one third from atmospheric O₂ (+23.5‰ (Kroopnick and Craig, 1972)), this would produce NO₃⁻ with δ¹⁸O_{NO3} = +2‰ for Site 1. In contrast, the snowpack NO₃⁻ ranged from δ¹⁸O_{NO3} = +60 to +85‰ (Heaton et al. 2004). The pure silver nitrate end-member for Stream 1 waters in Figure 7, having δ¹⁸O_{NO3} values of about -4 to +1‰, is therefore very similar to the value expected for NO₃⁻ derived entirely from nitrification. The linear trend of all Stream 1 samples in Figure 7 indeed suggests that throughout the season the source of the stream NO₃⁻ was entirely of microbial origin, with no evidence of atmospheric, snowpack NO₃⁻. Thus, whilst about 50 g NO₃-N ha⁻¹ is deposited in the winter snowpack, with further deposition in summer precipitation, this NO₃⁻ was entirely taken up into the soil bacterial nitrogen pool, and did not run off directly into the stream water.

The lack of evidence for snowpack NO₃⁻ in the Stream 1 waters is considered a result of the relatively low NO₃⁻ inputs. The chemistry and δ³⁴S_{SO4} values of the earliest stream waters collected in both 2001 and 2002, which largely consisted of overland flow, had definite snowpack characteristics. Therefore, it seems that the size of the input of snowpack NO₃⁻ to the tundra was small enough to allow the majority of it to be immobilised by assimilation into the plant / soil biomass. Plants and the microbial biomass can start to become active whilst still snow covered, and recent work has demonstrated the effectiveness of alpine and arctic tundra as sinks for inorganic N released from the snowpack (Bilbrough et al. 2000; Tye et al. 2005). Tye et al. (2005) applied ¹⁵N-labelled inorganic NO₃ and NH₄ at the last stages of snowmelt to tundra close to Streams 1 and 3 of this study, and subsequently recovered about 60% of this nitrogen from the microbial biomass, bryophytes and lichens, even though the applications of 1 and 5 kg N ha⁻¹ greatly exceeded snowpack inputs.

Earlier studies utilising $\delta^{18}\text{O}_{\text{NO}_3}$ analysis of silver nitrate samples prepared from high elevation or alpine tundra catchments have tended not to report sample purity, or consider how organic O contaminants might affect interpretation (Burns and Kendall, 2002; Campbell et al. 2002; and Sickman et al. 2003). Taken at face value, however, their conclusions differ slightly from those for Stream 1, in that they do detect a component (< 50 %) of snowpack NO_3^- in stream waters draining catchments after snowmelt. This may reflect differences in the soil/plant biomass, and/or in the relative amounts of snowpack N. Thus many of the previous studies were in catchments with a large amount of bare rock, where biological modification of the snowmelt chemistry will be minimised. Sickman et al. (2003) found that ~20-30% of stream water NO_3^- in the first stages of snowmelt was from the snowpack, but this was for an area where the amount of snowpack $\text{NO}_3\text{-N}$ was $\sim 260 \text{ g ha}^{-1}$, almost 5 times the inputs in this study. Therefore, in environments with less soil cover, or greater snow depths or NO_3^- concentrations than those near Stream 1, saturation with respect to the NO_3^- assimilation abilities of the microbial and plant populations may occur during snow melt.

Hodson et al. (2002) reported an increase in $\text{NO}_3^-/\text{Cl}^-$ ratios during mid-July in drainage through the developing active layer of moraine soils in a glacial forefield 4 km west of Ny Alesund. The increase in NO_3^- concentrations in samples from Stream 1 started in mid to late July and corresponded to a time of maximum active layer development and increased soil dryness when plants were becoming senescent. This increase could be explained by Sickman *et al.*'s (2003) proposal that increased NO_3^- concentrations in alpine catchment streams were brought about by continued mineralization/nitrification by the soil microbial biomass at a time when plant demand for nitrogen uptake was being reduced through senescence. Such a microbial nitrification origin is clearly indicated for the unusually high NO_3^- concentrations for Stream 1 on 20 July and 19 August 2002 (Table 2, Figure 6). In both cases the samples were taken on days when rainfall occurred after a prolonged dry spell. The $\delta^{18}\text{O}_{\text{NO}_3}$ values close to 0‰ rule out any contribution from atmospheric NO_3^- , and the lack of increased chloride

concentrations excludes evaporative enrichment as a cause of the high NO_3^- . The microbially-produced NO_3^- had presumably been accumulating in the catchment soils until it was flushed out with the start of rainfall.

4.4.2. Ammonium

Apart from a single early sample in 2001 (day 173), associated with heavy rainfall, NH_4 concentrations and NH_4/Cl^- ratios remained constantly low (Fig. 2h). Unlike NO_3^- , there was no rise in NH_4 towards the end of summer, and no flush-out of accumulated NH_4 by rainfall following dry periods. The isotopic characteristics of ammonium in geo-hydrological studies is much less well studied than nitrate, and the limited $\delta^{15}\text{N}$ data for ammonium in Stream 1, six samples from 2002 with values -7.2 to -0.7‰, can not be unambiguously interpreted. Ammonium produced by mineralisation in N-limited soils is thought to have, like nitrate, a $\delta^{15}\text{N}$ value similar to that of the organic N (Kendall, 1998), and on this basis the $\delta^{15}\text{N}$ values for Stream 1 ammonium were much lower than that of the organic N (+1 to +2‰ in Table 6). In addition, the Stream 1 sample $\delta^{15}\text{N}_{\text{NH}_4}$ values were also lower than that of the 2002 snowpack (-0.3‰); though they are within the range for other snow samples (2001 snowpack, and individual snow events in Table 1) and within the published range for rainfall (Heaton et al. 1997). It is possible that some process of isotope fractionation has occurred, operating either on soil-derived or atmospheric ammonium.

4.4.3. Organic nitrogen

Consideration of overall N budgets must include the role of dissolved organic nitrogen (Neff et al. 2003). No data are available for the snowpack at Site 1, but analyses of snow on nearby glaciers found that concentrations of DON were generally less than those of inorganic N (Hodson et al. 2005). In contrast, and in common with many low N systems, concentrations of DON in the stream generally exceeded those for total inorganic N (Table 2b). A strong correlation between DOC and DON ($r^2 = 0.92$) in Stream 1, together with the relatively high

DOC/DON ratios (Table 2b), suggest that much of this DON may have derived from humic substances in soil organic matter. These features accord with studies showing that DON of predominantly soil humic origin is the main form of N loss via rivers draining the Arctic tundra (Dittmar et al. 2001; Kawahigashi et al. 2004).

Perakis & Hedin (2002) suggested that in ecosystems with low N inputs, inorganic N is largely retained within the ecosystem, whereas less biologically-available forms of DON may dominate in stream waters. Thus N-limited ecosystems with a high biotic demand for N may nevertheless lose DON. The forms of DON lost will tend to be the more complex organic components resistant to biochemical breakdown, and the factors controlling their loss may be less subject to biotic influences (mineralization or biotic uptake) than factors controlling inorganic N. Instead, DON concentrations in streams may be more closely linked to factors influencing the organic retentivity of soil mineralogy – sandy soils such as those at Site 1 being less retentive - and hydrological parameters (Hedin et al. 1995; Neff et al. 2003). These factors may explain the relative constancy of the DON/Cl ratio in Stream 1 throughout the season, and the similar response of both NO_3^- and DON concentrations to significant rainfall events where a positive correlation in molar concentration of NO_3^- and DON was found ($r^2=0.78$). However, whereas the ratio of DON/Cl⁻ remained relatively constant through the summer, the NO_3^- /Cl⁻ ratio clearly increased towards the end of the season.

5. CONCLUSIONS AND IMPLICATIONS

Results from this study have increased understanding of the mechanisms involved in weathering reactions and nitrogen release in thin organic soils overlying sediment in tundra. In particular, the stable isotope analyses provide insights into how biogeochemical and weathering processes may evolve with climate change and the expected increases in the depth of the active layer (Anisimov et al. 1997). Snowpack on a near-shore site in the High Arctic has a major element composition dominated by seawater. This seawater chemistry is evident in

the earliest stream waters draining the tundra at the onset of snowmelt, but is gradually modified by weathering reactions. The main chemical change is associated with solution of Ca-Mg carbonate. The $\delta^{13}\text{C}$ values of the resulting bicarbonate in the streams are unusually high, and are presumed to reflect the particular characteristics of these tundra soils. Thus in parts of the globe where soils are deeper and better developed, 'closed system' carbonate solution dominated by plant/soil-respired CO_2 is common. In contrast, the chemistry and $^{13}\text{C}/^{12}\text{C}$ ratios of three streams sampled near Ny-Ålesund in 2002 can be accounted for by a largely 'open system' model in which the CO_2 is derived about equally from atmospheric and plant/soil sources. As these sources of CO_2 are essentially restricted to a very thin plant/soil cover in the top few centimetres of the active layer, the progressive deepening of the active layer as the permafrost melts during the summer will probably not promote any increase in carbonate solution. This may account for the fact that the Ca-Mg- HCO_3^- concentrations in the stream waters are established early in the season, and display only limited increases in the later part of summer. Increases in the depth of the active zone predicted with climate change will result in new mineral surfaces and easily soluble minerals being exposed (Keller et al., 2007). However, results from this study suggest that the weathering of carbonates in the deepening active zone through solution of CO_2 from atmospheric or biological sources may be limited by its diffusion as demonstrated with the 'open system' model.

In glacial systems the solution of carbonate by CO_2 is limited by the relative scarcity of biogenic sources of CO_2 , and restricted access of atmospheric CO_2 to the water-saturated bed of a glacier. Sulphide oxidation may therefore be a major contributor to carbonate solution in glacially-derived streams (Tranter et al. 2002). Although its role in the non-glacial streams of this study appears to be less important, sulphide oxidation nevertheless represents the second major weathering reaction whose understanding benefits from isotope data. The $\delta^{34}\text{S}$ values of the stream water sulfate follow a clear two end-member mixing pattern: a seawater sulfate component dominant in the earliest part of the summer drainage, with sulfate derived from

oxidation of reduced sulfur in coal being progressively added through the rest of the summer. If the fragments of coal are uniformly distributed through the subsoil, as might be expected in glacially-derived gravels, more coal will be exposed to sulfur oxidation as the active layer deepens. This may explain why $\text{SO}_4^{2-}/\text{Cl}^-$ ratios, unlike $\text{HCO}_3^-/\text{Cl}^-$ ratios, rise progressively through the summer drainage. The $\delta^{18}\text{O}$ values of the sulfate are consistent with the oxidation being entirely aerobic, which would be expected given the easy exchange of the atmosphere with a shallow active layer. This is in contrast to the formation processes ascribed to sulfate in glacial runoff, where $\delta^{18}\text{O}$ data have been used to suggest that sulphide oxidation at the bed of a glacier, cut off from the atmosphere, is at least partially anaerobic (Bottrell and Tranter, 2002; Wynn et al. 2006). Thus, with increases in the depth of the active layer expected with increasing temperatures, the distribution and weathering of newly exposed sulphide minerals in the sediment underlying the thin soils may play an important role in the production of acidity required for carbonate solution and may be a mechanism that increases losses of Ca-Mg- HCO_3^- and SO_4^{2-} to surface waters.

In contrast to other studied alpine and arctic catchments, the isotope composition ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values) of NO_3^- in drainage waters in this study suggests that none of it is derived directly from atmospheric NO_3^- . Possibly because of the low NO_3^- input, and the existence of a continuous (if thin) soil cover, the snowpack NO_3^- was assimilated and re-mineralised before being released into the stream. The export of this soil-derived NO_3^- increased during the latter part of summer as plant senescence progressed and ecosystem demand for NO_3^- diminished. Results have demonstrated that there are increased losses of NO_3^- derived through microbial activity from early to mid August. Warmer temperatures would be expected to extend the length of time each summer in which high microbial activity is present. It will also produce a shorter frozen period when drainage waters would not be present. This would be expected to increase NO_3^- losses. However, the extent of NO_3^- losses in drainage waters may be a balance

between microbial activity and the effect of warming on senescence in tundra plants. For example, Marchard et al. (2004) suggested that climate warming may extend the growing season and postpone senescence in plants of the High Arctic, contrary to previous research suggesting that late season phenology is solely controlled by photoperiod. No seasonal change was evident in dissolved organic nitrogen, the other major form of N loss to drainage. This might be a consequence of the DON being largely unreactive, with its concentrations mainly subject to abiological controls. However, increases in microbial activity and the length of the drainage period as a result of increasing temperatures will increase the overall losses of organic C and N species in drainage waters to aquatic ecosystems.

ACKNOWLEDGEMENTS

The authors would like to thank the UK Natural Environment Research Council (NERC) for funding this work through the GANE programme (grant GST/02/2725). The project operated out of the NERC Arctic Research Station in Ny-Ålesund and we would like to thank Nick Cox, Johanna Laybourn-Parry and Maggie Annat for their project and logistical support. John Corrie and Mike Gubbins provided analytical and technical support at the University of Nottingham. Carol Arrowsmith and Carolyn Chenery helped with isotope analyses at the British Geological Survey. Patrice de Caritat and one anonymous reviewer provided valuable comments and suggestions to improve the paper.

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Table 1. Composition of snowpack, ice layers and snowfall at Site 1

	Na	K	Ca	Mg	NH ₄	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	δ ² H _{H2O}	δ ¹⁸ O _{H2O}	δ ³⁴ S _{SO4}	δ ¹⁸ O _{SO4}	δ ¹⁵ N _{NO3} *	δ ¹⁸ O _{NO3} *	δ ¹⁵ N _{NH4}	
	μmol/L								%vSMOW	%vSMOW	%CDT	%vSMOW	%AIR	%vSMOW	%AIR	
Snowpack, 2001																
Mean	398	9.3	12.8	43.5	1.7	481	34.1	3.1	-65	-10.0	+17.0	+9.7	-13.5	+75.5	-3.1	
±1 SD	112	4.6	5.6	15.0	1.1	157	10.7	2.2	13	1.6	0.4	0.5	1.2	4.7	2.0	
No. of samples	15	15	15	15	15	15	15	15	15	15	4	4	4	4	5	
ion/Cl ratio	0.83	0.019	0.027	0.091		1	0.071									
Seawater ion/Cl ratio	0.86	0.018	0.019	0.098		1	0.052									
Snowfall, 23/04/01	80	1.6	14.3	11	1.7	59	11	2.3	-58	-9.5	+11.9	+9.7	-17.8	+77.8	-4.3	
Snowpack, 2002																
Mean	486	11.5	15.2	47.9	1.2	553	34.5	1.7	-88	-12.4	+18.0	+9.5	-6.9	+76.8	-0.3	
±1 SD	216	4.8	6.5	20.6	0.5	219	17.3	0.8	6	1.1	0.3	1.1	2.0	6.7	1.7	
No. of samples	18	18	18	18	18	18	18	18	4	4	3	3	4	4	4	
ion/Cl ratio	0.87	0.021	0.027	0.085		1	0.061									
Seawater ion/Cl ratio	0.86	0.018	0.019	0.098		1	0.052									
Ice layers, 2002																
Mean	199	7.6	28.5	26.2	0.4	328	19.8	1.5	-64	-9.3						
±1 SD	114	3.5	10.8	9.2	0.3	215	15.6	0.5	4	0.4						
No. of samples	4	4	4	4	4	4	3	4	4	4						
Snowfall, 05/04/02	131	3.4	14.7	33	5.4	144	28	3.9			+12.8	+11.9	-8.6	+73.8	-6.6	

* Data from Heaton et al. (2004)

Table 2: Composition of waters sampled from stream 1 in (a) 2001 and (b) 2002.

(a) 2001

Date	Day no.	pH	Na	K	Ca	Mg	NH ₄	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	δ ² H _{H2O}	δ ¹⁸ O _{H2O}	δ ³⁴ S _{SO4}	δ ¹⁸ O _{SO4}	δ ¹³ C _{DIC}
												μmol/L	‰VSMOW	‰VSMOW	‰CDT	‰VSMOW
18-06	169	6.7	246	10	249	124	1	395	26	1.6	447	-71	-10.5	+15.1	+6.1	-8.7
22-06	173	6.9	136	8	306	156	6	144	15	1.4	766	-66	-9.5	+9.0	+1.2	-6.4
02-07	183	7.0	196	9	417	288	2	216	32	0.7	1284	-61	-8.9	+5.4	+0.6	-2.2
09-07	190	6.8	202	8	417	288	N/A	177	23	0.1	1284	-65	-9.1	+7.1	-0.3	-2.4
12-07	193	7.2	215	10	479	363	1	223	34	1.2	1204					
22-07	203	7.1	235	12	671	529	1	259	58	0.9	2161	-63	-8.4			-2.1
05-08	217	7.2	197	9	585	399	1	246	49	1.8	1683	-80	-11.7	+4.5	+0.9	-2.5
12-08	224	7.4	227	13	795	542	1	293	84	2.7	2361	-72	-9.5	+1.7	+0.8	-2.9
21-08	233	7.0	214	12	828	577	1	274	86	7.7	2560	-70	-9.3	+1.7	+1.4	-4.4
26-08	238	7.2	200	12	784	517	1	271	91	7.9	2281	-70	-9.4	+2.4	+0.2	-1.9
02-09	245	7.3	157	12	767	517	1	285	99	13.1	2465	-68	-8.8			

(b) 2002

Date	Day no.	pH	Na	K	Ca	Mg	NH ₄	Cl-	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	DOC	DON	δ ² H _{H2O}	δ ¹⁸ O _{H2O}	δ ³⁴ S _{SO4}	δ ¹⁸ O _{SO4}	δ ¹³ C _{DIC}	δ ¹⁵ N _{NH4}	
														μmol/L-----	%oVSMOW	%oVSMOW	%oCDT	%oVSMOW	%oPDB	%oAIR
13-06	164	7.3	190	10	250	139	1.3	199	17.8	1.5	686	281	11	-75	-10.3	+8.7	+1.2	-7.5	-1.9	
17-06	168	7.7	234	10	401	235	1.0	219	61.5	0.9	1204	267	9	-87	-11.5	+3.8	-0.2	-2.3		
24-06	175	7.8	215	9.9	411	243	0.7	233	38.4	0.29	1284	250	9	-77	-10.3			-1.5		
28-06	179	8.0	251	14	503	288	1.0	257	39.1	0.79	1483	323	11	-70	-9.1	+4.0	0.0	-2.4		
04-07	185	8.0	317	17	682	387	1.3	300	51.4	7.6	2121	339	14	-71	-7.9			-3.9		
06-07	187	8.0	244	16	714	407	1.0	311	56.6	2.3	2161	292	13	-59	-7.6	+2.0	-0.3	-3.7		
20-07	201	8.1	373	26	799	487	1.5	386	89.2	34.7	2440	426	31	-63	-7.6	+2.1	+1.2	-4.4	-5.8	
01-08	213	8.2	457	18	922	563	1.6	459	145.8	8.0	2759	397	22	-55	-6.8	+0.6	+1.1	-3.1		
06-08	218	8.4	472	22	978	582	1.3	450	173.3	10.9	2919	337	16							
15-08	227	8.2	513	24	1072	633	1.6	464	217.8	10.1	3198	337	19	-59	-7.1	-0.9	+1.2	-3.9	-0.7	
19-08	231	8.2	356	19	793	533	1.1	372	113.2	21.1	2400	392	27	-62	-7.8	+0.8	+1.1	-3.8	-7.2	
22-08	234	8.2	304	15	674	440	0.9	307	79.3	11.4	2001	358	18	-73	-9.5	+2.4	-0.2	-3.5	-5.2	
27-08	239	8.2	249	11	525	330	0.5	264	75.8	7.4	1523	302	11	-67	-8.9			-2.8		
29-08	241	8.0	209	13	633	397	0.8	288	94.0	7.9	1842	315	14	-70	-9.1	+1.4	-0.3	-2.3	-2.8	
03-09	246	8.0	296	14	731	465	0.6	301	115.1	12.4	2041	300	13	-68	-8.8					

Table 3. Composition of silver nitrate of varying purity prepared from NO_3^- of Stream 1 water in (a) 2001 and (b) 2002

(a) 2001

Date	Day no.	$\delta^{15}\text{N}_{\text{NO}_3}$ ‰ _{AIR}	$\delta^{18}\text{O}_{\text{NO}_3}$ ‰ _{VSMOW}	C/N weight	N/O atomic
18/6	169		+12.3		0.13
22/6	173		+8.1		0.12
2/7	183		+12.0		0.04
9/7	190		+11.2		0.04
22/7	203		+11.3		0.04
5/8	217		+10.1		0.09
12/8	224		+2.4		0.19
21/8	233	-1.5	-4.4	0.07	0.32
26/8	238	-1.4	-4.5	0.05	0.33

(b) 2002

Date	Day no.	$\delta^{15}\text{N}_{\text{NO}_3}$ ‰ _{AIR}	$\delta^{18}\text{O}_{\text{NO}_3}$ ‰ _{VSMOW}	C/N weight	N/O atomic
13/6	164	-1.9	+4.7	0.66	0.22
17/6	168	-0.9	+1.0	>1	0.16
28/6	179		+11.0		0.08
6/7	187	-0.2	+2.8	1.25	0.24
20/7	201	-0.8	-1.4	0.31	0.31
1/8	213	+0.2	+1.4	0.44	0.24
15/8	227	+1.7	+0.9	0.38	0.26
19/8	231	+1.6	-0.6	0.28	0.33
22/8	234	+1.9	-1.7	0.25	0.34
29/8	241	+1.1	-1.5	0.15	0.28

Table 4: Composition of waters sampled from Stream 2 in 2002

Date	Day no.	pH	Na	K	Ca	Mg	NH ₄	Cl-	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	δ ² H _{H2O}	δ ¹⁸ O _{H2O}	δ ¹³ C _{DIC}
----- μmol/L -----												‰ _{VSMOW}	‰ _{VSMOW}	‰ _{PDB}
13-06	164	7.8	178	15	365	179	0.9	182	23.8	0.4	965	-68	-9.4	-7.8
17-06	168	7.7	158	11	346	140	0.7	161	12.3	3.1	766	-81	-11.2	-5.2
24-06	175	7.8	133	13	373	141	0.7	120	14.4	3.1	965	-72	-10.0	-3.4
28-06	179	7.7	117	12	312	107	0.5	98	13.8	5.1	766			-5.1
19-08	231	8.1	329	31	966	416	1.1	298	117	17.1	2441	-67	-8.9	-4.9
22-08	234	8.2	262	29	944	400	0.6	242	103	30.2	2361	-71	-9.6	-5.3
27-08	239	8.2	233	23	865	377	0.4	179	105	10.6	2161	-81	-9.4	-5.4
29-08	241	8.2	253	26	950	412	0.5	201	139	11.7	2321	-73	-9.6	
03-09	246	8.2	277	28	993	433	0.7	224	153	12.3	2401	-72	-9.4	

Table 5: Composition of waters sampled from Stream 3 in 2002

Date	Day no.	pH	Na	K	Ca	Mg	NH ₄	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	DOC	DON	δ ¹³ C
----- μmol/L -----														
‰ _{PDB}														
22-06	173	7.9	125	9	548	104	0.5	125	15	3.0	1204	166	<7	-5.3
25-06	176	7.9	106	8	503	92	0.3	86	12	3.0	1125	200	<7	-4.0
05-07	186	7.9	83	8	609	114	0.5	59	17	2.0	1364	185	<7	-4.2
13-07	194	8.0	81	10	676	128	0.2	58	22	3.2	1723	204	<7	-4.3
20-07	201	8.0	79	9	686	138	0.5	58	25	5.5	1523	191	<7	-4.3
08-08	220	8.2	95	11	876	183	0.1	73	47	7.5	1922	169	<7	-4.8
22-08	234	8.2	95	11	971	201	0.2	103	57	10.3	1882	165	<7	-4.3
28-08	240	8.2	106	11	993	213	0.3	117	67.	8.6	2042	171	<7	-4.7

Table 6. Isotopic analyses of rock gravel fragments and soils near Stream 1

Sample	Total S		Carbonate		Total organic	
	Amount (ppm)	$\delta^{34}\text{S}$ (‰ CDT)	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ PDB)	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{15}\text{N}$ (‰ AIR)
Sandstone	<10	-	-	-	-	-
Granodiorite	<10	-	-	-	-	-
Schist 1	50	+17.9	-	-	-	-
Schist 2	30	+13.6	-2.8	-19.3	-	-
Coal	1580	-0.9	-	-	-	-
Limestone 1	-	-	+3.3	-13.7	-	-
Limestone 2	-	-	+2.1	-14.1	-	-
Soil 1	-	-	-	-	-27.4	+1.2
Soil 2	-	-	-	-	-26.5	+2.1

Figure Captions

Figure 1: Map of Kongsfjorden showing the sites of the three sampled streams. Snow sampling was carried out in a 100 x 100m area in the catchment of stream 1.

Figure 2: Daily precipitation (-) and flow (●) rates measured at the time of sampling for Stream 1 during the summers of 2001 and 2002.

Figure 3: Temporal changes in the composition of Stream 1 in 2001 (●) and 2002 (□). The chemistry is expressed as ion/Cl⁻ molar ratios: (a) Ca/Cl⁻, (b) Mg/Cl⁻, (c) Na/Cl⁻, (d) K/Cl⁻, (e) HCO₃⁻/Cl⁻, (f) SO₄²⁻/Cl⁻, (g) NO₃⁻/Cl⁻, (h) NH₄/Cl⁻, (i) DON/Cl⁻, (j) DOC/Cl⁻ and (k) DOC/DON. Drainage water values are compared with snowpack chemistry (arbitrarily plotted at day 150) for 2001 (▲) and 2002 (◇). Bars signify the propagated error associated with the analytical precision of the ion and chloride measurements. Where bars are absent the error is less than the symbol size.

Figure 4. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of Stream 1 during 2001 (●) and 2002 (□). The mean values for the snowpack (▲, ◇) are arbitrarily plotted at 150 days.

Figure 5. $\delta^{34}\text{S}_{\text{SO}_4}$ values for sulfate in Stream 1 in relation to the percentage of non-sea-salt sulfate (calculated from $[1 - (0.052 \cdot \text{Cl}^-/\text{SO}_4^{2-})] \cdot 100$; Newman et al. 1991). ● = 2001; □ = 2002; ▲, ◇ = 2001 and 2002 snowpack.

Figure 6. Measured $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) in Stream 1 waters in 2002 (□), compared with $\delta^{13}\text{C}$ values calculated for DIC assuming an open system model described in the text (stars).

Figure 7: $\delta^{18}\text{O}$ values of silver nitrate of varying purity prepared from NO₃⁻ of Stream 1 waters during 2001 (●) and 2002 (□) with day/month in parentheses. Purity is expressed as N/O atomic ratio which equals 0.33 for pure NO₃⁻ and trends towards 0 as proportion of contaminant oxygen increases. Bar shows range of $\delta^{18}\text{O}_{\text{NO}_3}$ for 2001 and 2002 snowpack, corrected for contamination, from Heaton et al. (2004).

Figure 1:



Figure 2:

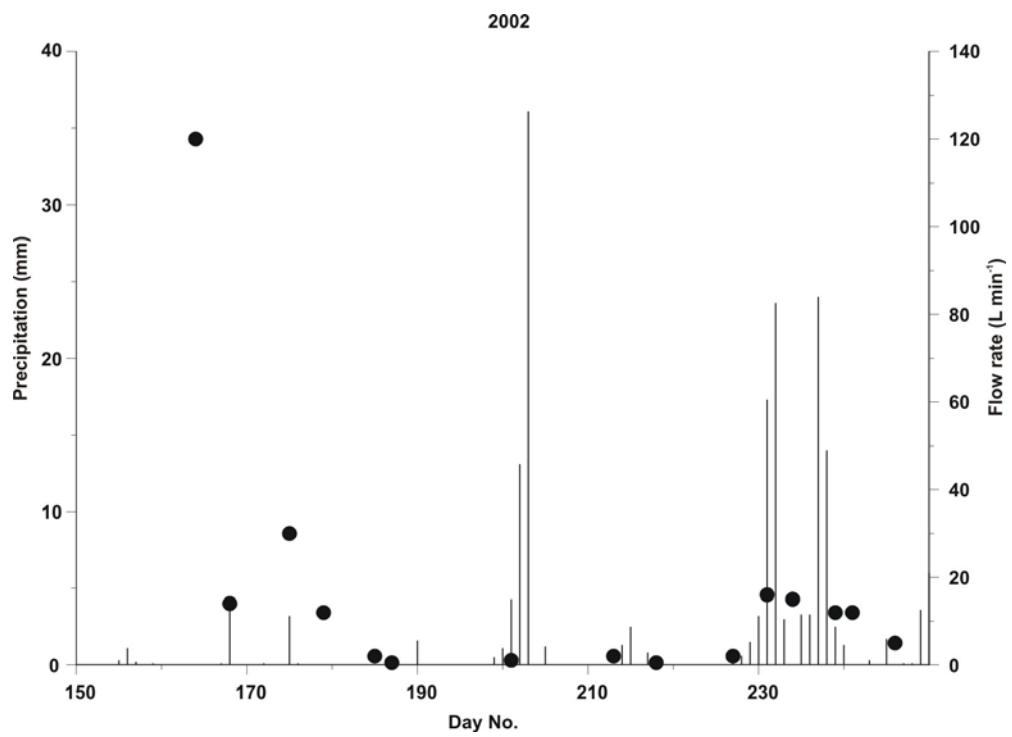
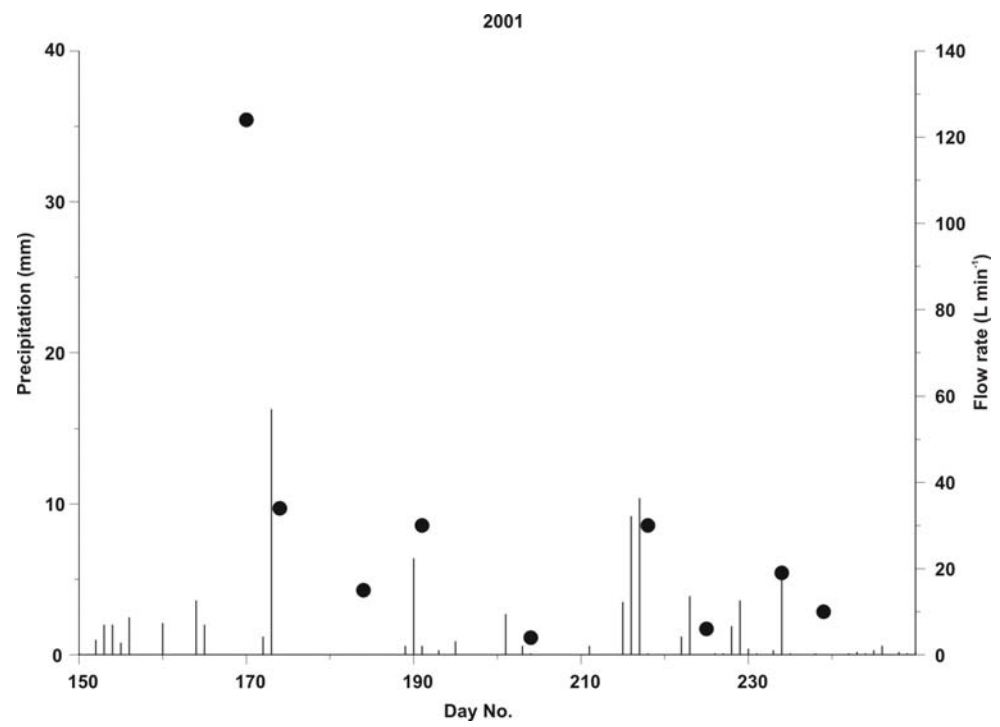
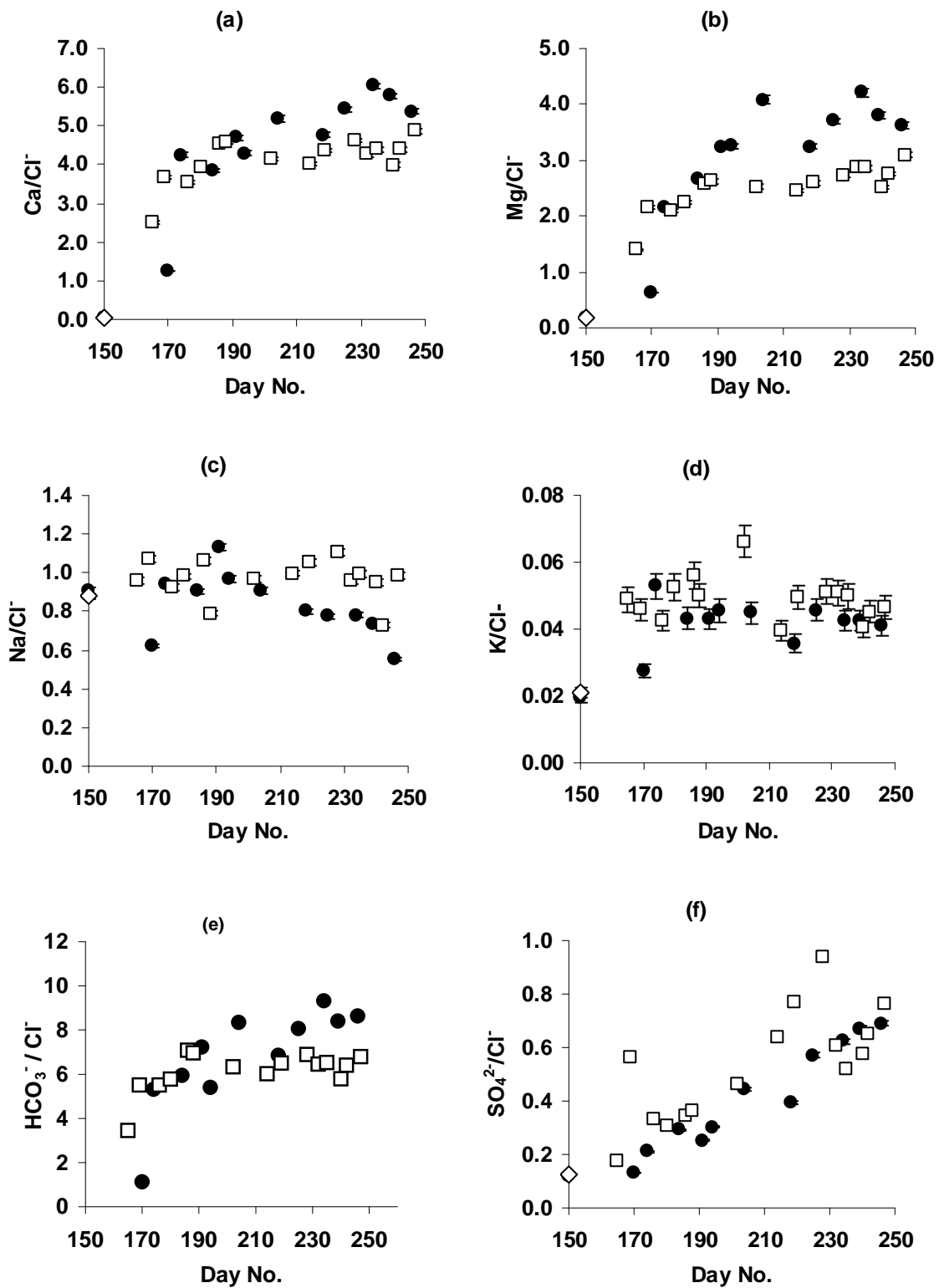


Figure 3:



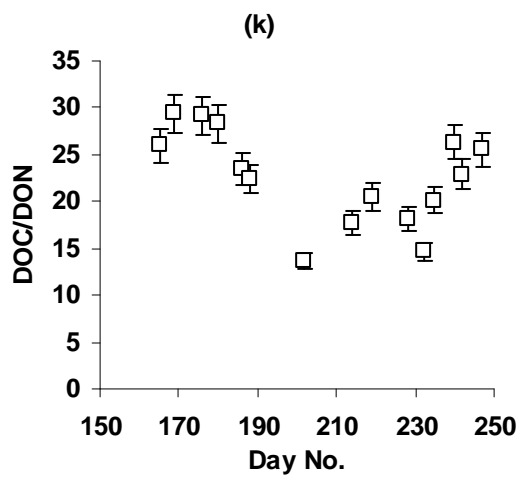
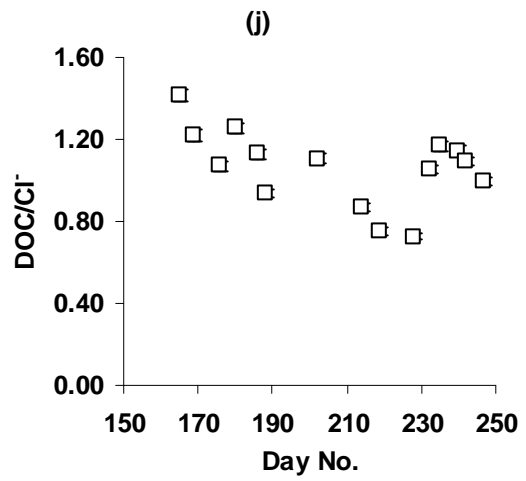
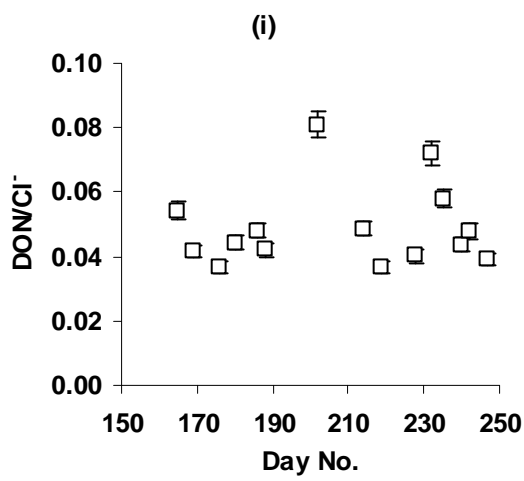
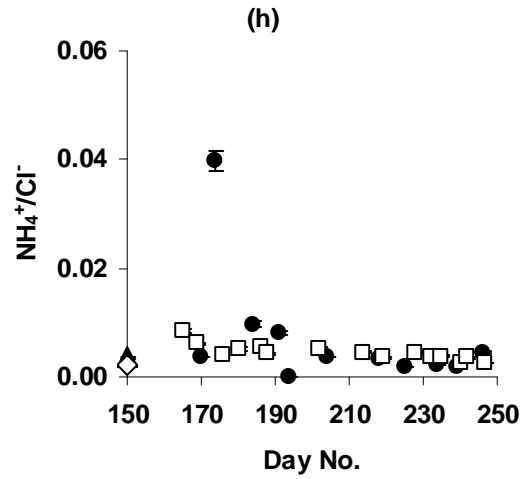
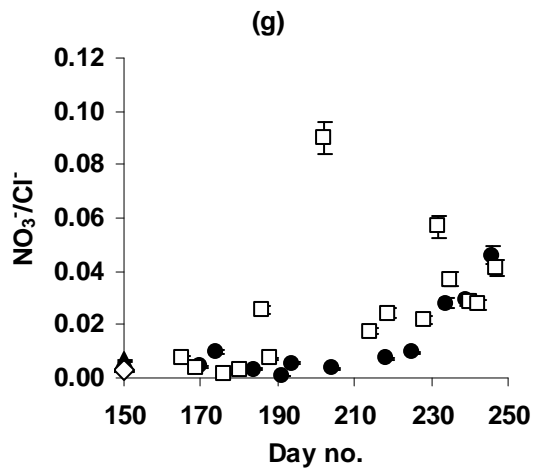


Figure 4.

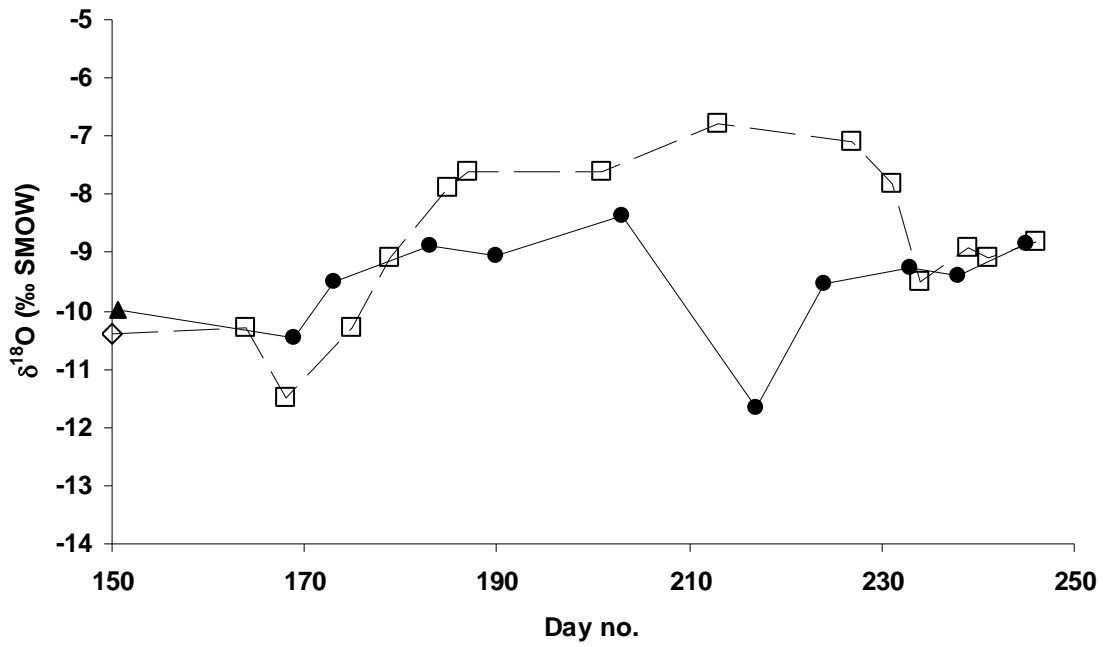


Figure 5.

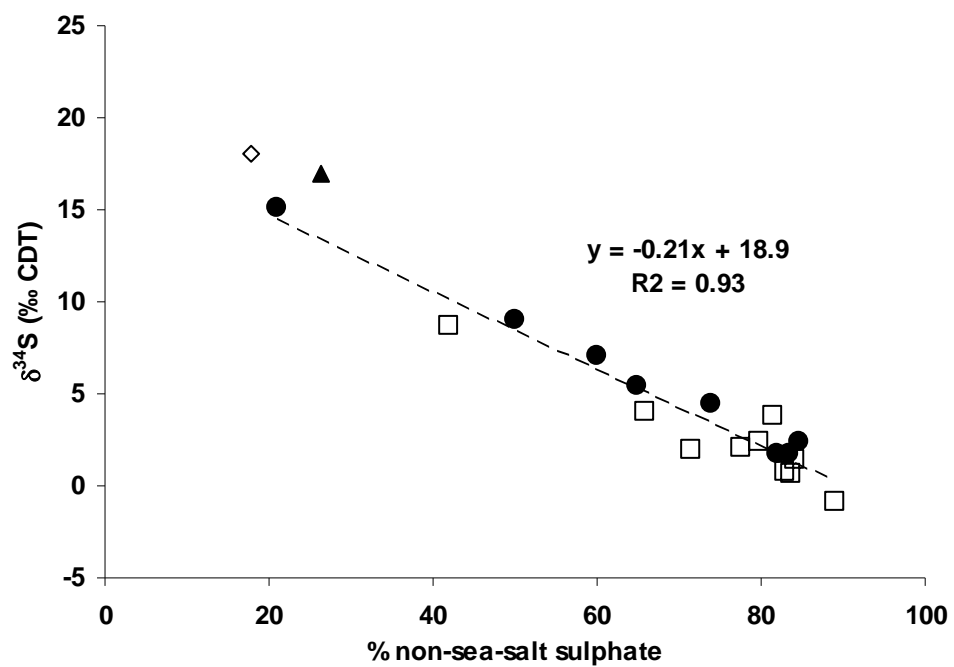


Figure 6.

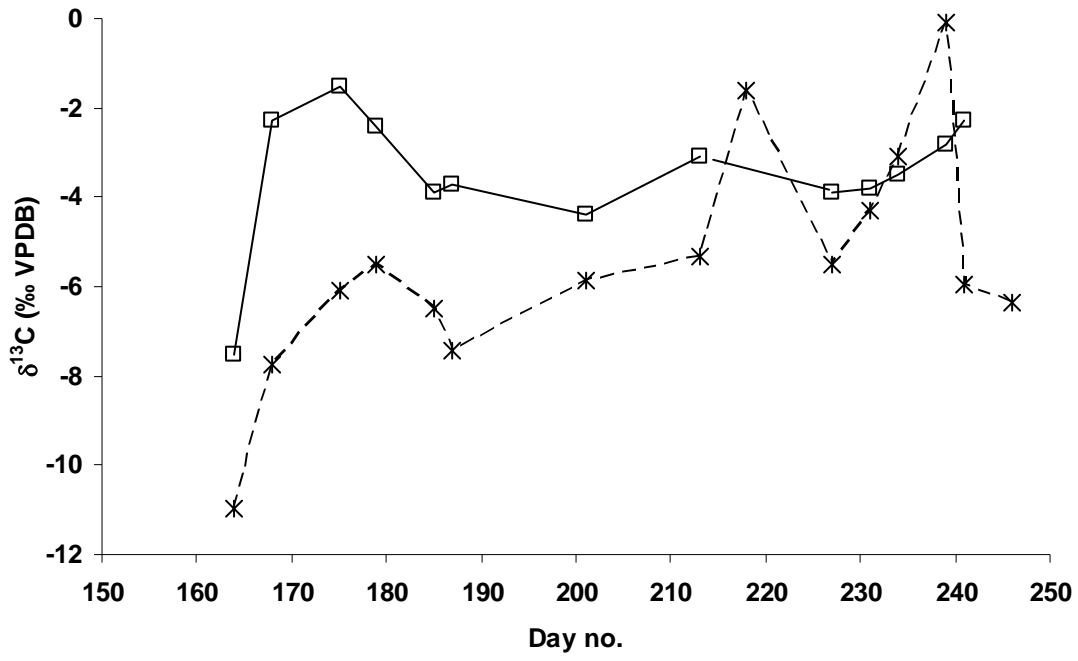


Figure 7:

