POLISH POLAR RESEARCH
vol. 29, no. 2, pp. 149–162, 2008

Rain water chemistry at Calypsobyen, Svalbard

Wiesława Ewa KRAWCZYK [1], Stefan A. BARTOSZEWSKI [2] and Krzysztof SIWEK [2]

[1] Wydział Nauk o Ziemi, Uniwersytet Śląski, Będzińska 60, 41-200 Sosnowiec, Poland
<wieslawa.krawczyk@us.edu.pl >

[2] Instytut Nauk o Ziemi, Uniwersytet Marii Curie-Skłodowskiej,
Akademicka 19, 20-033 Lublin, Poland
<Stefan.Bartoszewski@umcs.lublin.pl> <Krzysztof.Siwek@umcs.lublin.pl>

Abstract: Measurements of pollutants scavenged from air masses over southern Svalbard in summer precipitation are presented. Rainfall was sampled in July and August 2002 at Calypsobyen, Bellsund. Specific conductivity (SpC) and pH were measured and ion concentrations were determined by ion chromatography. Ions of marine origin were subtracted, assuming that all chlorides were of marine origin. The FLEXTRA trajectory model was applied to discover the sources of air masses arriving at Svalbard and track the paths of pollutant transport. Average (v/w) rainfall pH was 4.94, mean SpC amounted to 34.8 µS cm^{-1}. Total dissolved solids concentration (TDS) ranged from 12.6 to 67 mg L^{-1}, with ions of marine origin (Cl^-, Na^+, Mg^{2+}) prevailing. Rains with the highest percentage of marine salts occurred with winds from the East at above average velocities. Non-sea salt (nss) sulphate concentrations ranged from 0.5 µeq L^{-1} to 23 µeq L^{-1}, (v/w) average was 17 µeq L^{-1}. Nitrate concentrations ranged from 0 to 24 µeq L^{-1}. The highest concentrations of nss-SO_4^{2-} and NO_3^- were measured on 25 August, when the highest rainfall occurred (27 mm) and pH was the lowest (4.65). Rainfall at Calypsobyen deposited 194 kg km^{-2} of acidifying anions and 263 kg km^{-2} of base cations over the recording period. The polluted air masses were mostly from northern and central Europe. Rainfalls scavenging air masses formed over Greenland and Norwegian Seas displayed similar concentrations, being probably polluted by SO_x and NO_x from ship emissions.

Key words: Arctic, Svalbard, Bellsund, precipitation, long-range transport of pollutants.

Introduction

Polluted air masses from Eurasia are transported to Arctic regions and are the principal contributor to the phenomenon known as Arctic haze (Pacyna 1995; Stohl *et al.* 2002; AMAP 2006; Law and Stohl 2007). The haze is at a maximum in late winter and early spring. Its main components are sulphates and particulate organic matter, plus some ammonium, nitrate, black carbon and dust (Law and Stohl 2007). Arctic haze may also be returned to its initial source region, as was observed in Leipzig, Germany in April 2002 for example (Heitzenberg *et al.* 2003). The North Atlantic Oscillation (NAO – an index based on the difference of normalized sea level pressures between Azores and Iceland) controls pollution transport into the Arctic, particularly in winter and spring. During its positive phase net transport from the northern hemisphere continents is enhanced, leading to higher Arctic pollutant levels (Eckenhardt *et al.* 2003). The contribution of European emissions to Arctic pollution is considered to be greater than the Asian and North American contributions combined (Eckenhardt *et al.* 2003).

One of the regions easily reached by polluted European air is the Svalbard archipelago. Biomass burning in Eastern Europe was identified as a source of Arctic haze in Ny-Ålesund there in April/May 2006 (Stohl *et al.* 2007; Law and Stohl 2007). The lower tropospheric circulation over Svalbard differs between summer and winter. In winter it is dominated by high pressure over the continents and lows over the oceans. This results in atmospheric conduits transporting polluted air masses from Siberia and Eastern Europe to Svalbard (AMAP 2004). In summer northward transport from low latitudes weakens because the continental high pressure cells disappear. The Polar Front shifts further north, creating a partial meteorological barrier against air from the southern, more polluted regions (AMAP 2004). Summer precipitation should therefore be less polluted.

There are three alternative pathways along which pollutants can be transported to the Arctic: initial low-level transport followed by ascent within the Arctic region, uplift outside and then descent into the Arctic, and entirely low-level transport. In summer European pollution may reach the Arctic along the first two pathways (Stohl 2006).

Precipitation scavenges aerosols and gases from the atmosphere and deposits them at the Earth's surface (Mcdonald *et al.* 2005). One important indicator of atmospheric pollution is the pH of precipitation. But when base cations are present precipitation pH may be neutralized or raised higher, even in the presence of acidifying sulphate and nitrate anions. Such alkaline pH values were found in snow samples collected near to subarctic town of Vorkuta, NE European Russia (Walker *et al.* 2003). These anions are indicators of atmosphere pollution with sulphur and nitrogen oxides – SO_x and NO_x. In stations located close to the sea a proportion of the sulphates will be of marine origin, requiring procedures to subtract the marine component before determining concentrations of non-sea salt (nss) sulphates (Walker et al. 2003).

There are few data on precipitation chemistry in most of the High Arctic because of the problems of accessibility and of collecting reliable and representative samples (AMAP 1998). There are two localities on Svalbard with long-term research data: Ny-Ålesund (78°55'N 11°55'E) and Hornsund (77°00'N 15°33'E). Mean summer (June–July–August) and winter (January–February–March) sulphate concentrations in precipitation at Ny-Ålesund over 1980–2002 show no significant trends (AMAP 2006). Winter concentrations are higher but data after 1996 are missing. Summer concentrations of SO_4^{2-} were below 20 µeq L^{-1} (AMAP 2006). Summer nitrate concentrations show a statistically significant ($P < 0.1$) increasing trend over 1990–2003 at Ny-Ålesund; it is the only one amongst eleven Arctic stations monitoring nitrates that displays such a trend (AMAP 2006). Precipitation is sampled there only on a weekly basis, a strategy that does not allow tracing of the pollution sources. Monitoring at Ny-Ålesund has shown that it receives small but significant amounts of acidifying components such as sulphate and nitrate (Lien *et al.* 1995). In freshly fallen snow on August 30, 2000, for example, sulphate concentrations amounted to 12 µeq L^{-1} (Krawczyk *et al.* 2003). Recently published results from single samples of snow in April/May 1997 at 17 other localities widely around the Arctic found that the median concentration of nss sulphate was only 1.7 µeq L^{-1} (de Caritat *et al.* 2005) but sulphate concentrations from Svalbard sites were among the highest ones.

Precipitation samples have been collected at Hornsund since 1989 but before the summer of 2000 only pH, specific electric conductivity (SpC) and the concentration of chlorides were measured. A preliminary elaboration of results covering the expedition years 1993/94 and 1998/99 was published by Burzyk *et al.* (2002). The first comprehensive chemical analyses of single summer rainfall events were made in 2000, and have been discussed in relation to atmospheric circulation patterns by Krawczyk *et al.* (2002); Głowacki and Krawczyk (2002). Mean precipitation-weighted pH was 4.70 and nearly half of all rainfalls had pH <5. Precipitation with pH <5 in the summer of 2000 occurred in cyclonic situations with advection of air masses from S-SW (Krawczyk *et al.* 2002). Research on the inorganic ions was complemented by determination of the organic compounds in rainfall from September 2003 (Krawczyk and Skręt 2005).

The aim of this paper is to provide data on the chemical composition of rainfall and atmospheric deposition from a new location in southern Svalbard, Bellsund, to determine whether there are significant differences in chemical composition from those at Hornsund, reflecting effects of local sources. The strategy of sampling daily rainfalls permits tracing of the origins of polluted air arriving at the site and estimation of the effects of its scavenging by precipitation. Determining the ionic concentrations in atmospheric precipitation is also necessary for accurate estimates of terrestrial chemical denudation rates; data from the Calypsobyen station discussed below are being used for this purpose in the Scottelva basin (Krawczyk and Bartoszewski in press).

Methods

Rainfall samples were collected in July – August 2002, at a meteorological station located at the Maria Curie Skłodowska University base in Calypsobyen (77°33’N, 14°31’E). The station is at 23 m a.s.l., around 200 m from the shores of

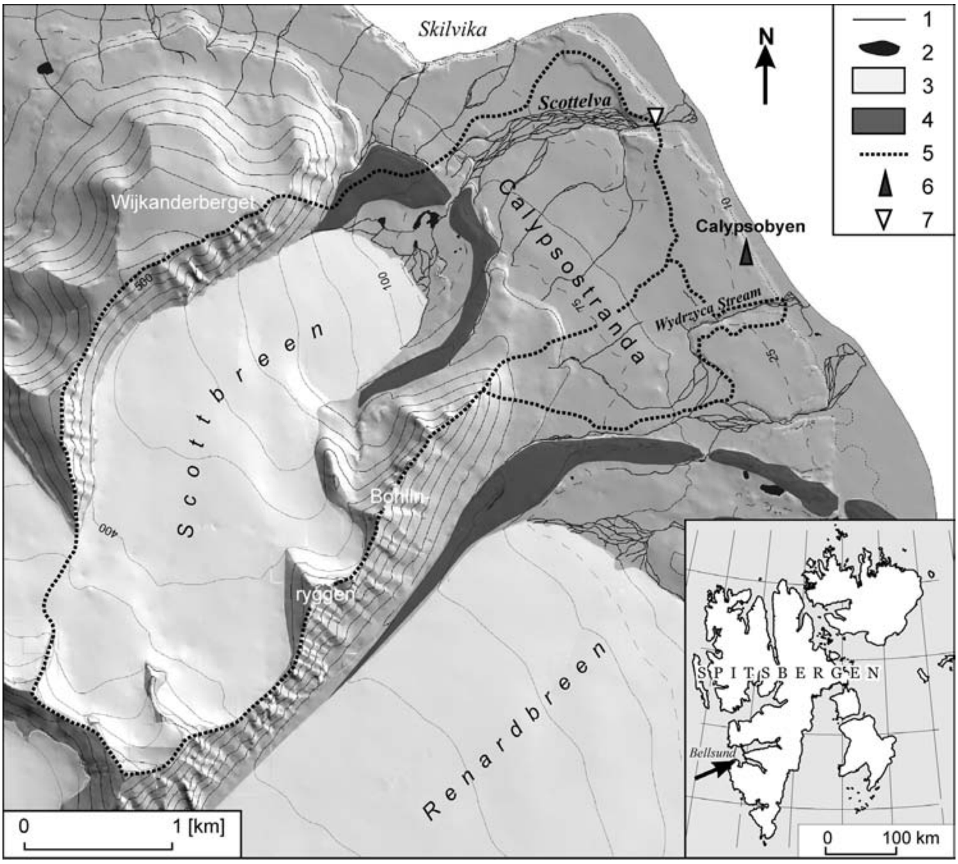

Fig. 1. Location of Calypsobyen Station, Bellsund: 1 – rivers and streams, 2 – lakes, 3 – glaciers, 4 – moraines, 5 – watershed, 6 – meteorological station, 7 – Scottelva gauging site.

Recherchefjorden in southern branch of Bellsund fjord (Fig. 1). Rainfall was collected daily and, immediately after sampling, pH (Elmetron CP-103) and SpC (Elmetron CC-318) were measured. Sub-samples were passed through 0.45 µm membrane filters, stored in 100 mL polythene bottles and transported to Poland. In the laboratories of the Faculty of Earth Sciences, University of Silesia, Sosnowiec, the samples were analyzed by ion chromatography using a Compact IC 761 (Metrohm, Switzerland). Anions were determined in untreated samples, in suppressor mode, using an ASUPP5 column and 3.2 mM $NaHCO_3$/1.0 mM Na_2CO_3 eluent. Detection limits and precision of analysis were 0.02 mg L^{-1} for Cl^- and 0.01 mg L^{-1} for SO_4^{2-} and NO_3^-. Bicarbonates were determined by titration, with 0.01 M HCl and methyl red/malachite green indicator. Cations were analyzed in samples acidified with HNO_3, using Cation 1–2 column and 4 mM tartaric acid/1 mM dipicolinic acid eluent. Detection limits and precision of analysis were 0.01 mg L^{-1} for Ca^{2+}, Mg^{2+} and Na^+, and 0.03 mg L^{-1} for K^+.

To find the origin of air masses arriving in Svalbard and track the pollutant paths the FLEXTRA trajectory model (Stohl *et al.* 1995; Stohl and Seibert 1998) was used. This model is accessible on the web pages (www.nilu.no/trajectories) of the Norwegian Institute for Air Research (NILU). FLEXTRA produces air-mass backward trajectories based on meteorological data from the European Centre for Medium Range Weather Forecasts (ECMWF). Hindcast trajectories are computed every six hours for the Hornsund location.

Results

Meteorology. — In the summer of 2002 the Calypsobyen (Bellsund) meteorological station operated between 8 July and 10 September; 65 days in total. Mean daily air temperature for this period was 5.4°C; the highest temperature was 10.2°C on 13 July and the lowest was -1.8°C on 7 September. The total atmospheric precipitation was 79 mm. The highest rainfall (23 mm) occurred on 25 August.

The plot of daily precipitation records (Fig. 2) shows that July was quite dry, with total precipitation of only 15 mm, whereas in August precipitation totalled 54 mm. There were 24 days with rainfall, with totals exceeding 1 mm on 16 of them; most of the big rains were sampled (Fig. 2). At the beginning of September a snowfall covered Calypsostranda with a few centimetres of snow, locally drifting to depths of one meter.

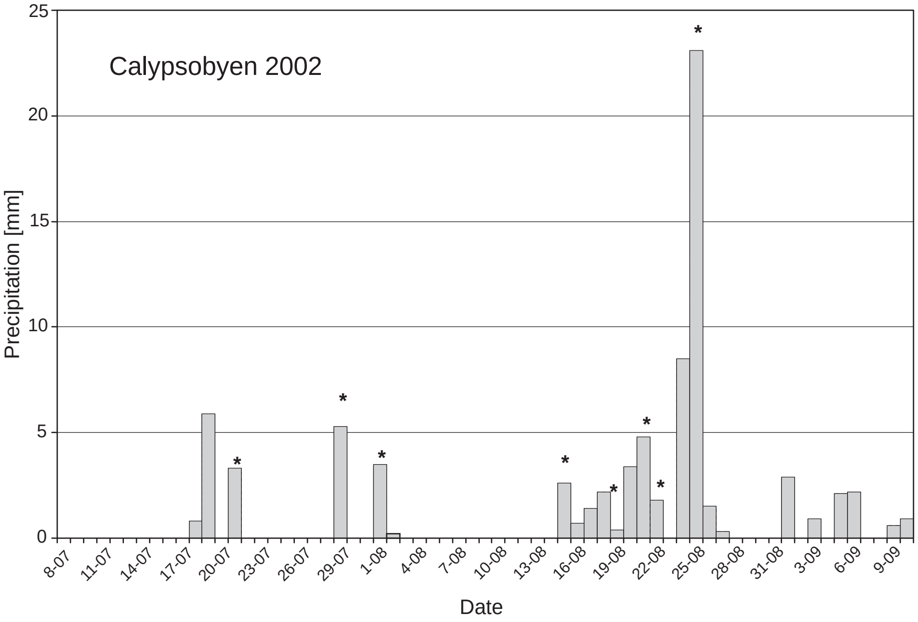

Fig. 2. Daily precipitation totals in Calypsobyen, Bellsund, in the summer of 2002. Asterisks indicate the rainfalls that were analyzed in this study.

Table 1

Ion concentrations (μeq L^{-1}) and total dissolved solids concentration (TDS, mg L^{-1}) in rainfall collected in Calypsobyen, Bellsund in the summer of 2002

Date	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
21 July	108	43	159	8	130	28	154	0	21.4
29 July	615	102	643	22	137	53	512	0	58.3
1 August	308	118	74	6	220	30	69	0	26.9
15 August	157	197	699	29	190	93	796	0	67.0
19 August	272	81	351	11	150	44	254	9	35.8
21 August	47	26	70	7	190	14	57	11	18.1
22 August	31	26	76	3	100	19	72	4	12.6
25 August	26	14	50	6	190	27	40	24	17.9
Min	26	14	50	3	100	14	40	0	12.6
Max	615	197	699	29	220	93	796	24	67.0

Mean wind speed over the observing period was 4.3 m s^{-1} but for 19 of the days it was higher than 5 m s^{-1}. Two wind directions dominated: from E (28%) and NW (18%); less frequent were NE and N winds. Mean cloud cover was 8.4; only one day was fine (<2.0). Forty-two days were cloudy (>8.0), 65% of all days. Stratocumulus and stratus clouds prevailed.

Ion concentrations in rainfall. — In the sampled rains pH ranged 4.65–7.57, with a mean volume-weighted (v/w) value of pH = 4.94; mean concentration of H^+ was 12 μeq L^{-1}. Six samples had pH>7, which can be explained by the dissolution of tiny atmospheric $CaCO_3$ particles. Only the final rain event of 25 August had a much lower pH, 4.65; as it was also much the highest volume event (23 mm) it strongly influenced the weighted mean pH. The SpC ranged from 14.7 to 121 μS cm^{-1} (mean v/w SpC = 34.8 μS cm^{-1}). Ranges of ion concentrations (Table 1) were the widest for sodium (50–699 μeq L^{-1}), calcium (26–615 μeq L^{-1}) and chlorides (40–796 μeq L^{-1}). Nitrate concentrations were low (0–24 μeq L^{-1}) but these particular values may have been affected by the time elapsed between sampling and laboratory analysis. TDS in the rains ranged from 12.6 to 67.0 mg L^{-1} (Table 1), similar to those found in rainfall at Hornsund in the summer of 2000 (11–50 mg L^{-1}; Krawczyk *et al.* 2002).

Discussion

Marine component. — Ions of marine origin (Na^+, Mg^{2+} and Cl^-) prevailed in all rainfalls. There were strong linear relations between them and SpC (Fig. 3). The relation between SpC and sulphates was:

$$SpC = 1.46 \times SO_4^{2-} - 7.1 \quad R^2 = 0.89 \qquad [1]$$

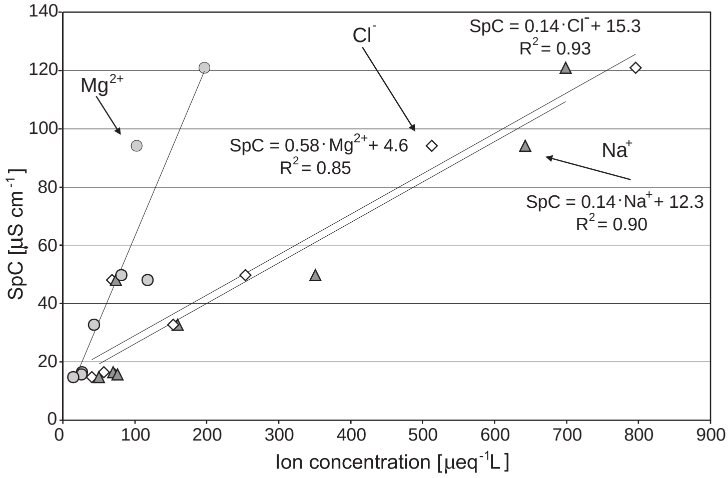

Fig. 3. Relations between specific conductivity (SpC) and concentration of marine ions (Cl^-, Na^+, Mg^2) in rainfall at Calypsobyen, Bellsund.

Assuming that all chlorides are of marine origin, the concentration of NaCl (in mg L^{-1}) dissolved in each rainfall where SpC is recorded may be calculated from:

$$\mathrm{NaCl} = 0.39 \cdot \mathrm{SpC} - 0.08 \qquad [2]$$

The equations for eleven Hornsund rainfalls in the summer 2000 are almost identical, only the intercepts being different (Krawczyk *et al.* 2002). The comparison shows that concentrations of all ions were higher at Bellsund, however (Table 2). This is probably due to a sampling point closer to the sea and to wind directions favouring inflow of marine aerosols; the Calypsobyen station is only 200 m from the outlet of Recherchefjorden whereas the Hornsund station is around 3500 m from the mouth of Hornsund fjord.

The Cl^-/Na^+ ratio in most Bellsund rains was lower than in typical seawater (1.14), which thus excludes any anthropogenic sources for the chlorides (*e.g.* from industrial HCl). Only in one event (August 15) did it attain 1.14, and the fact that the highest measured concentrations of chlorides, sodium and magnesium also occurred in this rainfall (Table 1) indicates that ions of marine origin were dominant.

Table 2

Average (v/w) ion concentrations (µeq L^{-1}) in rainfall at Calypsobyen, Bellsund, in the summer of 2002. Average (v/w) concentrations in rainfall at Hornsund in the summers of 2000 (H 2000) and 2001 (H 2001) are shown for comparison. Hornsund data from Głowacki and Krawczyk (2002); n-number of samples, nd-not determined.

	n	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
Bellsund	8	136	48	174	9	178	33	155	14
H 2000	18	12	26	117	4	nd	21	134	1
H 2001	12	10	6	40	2	nd	11	44	6

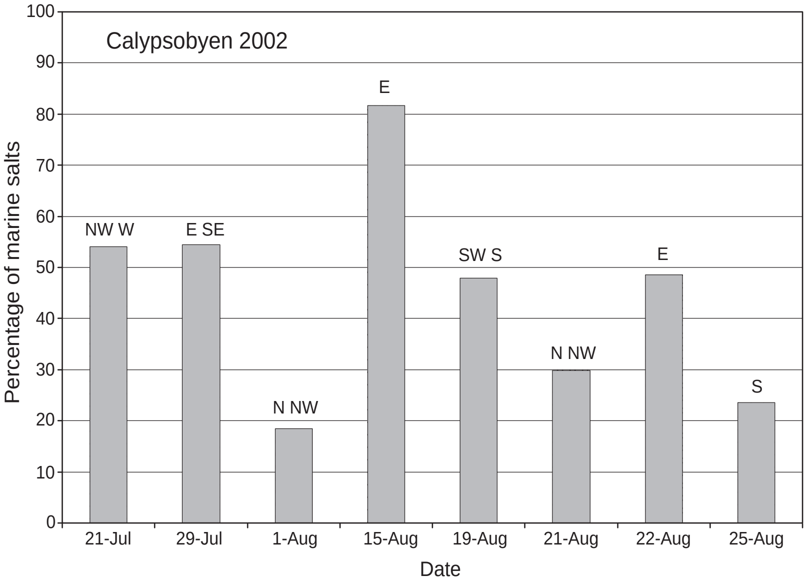

Fig. 4. Percentage of marine salts in rainfall at Calypsobyen, Bellsund. Wind directions are marked above bars.

Table 3

Average non sea salt (nss) ion concentrations (μeq L^{-1}) in rainfall at Calypsobyen, Bellsund, in the summer of 2002 and its percentage in total ion concentration

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	NO_3^-
nss	130	18	41	6	178	17	14
% of total	94	38	24	67	100	52	100

To estimate the proportion of ions resulting from seawater and marine aerosols it was thus assumed that all chlorides were of marine origin. The ionic equivalent ratios calculated from global mean seawater composition (*e.g.* Stumm and Morgan 1996) used to subtract the marine components were: $Ca^{2+}/Cl^- = 0.038$, $Mg^{2+}/Cl^- = 0.195$, $Na^+/Cl^- = 0.86$, $K^+/Cl^- = 0.019$ and $SO_4^{2-}/Cl^- = 0.103$. The marine proportion of each ion concentration was obtained by multiplying these ratios by chloride concentration. Marine concentration was then subtracted from total ion concentration to derive the average nss ion concentrations shown in Table 3. In the corrected rainfall bicarbonate, calcium and magnesium ions are dominant, confirming that there has been dissolution of significant quantities of atmospheric $CaCO_3$ and $MgCO_3$ particles. Nss-sulphates explain roughly one half of the total sulphate concentration.

A plot of percentage of marine salts in each rain event in Bellsund (Fig. 4) shows that these salts ranged from as little as 18% of TDS (1 August) to 82% (15 August). Rains with the highest percentage of marine salts occurred when the wind was blowing from the East with high mean speed ~10 m s^{-1} and maxima reaching 16 m s^{-1}. The lowest percentage of marine salts (18%) was in rainfall when wind speeds were only 5 m s^{-1} and the wind direction was N-NW. Winds from the East have the longer fetch over sea water.

Origin of the ions in the rainfall can be explained with the correlation coefficients. The sodium is mostly of marine origin; $R^2 = 0.94$ for its correlation with chlorides and $R^2 = 0.92$ with potassium. But sodium is also well correlated with sulphate ($R^2 = 0.82$), which suggests that the SO_4^{2-} also may be partly of marine origin. One of the natural sources of sulphates in rainfall collected at seaside stations may be the oxidation of dimethyl sulphide (DMS), hydrogen sulphide and organic sulphur compounds above the ocean (Berner and Berner 1996). The correlation between sulphates and chlorides at Bellsund ($R^2 = 0.93$) tends to support this argument. Sulphates correlate well with potassium ($R^2 = 0.89$), sodium ($R^2 = 0.82$) and magnesium ($R^2 = 0.81$). Correlation coefficients between Mg^{2+} and Cl^- ($R^2 = 0.71$), Mg^{2+} and Na^+ ($R^2 = 0.60$) and Mg^{2+} and K^+ ($R^2 = 0.69$) indicate that the magnesium ions are also partly of marine origin.

Origin of sulphates and nitrates in rainfall at Calypsobyen.— From the perspective of atmospheric pollution nss sulphates are most important and nitrates are second. Nss-sulphate concentration ranged from as little as 0.5 μeq L^{-1} on 29 July to 23 μeq L^{-1} on 1 and 25 August (Fig. 5). Nitrate concentration ranged from 0 to 24 μeq L^{-1}, the highest concentration also occurring in the precipitation of 25 August.

Higher concentrations of sulphates and nitrates in the summer of 2002 may be the result of positive phase NAO conditions favouring transport of pollutants from the northern hemisphere. In July and August 2002 the NAO indices were positive at 0.62 and 0.38 respectively, whereas in the same months in 2000 and 2001 they were negative, being -1.03, -0.29 and -0.25, -0.07 respectively (NAO indices taken from an internet website: http://www.cpc.noaa.gov).

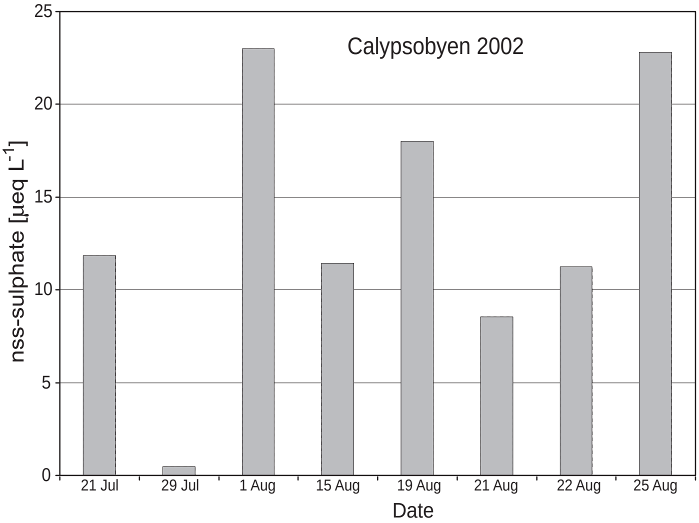

Fig. 5. Non-sea salt (nss) sulphate concentrations (μeq L^{-1}) in Calypsobyen rainfall.

The average summer sulphate concentrations at Calypsobyen (Table 2) were four times higher than average summer SO_4^{2-} of 0.41 mg L^{-1} in the Atlantic sector of the Russian Arctic in 1990–2004 reported in AMAP (2006). Even more striking, the average nitrate concentration was more than 10 times higher, being <0.07 mg L^{-1} for the AMAP region.

Hindcast trajectories for air masses reaching Svalbard were produced with FLEXTRA for each of the rainfalls. At 0:00 hrs on 29 July an air mass originated in Boothia Bay, Canada, and then flowed over SW Greenland and the Atlantic, passing east of Iceland and next over the Greenland Sea. This air mass arrived at Svalbard from the southwest and was not polluted with sulphur oxides (Fig. 6). The rain collected from it at Calypsobyen had the lowest nss-sulphate concentration recorded (0.5 μeq L^{-1}), and no nitrates were detected.

In the four rain storms of 21 July, and 15, 21, 22 August nss-sulphates were similar in amount at 9–12 μeq L^{-1} (Fig. 5). Between 19 and 21 July a low pressure centre was situated over NE Svalbard, forcing an inflow of arctic air masses from the northwest. FLEXTRA shows that at 0:00 hrs on 21 July air masses were moving towards Svalbard from the eastern coast of Greenland, over the Greenland Sea and then the Norwegian Sea (Fig. 6). Later on there was a new origin over the Norwegian Sea and the air flowed over northern Greenland before reaching Svalbard.

On 15 August at 0:00 hrs three air streams were formed, one above southern Norway, the second above the Kola Peninsula and the third above the Lena River mouth in northern Asia (Fig. 6). Six hours later another stream began in western Russia and moved over Byelorussia, Lithuania and the Scandinavian Peninsula; this direction predominated for the next six hours.

For the 21 August event, the air masses came from the Bay of Biscay, passing over Great Britain and Ireland then the Greenland Sea (Fig. 6). Six hours later (at 12:00) a low level air stream (around 500 m a.s.l.) originated in NW Germany. Nitrates were detected in this rainfall (11 μeq L^{-1}). For the 22 August rains the air masses arrived from Greenland and the Greenland Sea but for a short period around 12:00 FLEXTRA shows three streams formed over Atlantic, northern Spain and Gulf of Bothnia. A low level stream originating in the Gulf of Bothnia turned south, passing over the Baltic Sea and touching northern Poland and Germany, before completing a semi-circular course over the Norwegian Sea and on to Svalbard (Fig. 6).

When, in the rain of 19 August, nss-sulphates amounted to 18 μeq L^{-1} and nitrates to 9 μeq L^{-1}, there was a High pressure system over Scandinavia and a Low pressure system west of Svalbard, forcing inflow of air masses formed over Great Britain and the northern Atlantic. Hindcast trajectories here show that air masses circulated above the Greenland Sea and the Norwegian Sea. For short periods air streams were arriving from northern Great Britain, Ireland, northern and southern Norway. Pollutant concentrations in this rainfall may originate partly in shipping

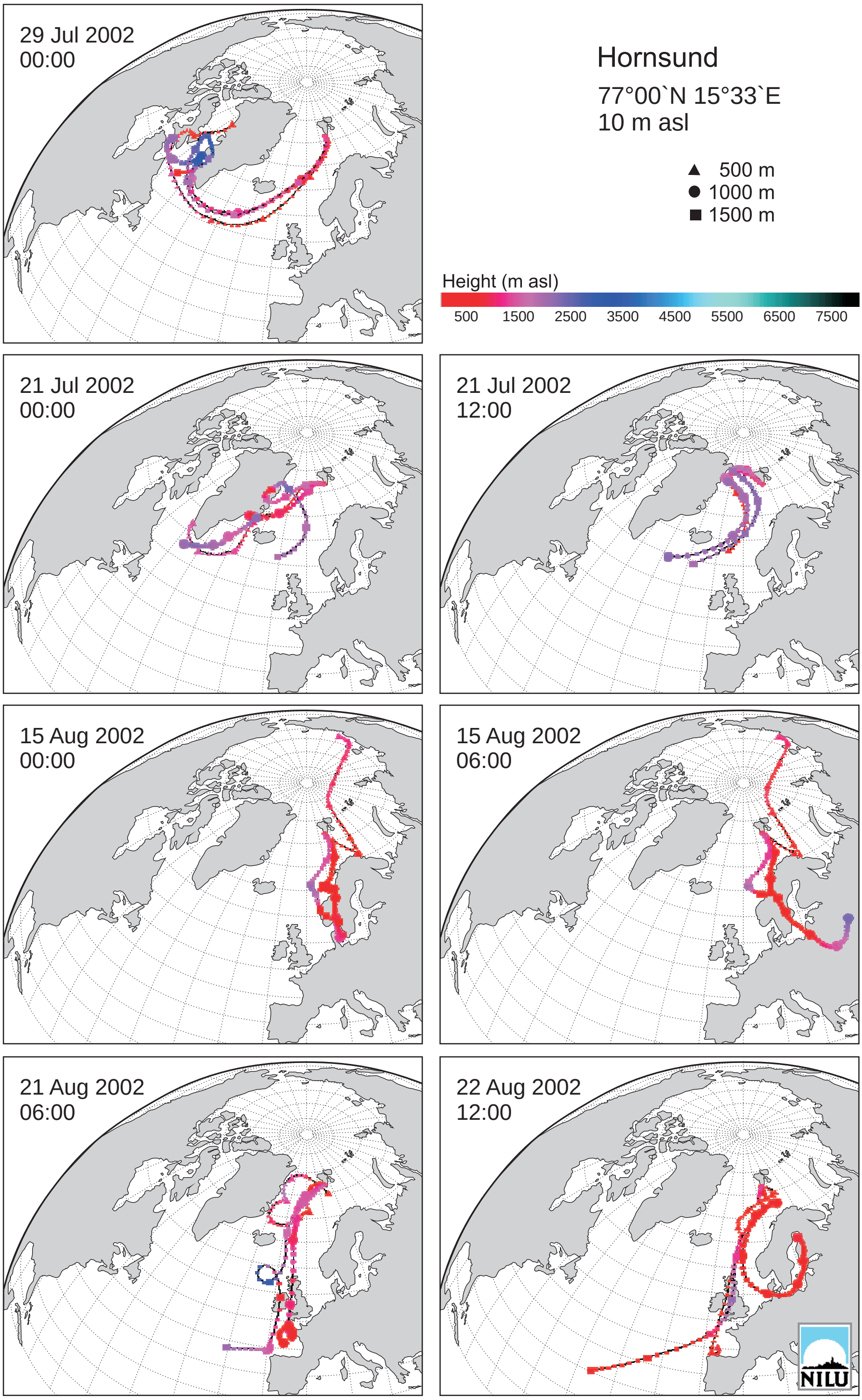

Fig. 6. FLEXTRA back (hindcast) trajectories for air masses reaching Svalbard at the time of the rainfalls sampled at Calypsobyen.

emissions. Part of the nss-sulphates may be from oxidation of DMS but to confirm this methanesulphonic acid (MSA) should be determined in rainfall samples.

The highest nss-SO_4^{2-} concentrations in rainfall (23 µeq L^{-1}) occurred in the events of 1 and 25 August. On 1 August the air masses were arriving from the north where a deep Low pressure system had formed. Hindcast trajectories extend back over the Arctic Ocean to the Bering Strait and NE Russia. Later, air streams originating in Alaska and northern Greenland joined in. No nitrates were detected in this rainfall. The high concentrations of nss-SO_4^{2-} were accompanied by low concentrations of chlorides (40 and 69 µeq L^{-1}) that may exclude origin from oxidation of DMS from decay of marine phytoplankton.

On 25 August there was a High pressure system over Scandinavia and a Low pressure system over Iceland. The air masses arrived from the southwest, with their sources over northern Scotland, the Norwegian Sea and southern Greenland. At 6:00 one of the low level streams had formed over Russia (close to the Ukrainian border), flowed across the Ukraine, Slovakia, western Poland, the Baltic Sea and further north over the Norwegian Sea. Six hours later air streams shifted further west and flowed above Scotland. Nitrate concentrations amounted to 24 µeq L^{-1}. European sources and shipping emissions contributed to this pollution.

Average nss-SO_4^{2-} in Calypsobyen rainfall in the summer of 2002 was 17 µeq L^{-1}, nearly half of the total sulphate. In contrast, in Hornsund rainfall in the summer of 2000 nss-SO_4^{2-} concentrations were scarcely half this value, amounting to only 9 µeq L^{-1} (Krawczyk *et al.* 2003).

Deposition of ions at Calypsobyen. — We have assumed that the eight rainfall samples collected in the summer of 2002 were representative for this period. Average (v/w) concentrations were multiplied by the total summer rainfall of 79 mm to derive the ion deposition. The estimates show that bicarbonates are dominant, followed by chlorides and sodium (Table 4). The rain deposited 194 kg km^{-2} of acidifying anions (SO_4^{2-} and NO_3^-) at Calypsobyen, a figure that falls between those obtained for deposition in Hornsund in the summers of 2000 (345 kg km^{-2}) and 2001 (121 kg km^{-2}). There were 263 kg km^{-2} of base cations (Ca^{2+} and Mg^{2+}). The sulphate load of anthropogenic origin (nss-SO_4^{2-}) was half of such load in Hornsund in the summer of 2000 (Głowacki and Krawczyk 2002). Estimated monthly summer sulphate deposition at Calypsobyen (20.8 kg S km^{-2}) was slightly higher than the range of 12.8–19.1 kg S km^{-2} found in the summer of 1994 in four pristine catchments in northern Scandinavia (Chekushin *et al.* 1998).

Table 4

Ion deposition (kg km^{-2}) derived from the atmosphere in Calypsobyen, Bellsund region in the summer of 2002

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
total	216.5	46.0	317.2	27.8	864.4	125.3	436.2	69.0
nss	207.0	17.4	74.5	19.0	864.4	65.0	0	69.0

Conclusions

Polluted air masses arrived at southern Svalbard in the summer of 2002, coming mostly from northern and central Europe but occasionally also from Asia. It was found that air masses formed over the Greenland Sea and the Norwegian Sea were also polluted with SO_x and NO_x, most probably from ship emissions. When scavenged by rainfall these marine air masses produced nss-sulphate and nitrate concentrations similar to those from air masses arriving from northern Europe. The rain deposited an average of 194 kg km^{-2} of acidifying anions (sulphates and nitrates).

In all of the rainfalls ions of marine origin prevailed. After subtracting these marine components nss-sulphate concentrations ranged from 0.5 to 23 μeq L^{-1}, the average (v/w) being 17 μeq L^{-1}. Nitrate concentrations ranged from 0 to 24 μeq L^{-1}. Concentrations of nss-sulphate and nitrate in Calypsobyen in summer 2002 were higher than in Hornsund in summers of 2000 and 2001. This may be explained by the positive NAO index conditions that prevailed in July and August 2002.

Acknowledgements. — This work was supported by the Polish Committee on Scientific Research project (6PO4E 034 20) and a research grant from the University of Silesia (BW-34/03). M. Barczyk and P. Domagalska are thanked for IC analyses. Norwegian Institute for Air Research (NILU) is acknowledged for providing the FLEXTRA trajectories used in this study. Dr. P. Zagórski is thanked for Fig. 1. The manuscript was improved by constructive comments from Professor D.C. Ford and Dr. T.R. Walker.

References

AMAP 1998. *AMAP Assessment Report: Arctic Pollution Issue.* Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

AMAP 2004. *AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic.* Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

AMAP 2006. *AMAP Assessment 2006. Acidifying pollutants, Arctic Haze and acidification in the Arctic.* Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

BURZYK M., BURZYK J. and GŁOWACKI P. 2001. Comparative chemical characteristics of precipitation in the Hornsund region (SW Spitsbergen) in the years 1993–1994 and 1998–1999. *Polish Polar Research* 22 (3–4): 233–247.

CHEKUSHIN V.A., BOGATYREV I.V., DE CARITAT P., NISKAVAARA H. and REIMANN C. 1998. Annual atmospheric deposition of 16 elements in eight catchments of the central Barents region. *The Science of the Total Environment* 220: 95–114.

DE CARITAT P., HALL G., GISLASON S., BELSEY W., BRAUN M., GOLOUBEVA N., OLSEN H.K., SCHEIE J.O and VAIVE J.E. 2005. Chemical composition of Arctic snow: concentration levels and regional distribution of major elements. *Science of the Total Environment* 336: 183–199.

ECKENHARDT S., STOHL A., BEIRLE S., SPICHTINGER N., JAMES P., FORSTER C., JUNKER C., WAGNER T., PLATT U. and JENNINGS S.G. 2003. The North Atlantic Oscillation controls air pollution transport to the Arctic. *Atmospheric Chemistry and Physics* 3: 1769–1778.

GŁOWACKI P. and KRAWCZYK W. E. 2002. Long range transport of pollutants – evidences from rainfall chemistry in Hornsund (Svalbard). *In*: J.B. Orbaek (ed.) *The Changing Physical Environment. Pro-*

ceedings from the Sixth Ny-Ålesund International Scientific Seminar, Tromsø, Norway, Norsk Polarinstitutt Internrapport 10: 65–69.

HEITZENBERG J., TUCH T., WEHNER B., WIEDENSOHLER A., WEX H., ANSMANN A., MATTIS I., MÜLLER D., WENDISH M., ECKHARDT S. and STOHL A. 2003. Arctic Haze over Central Europe. *Tellus* 55B: 796–807.

KRAWCZYK W.E., GŁOWACKI P. and NIEDŹWIEDŹ T. 2002. Charakterystyka chemiczna opadów atmosferycznych w rejonie Hornsundu (SW Spitsbergen) latem 2000 r. na tle cyrkulacji atmosferycznych [Chemical characteristics of atmospheric precipitation in Hornsund region (SW Spitsbergen) in the summer of 2000]. *In*: A. Kostrzewski and G. Rachlewicz (eds) *Polish Polar Studies*. Poznań: 187–202.

KRAWCZYK W.E., LEFAUCONNIER B. and PETTERSSON L.-E. 2003. Chemical denudation rates in the Bayelva catchment, Svalbard in the fall of 2000. *Physics and Chemistry of the Earth* 28: 1261–1275.

KRAWCZYK W.E. and SKRĘT U. 2005. Organic compounds in rainfall at Hornsund, SW Spitsbergen: qualitative results. *Polish Polar Research* 26: 65–76.

LAW K.S. and STOHL A. 2007. Arctic air pollution: origins and impacts. *Science* 315: 1537.DOI: 10.1126/science.1137695.

LIEN L., HENRIKSEN A. and TRAAEN T.S. 1995. Critical loads of acidity to surface waters: Svalbard. *The Science of the Total Environment* 160/161: 703–713.

MCDONALD R.W., HARNER T. and FYFE J. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *The Science of the Total Environment* 342: 5–86.

PACYNA J. 1995. The origin of Arctic air pollutants: lessons learned and future research. *The Science of the Total Environment* 160/161: 39–53.

STOHL A. 2006. Characteristics of atmospheric transport into the Arctic troposphere. *Journal of Geophysical Research* 111: D11, 306.

STOHL A. and SEIBERT P. 1998. Accuracy of trajectories as determined from the conservation of meteorological tracers. *Quarterly Journal – Royal Meteorological Society* 124: 1465–1484.

STOHL A., BERG T., BURKHART J.F., FJERAA A.M., FORSTER C., HERBER A., HOV Ć., LUNDER C., MCMILLAN W.W., OLTMANS S., SHIOBARA M., SIMPSON D., SOLBERG S., STEBEL K., STRÖM J. TORSETH K., TREFFEISEN R., VIRKKUNEN K. and YTTRI K.E. 2007. Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring 2006. *Atmospheric Chemistry and Physics* 7: 511–534.

STOHL A., ECKHARDT S., FORSTER C., JAMES P. and SPICHTINGER N. 2002. On the pathways and timescales of intercontinental air pollution transport. *Journal of Geophysical Research* 107: D23, 4684.

STOHL A., WOTAWA G., SEIBERT P. and KROMP-KOLB H. 1995. Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories. *Journal of Applied Meteorology* 34: 2149–2165.

STUMM W. and MORGAN J. 1996. *Aquatic chemistry. Chemical equilibria and rates in natural waters.* 3rd ed. Wiley, New York: 1022 pp.

WALKER T.R., CRITTENDEN P.D. and YOUNG S.D. 2003. Regional variation in the chemical composition of winter snow pack and terricolous lichens in relation to sources of acid emissions in the Usa river basin, northeastern European Russia. *Environmental Pollution* 125: 401–412.

Received 29 April 2008
Accepted 2 June 2008