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Recommended Citation

J. E. Dibb, R. W. Talbot, and M. H. Bergin, "Soluble acidic species in air and snow at summit, Greenland," *Geophysical Research Letters*, vol. 21, no. 15, pp. 1627–1630, Jul. 1994.

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Soluble acidic species in air and snow at Summit, Greenland

Jack E. Dibb,¹ Robert W. Talbot,¹ and Michael H. Bergin²

Abstract. Simultaneous measurements of the concentrations of soluble acidic species in the gas, aerosol and snow phases at Summit, Greenland were made during summer 1993. Mean concentrations of gas phase HCOOH, CH₃COOH, and HNO₃ (49±28, 32±17 and 0.9±0.6 nmol m⁻³ STP, respectively) exceeded the concentrations of aerosol-associated HCOO⁻, CH₃COO⁻, and NO₃⁻ by 1-3 orders of magnitude. On average, SO₂ concentrations (0.9±0.6 nmol m⁻³ STP) were approximately 1/3 those of aerosol SO₄⁻, but this ratio varied widely due largely to changes in the concentration of aerosol SO₄⁻. Concentrations of aerosol SO₄⁻ plus SO₂ consistently exceeded the sum of aerosol NO₃⁻ plus HNO₃, yet NO₃⁻ was 3-20 times as abundant as SO₄⁻ in surface snow. Gas phase concentrations of HCOOH and CH₃COOH at Summit were unexpectedly as large as those previously reported for several high latitude continental sites. However, carboxylate concentrations in snow were lower than those of SO₄⁻. Our observation of post-depositional loss of these carboxylic acids within hours after a snowfall must partially explain the low concentrations found in snow. The relative abundance of soluble acids in summer snow at Summit was opposite of that in the overlying atmosphere. Our results highlight the need for improved understanding of the processes controlling transfer of soluble atmospheric species between air and snow.

Introduction

Deposition of aerosol NO₃⁻ (hereafter p-NO₃⁻) and gaseous HNO₃ is the major atmospheric sink for total reactive nitrogen (NO_y) [e.g., Logan, 1983]. Since NO_y is involved in many important atmospheric photochemical reactions [e.g., Logan, 1983], Greenland ice core records of nitrate (p-NO₃⁻ plus HNO₃) accumulation could provide insight into past photochemical and oxidative states of the troposphere. However, it is not clear that the relationship between NO₃⁻ concentration in snow and that of NO_y in the overlying atmosphere is straightforward, nor is it certain that ice cores preserve a simple record of the deposition of total tropospheric nitrate at the site [Wolff, 1993].

In this paper we report measurements of HNO₃, p-NO₃⁻ and snow NO₃⁻ made at Summit in summer 1993. Parallel results for HCOOH, CH₃COOH, SO₂ and SO₄⁻ in the three phases are also presented. We examine differences in air/snow transfer functions for these species in relation to their gas-aerosol partitioning and their behavior during snow and fog events. Early (hours to days) post-depositional changes in snow chemistry after such events are also discussed.

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Paper number 94GL01031
0094-8534/94/94GL-01031\$03.00

Methods

Gas phase concentrations of the soluble acids were determined by mist chamber sampling techniques, wherein the gases are concentrated into a small volume of ultrapure water. This technique quantitatively collects HNO₃, and the collection efficiencies for the other acids of interest exceed 95% [Keene *et al.*, 1988; Talbot *et al.*, 1990a; Klemm and Talbot, 1991]. The stripping solutions were all analyzed by ion chromatography, in the field for NO₃⁻ and some of the blanks, and back in New Hampshire for SO₂ and the carboxylates. The samples returned for analysis were frozen to -20°C within 30 minutes of collection and maintained frozen until just before analysis.

Four 3-hour samples day⁻¹ (volumes of 1.6-1.8 m³ STP) were collected (starting at 05:00, 11:00, 17:00 and 23:00 local time) for at least 3 consecutive days. A total of 36 samples were collected 20-22 June, 5-8 July and 18-20 July. No sampling was conducted until several blanks with acceptably low concentrations of NO₃⁻ were obtained before each sampling period. Uncertainties for HNO₃, SO₂, HCOOH and CH₃COOH concentrations were approximately 0.1, 0.3, 1.2 and 1.2 nmol m⁻³ STP, respectively.

During gas phase sampling, five replicate surface snow samples were collected at the mid-time of each mist chamber sample. A full suite of soluble organic and inorganic ions were measured in these samples by ion chromatography. Large volume aerosol samples were also collected through the first two intervals, on 8:00-20:00/20:00-8:00 and 8:00-24:00 schedules for the determination of natural radionuclides and soluble ionic species, respectively [Dibb *et al.*, 1992].

Results

Overview

Gas phase concentrations over Summit, Greenland are compared to those from previous studies in northern high latitudes in Table 1. The mean aerosol composition reported for Summit represents only 10 samples, 5 each from late June and early July. Reported values for p-NO₃⁻ and p-SO₄⁻ were lower than the seasonal averages (0.4 and 4.2 nmol m⁻³ STP, respectively), while the opposite was true for p-HCOO⁻ and p-CH₃COO⁻ (season means 0.3 and 0.06 nmol m⁻³ STP, respectively). It is unclear whether the reported mean gas phase concentrations are similarly biased.

Nitric acid concentrations were more than an order of magnitude higher than those of p-NO₃⁻ (Table 1), in accord with the denuder results of *Silvente* [1993]. However, the mean concentrations in 1993 were >3 times the background levels reported for 1991 [Silvente, 1993]. On the other hand, HNO₃ concentrations at Summit were ≤1/2 the free tropospheric (1-6 km) mean during ABLE 3A and about 1/2 the mean for "background" air during ABLE 3B (Table 1). Concentrations of p-NO₃⁻ at Summit were lower than any previously reported for the region (Table 1).

Table 1. Summary comparison of gaseous and aerosol acid concentrations (nmol m⁻³ STP) at Summit and other high northern latitude regions.

		HNO ₃	p-NO ₃ ⁻	SO ₂	p-SO ₄ ⁼	HCOOH	p-HCOO ⁻	CH ₃ COOH	p-CH ₃ COO ⁻	source
Summit, Greenland:										
Summer 1993										
72° 25' N	mean ± σ	0.9 ± 0.6	0.06 ± 0.06	0.9 ± 0.6	3.0 ± 2.3	49 ± 28	1.05 ± 2.31	32 ± 17	0.16 ± 0.33	<i>This Work</i>
36° 40' W	median	0.9	0.03	0.8	2.4	45	0.15	34	0.04	
	range	0.19 - 2.44	n.d. - 0.15	0.15 - 3.63	0.6 - 7.1	8.6 - 119.2	n.d. - 7.53	6.6 - 72.5	n.d. - 1.07	
ABLE 3A Airborne Campaign:										
Summer 1988										
High Arctic	mean ± σ	2.0 ± 1.1	0.98 ± 0.53		5.7 ± 3.4	7.3 ± 4.7	<0.2	9.2 ± 4.6	<0.4	<i>Talbot et al., 1992</i>
Sub-Arctic	mean ± σ	2.6 ± 1.4	0.67 ± 0.31		1.8 ± 1.0	8.5 ± 3.2	<0.2	10.0 ± 3.1	<0.4	
ABLE 3B Airborne Campaign:										
Summer 1990										
"Background" Air	mean ± σ	1.7 ± 0.1	0.2 ± 0.1		3.7 ± 4.4	20 ± 1	<0.2	25 ± 1	<0.4	<i>Lefer et al., 1994</i> <i>Gorzelska et al., 1994</i> <i>Talbot et al., 1994</i>
Burning Plumes	mean ± σ	26.0 ± 5.0	1.8 ± 2.6		10.0 ± 7.0	100 ± 5	<0.2	86 ± 4	<0.4	
ABLE 3B Schefferville Tower Site:										
Summer 1990										
54° 52' N	mean ± σ	4.2 ± 4.0	3.1 ± 2.9	2.1 ± 2.2	8.1 ± 6.7	49 ± 31	<0.4	42 ± 24	<0.9	<i>Klemm et al., 1994</i> <i>plus unpublished</i> <i>aerosol data</i>
66° 39' W	median	2.7	3.1	1.2	5.2	45		38		
	range	0.6 - 19.4	n.d. - 8.2	n.d. - 12.0	2.9 - 23.9	8.1 - 222.0		10.8 - 166.4		
Alert, Canada:										
Winter - Spring 1988										
82° 30' N	mean ± σ	1.3 ± 0.9	1.4 ± 1.0	20.0 ± 19.7	24.8 ± 15.8					<i>Bottenheim et al., 1993</i>
62° 18' W	median	1.0	1.2	13.3	18.6					
	range	0.04 - 2.9	0.1 - 4.2	0.5 - 86.9	4.9 - 65.4					
Barrow, Alaska:										
Winter - Spring 1986										
71° 19' N	mean ± σ		2.0 ± 0.2		10.8 ± 1.5		5.3 ± 0.7	12.4 ± 2.2		<i>Li and Winchester, 1989a,b</i>
156° 37' W	median		1.4		4.3		2.9	5.4		

Overall, p-SO₄⁼ was about 3 times as abundant as SO₂ at Summit (Table 1; Fig. 1). The seasonal mean concentration of p-SO₄⁼ at Summit was bracketed by previously reported values for the high-latitude summer troposphere (Table 1). Wintertime observations at Alert and Barrow are characterized by much higher concentrations of SO₂ and p-SO₄⁼, as well as higher values of the ratio SO₂/SO₄⁼, reflecting the influence of Arctic haze [e.g., *Barrie and Bottenheim, 1991*].

Both carboxylic acids were nearly entirely in the gas

phase over Summit (Fig. 1), in contrast to the high aerosol-associated concentrations at Barrow in winter (Table 1). *Li and Winchester [1989a]* suggested that formate and acetate were partitioned predominantly into the condensed phase due to polar nighttime temperatures near -25°C. However, temperatures at Summit during sample collection ranged -5 to -25°C, suggesting that air temperature is not the sole control on the partitioning of these carboxylic acids in the atmosphere.

The concentrations of HCOOH and CH₃COOH over the ice sheet at Summit were similar to those at Schefferville, Ontario, and more than twice those of "clean" free tropospheric air sampled during ABLE 3A and 3B (Table 1). These organic acids were well correlated at Summit ($r=0.93$), with the ratio HCOOH/CH₃COOH in the range of 1.1-2.1 (mean 1.5 ± 0.3).

Air-Snow Relationships. Contemporaneous sampling for gas, aerosol and snow phase chemistry was conducted during the late June and early July periods. Here we focus only on the first interval, but results were similar during July.

Beryllium-7 concentrations suggest that the air was relatively depleted of sub-micron aerosols at the beginning of the period (55-73 fCi ⁷Be m⁻³ STP) and became progressively cleaner during the first two days (13 fCi ⁷Be m⁻³ STP). When the inversion broke down on the morning of 22 June, ⁷Be concentrations increased by an order of magnitude (177 fCi m⁻³ STP), suggesting replenishment of surface-level air by downward mixing [e.g., *Dibb et al., 1992*].

Nitrate concentrations in surface snow steadily increased from midday 20 June through midday 21 June as flurries added new snow to the initial layer (Fig. 2). The jump in concentration between 12:30 and 18:30 on 21 June is partly a sampling artifact; at 12:30 the initial 3-4cm-thick layer plus new snow that was still accumulating was sampled as the representative surface layer; later only the thin layer of new snow was included. The sharp increase in NO₃⁻ concentration between 00:30 and 6:30 on 22 June reflects NO₃⁻ added by the deposition of rime ice during the fog event (1.3 nmol g⁻¹ increase in 6 h) (Fig. 2).

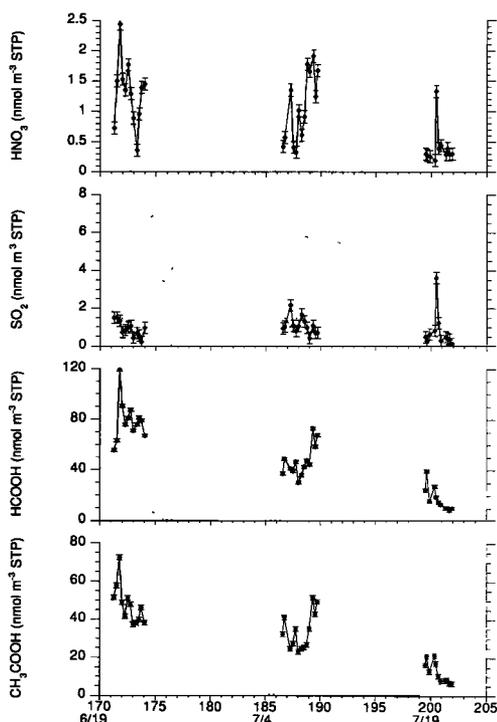


Figure 1. Concentrations of soluble acidic gases at Summit. For comparison, concentrations of aerosol-associated nitrate, sulfate, formate and acetate are shown in the dotted lines.

Nitric acid was always the dominant fraction of total atmospheric nitrate during these three days. Concentrations rose sharply during the first 12 hours, then decreased during the snow flurries (Fig. 2). Concentrations of HNO_3 dropped even lower during the fog event. After the inversion broke down, HNO_3 concentrations increased; at the same time p-NO_3^- became detectable.

Aerosol SO_4^{2-} concentrations were quite low and comparable to those of SO_2 early in the sampling period (Fig. 2). The period of snow flurries coincided with decreasing trends of p-SO_4^{2-} and SO_2 , but had little influence on SO_4^{2-} concentrations in surface snow. Deposition of rime ice increased SO_4^{2-} concentrations in surface snow, perhaps at the expense of a slight decrease in SO_2 concentrations (no aerosol samples for ionic species were collected overnight). After the fog dissipated, p-SO_4^{2-} concentrations increased with those of ^7Be and p-NO_3^- .

Concentrations of HCOOH and CH_3COOH exceeded concentrations of p-HCOO^- and $\text{p-CH}_3\text{COO}^-$ by nearly three orders of magnitude throughout the sampling period (Fig. 2). The snow flurries on 20-21 June coincided with decreasing trends of formate and acetate in both air and snow, in contrast to the opposing trends seen for nitrate in the two phases (Fig. 2). The fog event caused sharp increases in the concentration of carboxylates in the snow, but only slight depressions of gas phase concentrations. The small impact of fog on atmospheric concentrations of the carboxylic acids contrasts the decline in HNO_3 during this event, but is in accord with the fact that their equilibrium solubilities are several orders of magnitude less than that of HNO_3 [Klemm and Talbot, 1991]. Nearly all of the formate and acetate delivered to the snow by the rime event "disappeared" within 6 hours.

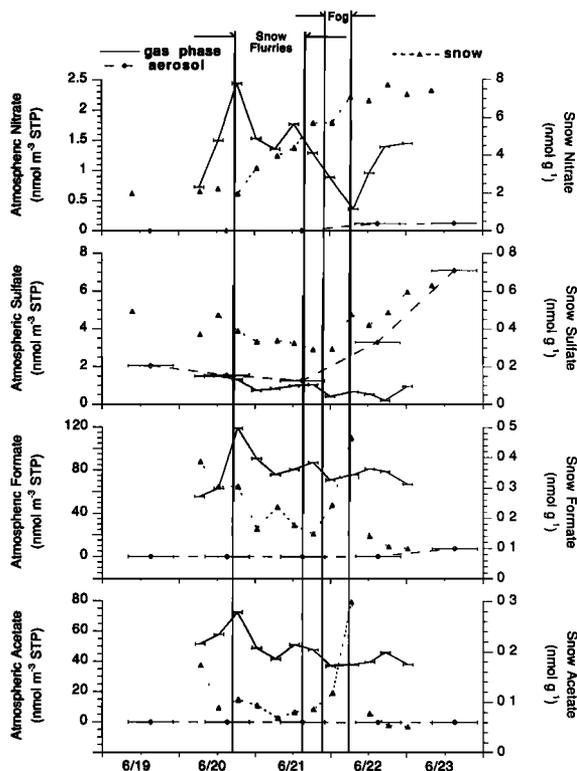


Figure 2. Relationships between the gas, aerosol and snow concentrations of nitrate, sulfate, formate and acetate during the 20 - 22 June intensive sampling period.

It should be noted that NO_3^- concentrations in snow were roughly an order of magnitude higher than those of SO_4^{2-} and the carboxylates (Fig. 2). In contrast, atmospheric concentrations of HNO_3 were $\leq(\text{SO}_2 + \text{p-SO}_4^{2-})$ and 20-50 times lower than those of HCOOH and CH_3COOH . In addition, the snow NO_3^- concentrations during this period (and throughout the summer) were considerably higher than those routinely reported for summer snow layers in snowpits and firn cores.

Discussion

The most intriguing findings of this study are the large enrichment of NO_3^- in snow relative to the atmospheric abundance of HNO_3 and p-NO_3^- , and the high gas phase concentrations of HCOOH and CH_3COOH . It is difficult to reconcile the observation of p-SO_4^{2-} being three times more abundant than HNO_3 plus p-NO_3^- (Table 1) with $\text{NO}_3^-/\text{SO}_4^{2-}$ in snow ranging 3-20. Part of this apparent discrepancy may be due to a sampling artifact. Dry deposition of HNO_3 to the surface can create steep concentration gradients, making measurements at 1.5 m non-representative of the concentrations at slightly higher elevations [e.g., Lee *et al.*, 1993]. However, Lee *et al.* [1993] report only a 2-fold increase in HNO_3 from 2 to 30 m over basalt, suggesting that loss of HNO_3 to the snow surface is not the only factor. It is possible that one, or more, of the NO_y species not measured in this study is contributing to NO_3^- measured in surface snow.

Keene and Galloway [1988] suggested that the atmospheric lifetimes of HCOOH and CH_3COOH are on the order of days, so it is surprising that their concentrations at Summit were similar to those at Schefferville and higher than mean concentrations in the Arctic summer free troposphere (Table 1). Lefer *et al.* [1994] have shown that biomass burning plumes in the northern high-latitude troposphere can contain elevated concentrations of both acids. Such plumes may reach Summit, but we would expect their influence to be episodic and not capable of maintaining such high concentrations for month-long periods (Fig. 1). Degassing of organic acids from surface snow (Fig. 2) might constitute a local source. However, this possible source appears too weak. For example, the 260 and 175 nmol m^{-2} of formate and acetate, respectively, apparently lost from the surface layer of snow on the morning of 22 June would only account for 7 and 5 nmol m^{-3} STP if they were well mixed through the boundary layer below the inversion observed at 50 m at 12:00. It may be that a deeper layer of surface snow is exchanging with near-surface air, but this explanation does not address the original source of carboxylates in Summit snow.

The partitioning of nitrate and the carboxylates just above the snow surface strongly favored the gas phase. The mean gas phase percentage of atmospheric formate and acetate was $>98\%$ (Table 1). Similarly, the fraction of total atmospheric nitrate present as HNO_3 at Summit (mean 93%) was higher than most previous results (Table 1). This presumably reflects the acidic nature of the aerosol at Summit, but it is unclear how much displacement of p-NO_3^- , p-HCOO^- and $\text{p-CH}_3\text{COO}^-$ occurs in the atmosphere rather than on the filters as they become loaded with acidic p-SO_4^{2-} .

On average, 75% of inorganic S in the atmosphere at Summit was present as p-SO_4^{2-} , a finding in accord with the seasonal decrease in $\text{SO}_2/\text{p-SO}_4^{2-}$ in the Arctic Basin [Barrie and Bottenheim, 1991]. Concentrations of SO_2 at Summit

varied much less than those of $p\text{-SO}_4^-$ (Table 1; Figs. 1 and 2), resulting in wide variations in their ratio. This implies that SO_2 is not efficiently removed from the air over Summit and that oxidation to SO_4^- is also suppressed (perhaps due to the very low humidity).

Summary

A pilot study in the harsh environment at Summit has demonstrated the feasibility of operating mist chamber samplers to provide data on the atmospheric concentrations of HNO_3 , HCOOH , CH_3COOH and SO_2 directly over the Greenland ice sheet. Nitric and the carboxylic acids were well over an order of magnitude more abundant than their aerosol-associated anionic forms, while SO_2 was only a small fraction of SO_4^- plus $p\text{-SO}_4^-$.

In snow, the relative abundance of these four acids was opposite their ranking in the atmosphere. Very low concentrations of the carboxylates in snow can be partially attributed to post-depositional loss processes operating on time scales of hours. We saw no convincing evidence of rapid NO_3^- loss from the snow during the summer season. However, observed concentrations in the surface layer much higher than those reported for summer layers buried in the snow pack (i.e., a year or more old) that NO_3^- losses must occur within the first 12 months after deposition. Additional sampling is needed to confirm and expand on these preliminary 1993 findings.

Acknowledgments. We thank M. Pender for assistance with sampling at Summit, and S. Whitlow, E. Scheuer and J.L. Jaffrezo for analysis of some of the samples. We are also grateful for the assistance of the GISP2 SMO, PICO and the 109th NYANG. We thank the Danish Research Commission for permission to study in Greenland. This work was partially supported by NSF grants DPP-9122555 to JED and DPP-9123082 to C. Davidson. This is contribution # 94-01 of the Greenland Ice Sheet Project 2 (GISP2).

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(Received January 25, 1994; accepted February 25, 1994.)