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Snow–Atmosphere Interactions in Arctic Snowpacks
Net Fluxes of NO_3, SO_4 and Influence of Solar Radiation

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ABSTRACT

Identical experiments on snow-atmosphere interaction were carried out at two arctic sites (open forest and tundra, Inuvik, Canada) prior to spring snowmelt, April 1992. The purpose of the experiments was to estimate the magnitude and direction of net fluxes (dry deposition/re-emission) of NO_3 and SO_4 between the snow surface and the atmosphere from changes in the concentrations of these species in the surface snow over periods of 36-48 hours. The experiment was also designed to determine the influence of solar radiation on fluxes of NO_3 and SO_4. The methodology included a procedure to homogenise surface snow; this served to normalise the initial chemical conditions for all sample sets used in the experiment. The homogeneous samples were exposed to the atmosphere in a series of mesh bags which allowed free exchange of water vapour, trace gases and aerosols between the atmosphere and the snow. The control study for the influence of solar radiation on the snow-atmosphere exchange was identical to that of the bagged snow under open sunny sky except that it was carried out in the shade of an opaque flysheet. The chemical composition and snow-water equivalent (SWE) of all bagged snows were determined before and after each experiment. The results from experiments at both sites show that solar radiation had no influence on snow-atmosphere exchange of NO_3 and SO_4. In the first experiment at the forested site sublimation of water vapour from the snow occurred. The mass loss of water vapour was equally offset in sun and shade by significant increases in NO_3 concentrations and no net loss or gain of this species by snow-atmosphere exchange thus took place. Changes in the concentrations of SO_4 were not significant indicating that no dry deposition of this species had occurred. In the second experiment at the tundra site there was no loss of mass by sublimation. However, in this case a significant net exchange of SO_4 from the atmosphere to the snow with a dry deposition velocity of 0.09 cm s^{-1} was measured.

INTRODUCTION

Snow cover is a major factor in mediating the transfer of gasses and aerosols between the atmosphere and circumpolar ecosystems. Snow cover acts as a reservoir which continuously accumulates atmospheric species by dry deposition and fallout prior to the release of the chemical components during the spring melt (Cadle, 1991). However, other processes such as sublimation (Pomeroy et al, 1991), snow-grain metamorphism (Laberge and Jones, 1991), snow-crystal charge distribution, gaseous re-emission (Neubauer and Heumann, 1988), photochemical reactions (Sigg and Neftel, 1988), meltwater infiltration (Tranter et al, 1991), wind redistribution, snow algal photosynthesis (Hoham et al, 1989) and heterotrophic metabolism (Jones, 1991) by other microorganisms can also cause changes in the chemical composition of the snowpack. The presence of these processes induce errors in the measurement of true dry deposition velocities (V_d cm s^{-1}) for the transfer of chemical species

between the snow and the atmosphere.

One of the competing process which has been suggested as a major factor in the chemical dynamics of snow cover in solar-radiation induced photochemical reactions at the snow surface. Neubauer and Heumann (1988) proposed such a hypothesis to explain losses of NO_3 from polar snows. The hypothesis states that NO_3-HNO_3 could be produced or degraded by photochemical reactions at the snow-atmosphere interface from N-species by shortwave radiation. Solar radiation may also influence SO_4 concentrations at the snow-atmosphere interface by increasing the oxidation rate of S(IV) to SO_4; this would occur if solar radiation produced oxidants such as H_2O_2 and O_3 in the quasi-liquid layers on grain surfaces. Possible pathways for S(IV) oxidation to SO_4 have been discussed by Bales (1991).

To test these hypotheses, Duchesneau and Jones (in press) carried out a series of experiments on snow-atmosphere exchange in the spring of 1990 and of 1991 on the Agassiz Ice Cap in Arctic Canada. Although the results did not show any direct photo-induced degradation of NO_3 they did indicate that some losses of this species occurred in sunlight. Influence of solar radiation on SO_4 concentrations was not observed.

In the spring of 1992 a similar experiment on snow-atmosphere exchange was set up at two sites close to Inuvik in the Canadian Arctic. In order to control the field experiment as closely as possible the experimental methodology was designed to minimise the initial heterogeneity of the snow samples by using homogenised fresh surface snow. Mass losses were determined by weight differences of discrete snow samples during the experimental period. Any effect of microbiological activity on nutrient species within the snow or on the exchange of species between the atmosphere and the snow was minimised by carrying out the experiment at air temperatures below -5°C when very little liquid water was present. The following paper describes the experiment and the conclusions of the study.

METHODOLOGY

The first field experiment was carried out in a shallow valley with open spruce woodland adjacent to the weather station of the Atmospheric Environmental Service of Canada, 10 km east of Inuvik (68°N 134°W), on April 15-16, 1992. The second experiment was carried out on April 25-26, 1992, at the GEWEX field station of the National Hydrologic Research Institute of Canada. The site is at Trail Valley Creek, 50 km north of Inuvik, in a tundra location with no tree cover. In both cases the depth of the snow cover was approximately 1 m.

Experimental Procedure

Surface snow (approximately 20 L of the top stratum, 2-3 cm) was homogenised by shifting and stirring with plastic scoops in a large plastic bucket which had previously been well rinsed with deionized water. The scoops were manipulated using plastic gloves. The homogeneised snow was divided into two halves (approximately 10 L each; series A and B; Table 1). The snow from each series was further divided into four sets (approximately 2-3 L each, A1..A4 and B1..B4). Each set was separated into six samples of between 200-400 g each (An-1..An-6 and Bn-1..Bn-6 where n = 1..4). Three of the snow samples from each set (e.g. A1-1..A1-3 or B4-1..B4-3) were hermetically sealed in plastic bags and conserved in the dark (-15°C) until melted for analysis. They represented the initial chemical condition of the snow at the start of the experiment. The three complementary samples from each set (e.g. A1-4..A1-6 or B4-4..B4-6) were placed in gauze bags made of polypropylene (mesh size, 200 µm; bag size 20 cm x 20 cm), weighed and placed on the surface of the snow cover, from which the original surface snow had been removed (approx. 1 m x 1 m), for 36-48 hours. Series A were placed in the sun, Series B were placed in the shade of a tarpaulin flysheet strung 0.5-1 m above the snow cover.

Immediately after the mesh bags had been laid on the surface at the beginning of the experiment, three mesh bags from each series (A, sun; B, shade) were retrieved and hermetically sealed in plastic bags before being replaced on the snow surface in their original position. This experimental subset was used as a control to verify mass losses due to the free exchange of water vapour between the mesh bags and the atmosphere. It also served as a control to the open mesh bags in the study of the chemical exchange between snow and the atmosphere.

TABLE 1: Series and subsets of snow samples used for the snow-atmosphere experiments, Inuvik, Canada, April 1992. Initial conditions refers to the samples used to establish the chemical composition of the snow at the start of the experiments; final conditions to the samples analyzed at the end of the experiment. The samples numbered as -N^H identify the mesh bags that were hermetically sealed in plastic at the start of the experiments.

	SERIES A Experiment in sun		SERIES B Experiment in shade	
	Initial conditions	Final conditions	Initial conditions	Final conditions
SUBSET 1	A1-1	A1-4	B1-1	B1-4
	A1-2	A1-5	B1-2	B1-5
	A1-3	A1-6	B1-3	B1-6
SUBSET 2	A2-1	A2-4	B2-1	B2-4
	A2-2	A2-5	B2-2	B2-5
	A2-3	A2-6	B2-3	B2-6
SUBSET 3	A3-1	A3-4^H	B3-1	B3-4^H
	A3-2	A3-5^H	B3-2	B3-5^H
	A3-3	A3-6^H	B3-3	B3-6^H
SUBSET 4	A4-1	A4-4	B4-1	B4-4
	A4-2	A4-5	B4-2	B4-5
	A4-3	A4-6	B4-3	B4-6

At the end of the experimental period, the bags were weighed, the snow transferred to plastic bags and kept in the dark at -15°C for 26 days (first experiment), 16 days (second experiment) and then melted for analysis. The results of the analysis represent the final chemical condition of the snow samples at the end of the experiment. The analyses of NO_3 and SO_4 were conducted by utilizing ion-chromatography - also used to analyze for other major anions (Cl, Br) and cations (Na, K, Mg, Ca). The pH was determined by the use of a Coleman pH meter and conductivity with a Radiometer CDM-2 meter.

Data Analysis

The chemical characteristics of the snow samples before or after the experiment are expressed either as ion concentrations ($\mu eq\ L^{-1}$) or as ion load (μeq_L, where μeq_L x SWE).

Statistical analyses (Student-T test) were carried out on the chemical data ($\mu eq\ L^{-1}$ or μeq_L) regrouped according to the two main considerations of the experiment. First, to determine if solar radiation influenced the chemical exchanges of NO_3 and SO_4 between the snow and the atmosphere, the chemical data for the A and B series were treated separately. If there is no significant differences in the initial chemical concentrations of the A and B series (normalised homogeneous snow substrate) then a comparative test between the increases in concentrations of the A series (in the sun) with the B series (in the shade) will show if solar radiation has any effect on snow-atmosphere exchange. Initial conditions for each series were

regrouped as 12 samples each (table 1, An-1..An-3 for series A and Bn-1..Bn-3 for series B where n = 1..4). The final chemical condition of the snow was represented by the 9 samples from each series which were exposed to the atmosphere only. These samples were drawn from the sets An-4..An-6 for series A representing the 12 mesh bags exposed to the sun, and samples Bn-4..Bn-6 for series B representing the 12 mesh bags exposed in the shade, *minus* the 3 mesh bags from each series which were chosen at the start of the experiment to be sealed in plastic bags. In these latter bags the snow had no contact with the atmosphere, dry deposition and re-emission were eliminated. However, comparative data analysis of the sealed bags in the sun versus those in the shade still served to evaluate the effect of solar radiation on snow in the absence of free atmospheric exchange.

The rate (deposition flux, $\mu eq\ m^{-2}\ day^{-1}$) of net snow-atmosphere exchange of NO_3 and SO_4 between snow and the atmosphere was determined from the increase in chemical load during the experiment. The chemical loads were only calculated if concentration changes of any series were statistically significant. Data from the A and B series were either treated separately or combined. In the separate case the initial and final conditions for each series were regrouped as in the case of the solar radiation experiment. In the event that there was no significant effect of solar radiation on the chemistry of the snow from the separate analysis of the data from the A and B series, the data from the A and B series were combined.

RESULTS AND DISCUSSION

General snow chemistry and data analysis

The first experimental period lasted for 36 hours (April 15-16) of which there were 24 hours of sunlight, and the second for 48 hours (April 25-26) of which there were 35 hours of sunlight. Meteorological conditions were similar during the two experiments; air temperature, -8 to -10°C for the first, -5 to -15°C for the second. Winds were very light during both experiments, very little redistribution of snow was observed. Veiled sun under light cloud occurred on April 15-16 in the first period while bright sun was experienced on April 25 and veiled sun behind high cloud on April 26.

At both sites the original chemical contents of the snows were extremely low (Table 2); conductivity was in the range of 0.5-4 μMHO and pH varied from 5.27 to 5.75. Major ion concentrations showed that both sea salt (Na, Cl) and local dust (Ca, Mg) were present, sea salt being more in evidence in the snow from the first experiment than in the second.

Calculation of SO_4 concentrations from sea salt content shows that 80% of the SO_4 content of the snows was in excess and was of terrestrial and anthropogenic origin.

Statistical analyses of data representing the initial chemical concentrations of NO_3 and SO_4 in snow regrouped either by discrete sample sets or by complete series showed that there was no significant differences between concentrations of all sample sets and/or series at the beginning of each experiment. The coefficient of variation of sample sets were low (2-10%), thus showing that the initial condition of homogeneity for the snow substrate was respected.

Water vapour losses from bagged snow

Figure 1a shows the change in SWE of snow samples at the end of the first experiment. In the case of the mesh bags open to the atmosphere there was a significant and consistent loss of water vapour by sublimation in all cases. A relatively greater loss of SWE from the mesh bags in the shaded location was measured in comparison to the losses from those in the sun (Figure 1a), but the overall loss was not significantly different for the two series. The consistent increase in sublimation for shaded snow samples may have been due, however, to the presence of the tarpaulin. The tarpaulin may induce different air movements and temperature gradients over the snow surface as compared to snow completely exposed to the atmosphere. There was very little weight loss from the control mesh bags which had been sealed in plastic at the start of the experiment.

In the second experiment no mass losses occurred from any of the snow samples. There was no difference between the weight of snow in the bags before and after the experimental period whether the bagged samples were in mesh bags open to the atmosphere in sun or in shade, or sealed in plastic (Figure 1b).

Table 2: Chemical characteristics (pH, units; mean concentrations, μeq L^{-1}; [ ], standard deviation) of the surface snows at the start of each experiment on snow-atmosphere exchange, Inuvik, Canada, April 1992.

pH or ION	First experiment	Second experiment
pH	5.41 [0.08]	5.61 [0.08]
Na	5.69 [2.04]	7.46 [1.59]
K	0.30 [0.41]	0.41 [0.38]
Ca	4.30 [0.50]	15.88 [2.92]
Mg	4.64 [1.17]	8.01 [1.73]
Cl	6.37 [1.55]	13.51 [7.01]
NO_3	1.86 [0.08]	4.48 [0.40]
SO_4	3.33 [0.27]	4.56 [0.43]

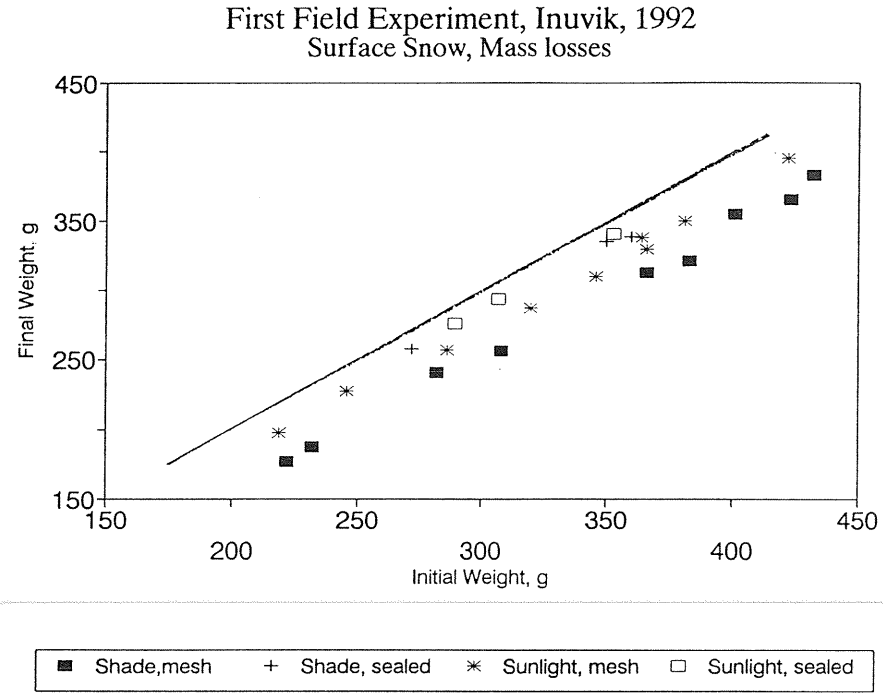

Figure 1a: Changes in weight of mesh bag samples of surface snow either exposed to the atmosphere or sealed in plastic, in sun and in shade, first field experiment, Inuvik, Canada, April 15-16, 1992. The line is a 1:1 regression which theoretically represents no weight loss during the experiment.

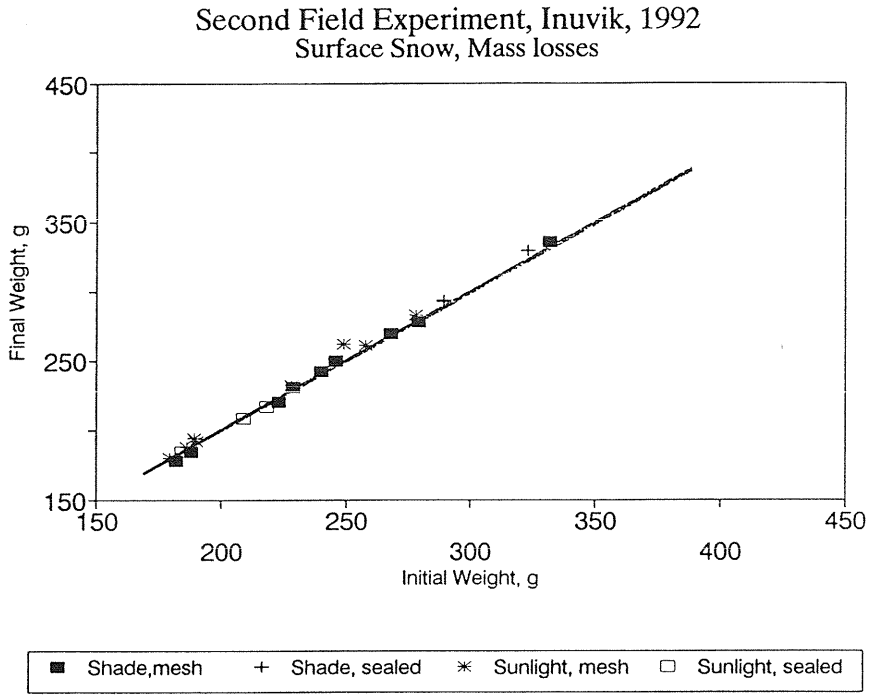

Figure 1b: Changes in weight of mesh bag samples of surface snow either exposed to the atmosphere or sealed in plastic, in sun or in shade, second field experiment, Inuvik, Canada, April 25-26, 1992. The line is a 1:1 regression which theoretically represents no weight loss during the experiment.

Although no air measurements were taken, the overall differences in sublimation rates between the two experiments must have been due to the different degrees of humidity of the ambient air during the two experimental periods.

Nitrate dynamics of bagged snow

In the first experiment significant increases in the concentrations of NO_3 in the snow in all the mesh bags exposed to the atmosphere in both the sun and the shade were recorded (Figure 2a). There was, however, no significant differences between the NO_3 increases in the series of mesh bags exposed in the shade to the series exposed in the sun, showing that there was no effect of solar radiation on the snow chemistry. The chemical loads of NO_3 at the beginning and at the end of the experiment were then calculated for each sample. The values of series A and B were combined to produce a regression which showed that no increase in NO_3 loads had occurred (Figure 2b). The increases in NO_3 concentrations could thus be attributed entirely to the decreases in SWE. The results show that there was no net dry deposition of NO_3 from the atmosphere to the snow during the experiment. The deposition flux of NO_3 is essentially 0 $\mu eq\ m^{-2}\ day^{-1}$.

It should be noted that some increases in NO_3 in the hermetically sealed mesh bags also occurred. However, the results were not significant due to the small sample set and were eliminated for purposes of comparison.

In the second experiment no significant increases or decreases in NO_3 concentrations of snow exposed to the atmosphere took place whether the samples were in sun or shade. As mass losses of water vapour from snow were not observed during this study the results suggest that net deposition of NO_3 did not occur in this experiment either. The conclusion, however, is only tentative as the changes in NO_3 concentrations were not significant and NO_3 loads were not calculated. No significant changes were observed in the case of the hermetically sealed mesh bags.

Sulphate dynamics of bagged snow

In the first experiment a trend in the increase of SO_4 concentrations in bagged snows exposed to the atmosphere was recorded; the

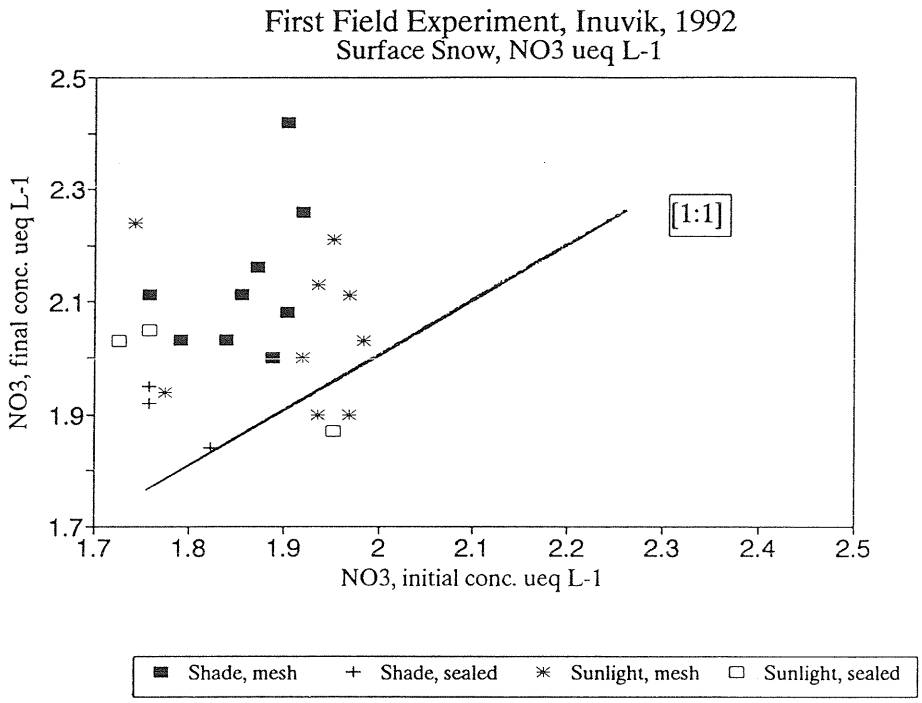

Figure 2a: *Changes in NO_3 concentrations of surface snow in mesh bags either exposed to the atmosphere or sealed in plastic, in sun or in shade, first field experiment, Inuvik, Canada, April 15-16, 1992. The line is a 1:1 regression which theoretically represents no concentration changes during the experiment.*

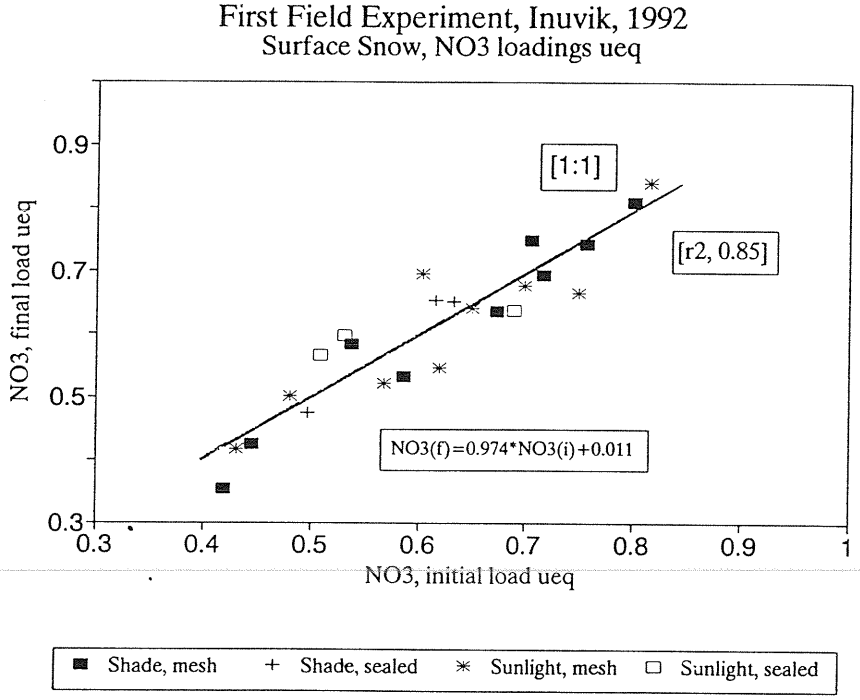

Figure 2b: *Changes in NO_3 loads of surface snow in mesh bags either exposed to the atmosphere or sealed in plastic, in sun or in shade, first field experiment, Inuvik, Canada, April 15-16, 1992. The relationship between the final load, NO_3 (f), and the initial load, NO_3 (i), is shown. There is no significant difference between this regression and the 1:1 regression which theoretically represents no changes in NO_3 load during the experiment.*

increase was of the same order as that expected from the loss in SWE. Although the increases in concentrations were not statistically significant enough to calculate changes in chemical load and deposition flux, they do indicate, however, that if any dry deposition had occurred it must have been minimal.

Conversely, in the second experiment significant increases in SO_4 concentrations in all bagged snows exposed to the atmosphere in both the sun and the shade were recorded (Figure 3a). There were, however, no significant differences between the SO_4 increases in the series of mesh bags exposed in the shade to the series exposed in the sun. The results of series A and B were then combined to calculate the increase in chemical loads of SO_4 (μeq_L) at the end of the experiment (Figure 3b). These increases are entirely due to net exchange between the atmosphere and the snow surface as there was no difference between increases in sun and shade. From the mean increase in load for series A and B (0.2 μeq), the area of the mesh bags (0.04 m^{-2}), and the time of exposure to the atmosphere (48 hrs), the mean deposition flux for SO_4 is calculated to be 2.5 μeq m^{-2} day^{-1}).

It should be noted that changes in the concentration of SO_4 in the hermetically sealed mesh bags were not significant.

NO_3 and SO_4 exchange at the snow-atmosphere interface

The results of both experiments show that solar radiation does not have an appreciable effect on the snow-atmosphere exchange of NO_3 and SO_4 under the conditions of each experiment.

The results of the first experiment show that the net exchange of NO_3 and SO_4 between the atmosphere and the snow surface was minimal.

The fact that NO_3 fluxes were not observed is consistent with the fact that atmospheric concentrations of NO_3 in Arctic air masses are very low (Barrie, 1986; Parungo et al. 1990). On the other hand SO_4 concentrations can be as high as those found in temperate industrial regions. From the published data on NO_3 concentrations in Arctic air and known values for dry deposition velocities, the calculated values for dry deposition increases of NO_3 to the snow samples during the experimental period would have been very small compared to the original concentrations of this species in the snow. In the case of SO_4, deposition may also have been small due to concomitant low concentrations of SO_4 in the air mass - the air having already lost much of its aerosol load by wet deposition prior to the date of the experiment. This is supported by the fact that the air mass was dry enough to cause sublimation of the snow.

The retention of NO_3 by the snow grains during the sublimation of snow suggests that the species is conservative. It is probably retained at the inter-grain boundaries and/or the ice surface quasi-liquid layers in the same manner as the non-volatile SO_4 (Mulvaney et al, 1988). These experiments, however, can only indicate the general behaviour of these solutes as the methodology does not rule out the possibility that concomitant processes of loss and gain of equal magnitude may have resulted in a null net exchange of NO_3 between the snow and the atmosphere.

In the second experiment no net exchange of NO_3 was in evidence again, but a significant net exchange of SO_4 from the atmosphere to the snow was measured. From the deposition flux of 2.5 μeq m^{-2} day^{-1} and the reported mean values for seasonal SO_4 concentrations in Arctic aerosol during spring (mean, 2 μg m^{-3}; Barrie, 1986; Parungo et al, 1990), the calculated dry deposition velocity of SO_4 is then calculated to be 0.09 cm s^{-1}. This falls in the range of reported values for this species of 0.04-0.16 cm s^{-1} (Cadle, 1991).

CONCLUSIONS

Solar radiation did not effect the exchange of NO_3 and SO_4 between the snow and the atmosphere in either of the two experiments. In the first experiment the losses of mass by sublimation of water vapour from bagged snow were equally offset by significant increases in NO_3 concentrations in both sun and shade. The results suggest that NO_3 was conservative during snow-atmosphere exchange. Changes in the concentrations of SO_4 were not significant enough to indicate whether losses or gains of the ion had occurred during the experiment. Dry deposition of this species was low during this experiment as the dry air mass had presumably lost most of its aerosol load by prior wet deposition.

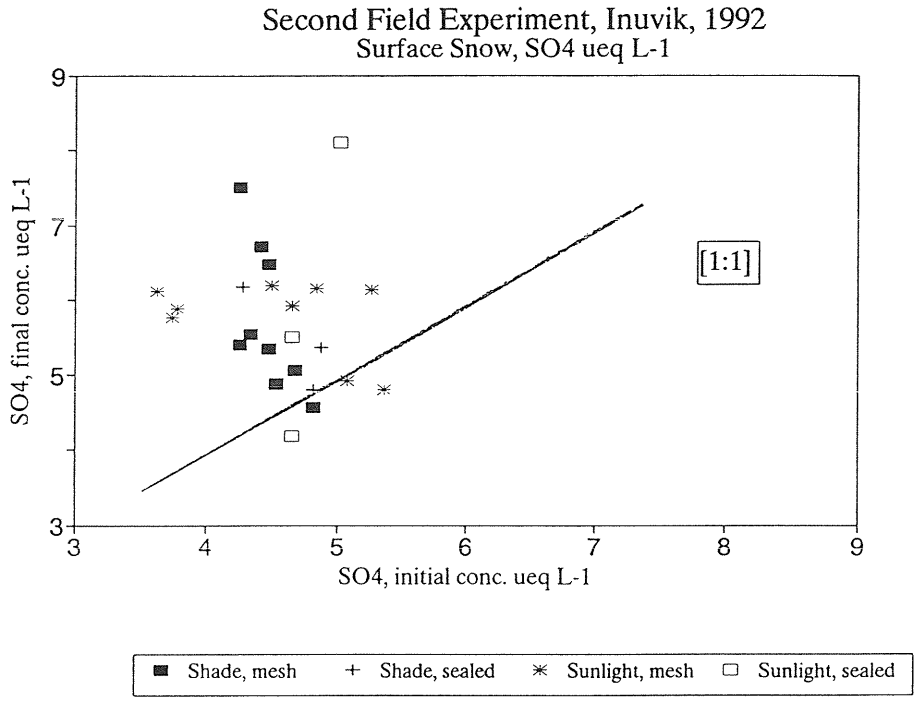

Figure 3a: *Changes in SO_4 concentrations of surface snow in mesh bags either exposed to the atmosphere or sealed in plastic, in sun or in shade, second field experiment, Inuvik, Canada, April 25-26, 1992. The line is a 1:1 regression which theoretically represents no concentration changes during the experiment.*

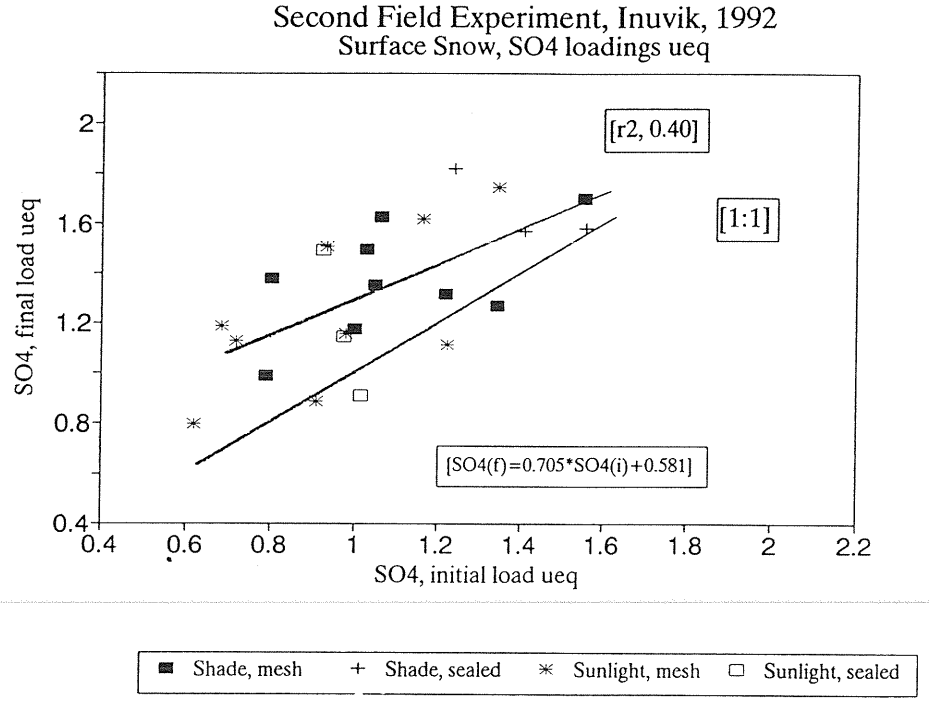

Figure 3b: *Changes in SO_4 loads of surface snow in mesh bags either exposed to the atmosphere or sealed in plastic, in sun or in shade, second field experiment, Inuvik, Canada, April 25-26, 1992. The relationship between the final load, SO_4 (f), and the initial load, SO_4(i) is shown. There is significant difference between this regression and the 1:1 regression which theoretically represents no changes in SO_4 load during the experiment.*

In the second field experiment there were no losses of mass by sublimation. No significant losses or gains of NO_3 occurred during the experiment. However, a significant net exchange of SO_4 from the atmosphere to the snow was measured in both sun and shade; the calculated dry deposition velocity of SO_4 to the snow surface is similar to that reported fro snow in other regions outside of arctic North America.

REFERENCES

Bales, R.C. (1991) Modelling in-pack chemical transformations. In: seasonal snowpacks; processes of compositional change. proceedings of a NATO Advanced Research Workshop, Maratea, Italy, July 23-27, 1990. Eds. Davies, T.D., Tranter, M and H.G. Jones. pp 139-164.

Barrie, L.A. (1986) Arctic air pollution: an overview of current knowledge. Atmospheric Environment 20: 643-663.

Cadle, S.H. (1991) Dry deposition to snowpacks. In: seasonal snowpacks; processes of compositional change. proceedings of a NATO Advanced Research Workshop, Maratea, Italy, July 23-27, 1990. Eds. Davies, T.D., Tranter, M and H.G. Jones. pp 121-66.

Duchesneau, M. and H.G. Jones (in press) La calotte de glace Agassiz: profils physico-chimiques et echanges neige-atmosphere. Musk Ox.

Hoham, R.W., Yatsko, C., Germain, L. and H.G. Jones (1989) Recent discoveries of snow algae in upstate New York and Québec Province and preliminary reports on related snow chemistry. In: Proceedings of the Eastern Snow Conference, 46th Annual meeting, Québec City, Québec, June 8 & 9, pp. 196-200.

Jones, H.G. (1991) Snow chemistry and biological activity: a particular perspective on nutrient cycling. In: seasonal snowpacks; processes of compositional change. proceedings of a NATO Advanced Research Workshop, Maratea, Italy, July 23-27, 1990. Eds. Davies, T.D., Tranter, M and H.G. Jones. pp 173-228.

Laberge, C. and H.G. Jones (1991). A statistical approach to field measurements of the chemical evolution of cold (< 0°C) snowcover. Environmental Monitoring and Assessment, 17: 201-216.

Mulvany, R., Wolff, E.W. and Oates, K. (1988). Sulphuric acid at grain boundaries in Antarctic ice. Nature 331: 247-249.

Neubauer, J. and K.G. Heumann (1988) Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddel Sea, Antarctica. Atmospheric Environment 22: 537-545.

Parungo, F.P., Nagamoto, C.T. and P.J. Sheridan (1990) Aerosol characteristics of Arctic haze sampled during AGASP-II. Atmospheric Environment 24A: 937-949.

Pomeroy, J.W., Davies, T.D. and M. Tranter (1991) The impact of blowing snow on snow chemistry. In: Seasonal Snowpacks. Processes of Compositional Change, T.D. Davies, M. Tranter and H.G. Jones (Editors), NATO Advanced Study Institute Series G, Vol. 28, Springer-Verlag, Berlin, pp. 71-114.

Sigg, A. and A. Neftel (1988) Seasonal variations of hydrogen peroxide in polar ice cores. Annals Glaciol. 10: 157-162.

Tranter, M., Tsiouris, S., Davies, T.D.and H.G. Jones (1992) A laboratory investigation of the leaching of solute from snowpack by rainfall. Hydrological Processes, 6: 169-178.