PTR-MS observations of photo-enhanced VOC release from Arctic and midlatitude snow

S. S. Gao,¹ S. J. Sjostedt,¹ S. Sharma,² S. R. Hall,³ K. Ullmann,³ and J. P. D. Abbatt¹

Received 14 November 2011; revised 3 February 2012; accepted 8 February 2012; published 31 March 2012.

[1] To evaluate the release mechanism of volatile organic species (VOCs) from solar illuminated snowpacks, this study used proton transfer reaction–mass spectrometry (PTR-MS) for the first time to study VOCs within Arctic snow and to compare these results to VOC release from illuminated snow in the laboratory. The field measurements were conducted in April during the 2009 Ocean–Atmosphere–Sea Ice–Snowpack (OASIS) campaign in Barrow, Alaska, whereas in the laboratory four natural snow samples, from the Arctic (Alert, Nunavut), a rural site (Egbert, Ontario), and an urban area (Toronto, Ontario), were exposed to a Xe arc lamp with a 295 nm longpass filter. Similar VOCs were observed in both the field and laboratory experiments suggesting that these light-driven processes occur not only in polar regions but in midlatitude snows as well. Also, because the laboratory samples were temperature controlled, we conclude that the release mechanism is primarily photochemical and not temperature mediated. The snow composition may have influenced VOC production because aged Toronto snow samples, with both the highest total organic carbon content and concentration of oxidant precursors (i.e., NO₃⁻), exhibited the largest production of VOCs upon irradiation.


1. Introduction

[2] While initial interest in snowpack photochemistry stemmed from its ability to affect the oxidative capacity of the overlying atmosphere through the emission of reactive species (e.g., NOₓ, HOₓ, and molecular halogens) [Honrath et al., 2000a, 2000b; Simpson et al., 2007; Yang et al., 2002], chemistry occurring within the snowpack and involving the transformation of species present in this environment has lead to numerous other field and laboratory studies. In polar regions, higher levels of volatile organic species (VOCs) have been measured within the interstitial air of the snowpack, in comparison to the ambient atmosphere, resulting in observed fluxes from the snowpack to the boundary layer. Release of species such as formaldehyde [Hutterli et al., 1999; Sumner and Shepson, 1999], acetaldehyde and acetone [Grananas et al., 2002; Guimbaud et al., 2002], carboxylic acids [Dibb and Arsenault, 2002], alkenes and alkyl halides [Swanson et al., 2002] have been suggested to arise from photochemical sources. Known gas-phase chemistry (i.e., the oxidation of hydrocarbons by OH or Cl radicals in the presence of NOₓ) underpredicts the measured VOC mixing ratios. Both temperature-dependent physical processes (e.g., desorption and degassing) and radiation-dependent photochemistry are believed to contribute to the snowpack emissions [Grananas et al., 2007]. Volatile species such as aldehydes can be an important source of HOₓ in dry, polar environments, affecting the lifetime of atmospheric chemical species by participating in the termination of ozone-destroying radical chain reactions involving halogens [Barrie et al., 1988].

[3] This work compares the observed production of VOCs from irradiated snow during the OASIS field campaign, which took place in Barrow, Alaska during April of 2009, to laboratory measurements of VOCs produced from the irradiation of urban, rural, and Arctic snow samples using a Xe arc lamp. Photochemical production of VOCs from natural and artificial snow/ice has been previously investigated in both field [Dibb and Arsenault, 2002; Guimbaud et al., 2002; Klán et al., 2003; Sumner and Shepson, 1999; Swanson et al., 2002] and laboratory [Grananas et al., 2004; Guzmán et al., 2007; Klán et al., 2000; Klánova et al., 2003; Matykiewiczová et al., 2007] settings, and mechanisms for this chemistry have been proposed. To our knowledge, this is the first study to measure real-time VOC production from snow using a proton transfer reaction – mass spectrometer (PTR-MS) and the first laboratory investigation of midlatitude snow as a photochemical source of VOCs.

[4] VOCs can be produced within the snowpack via photooxidation of organic species present, which can be of anthropogenic or biogenic origin. Large organic species within the snowpack are believed to be broken down...
photolytically to smaller volatile products [Gao and Abbatt, 2011; Sumner and Shepson, 1999]. Photochemically produced oxidants (e.g., OH) can react with the organics [Sumner and Shepson, 1999], and light-absorbing species can undergo direct photochemistry as well [Dubowski and Hoffmann, 2000; Guzmán et al., 2007; Klán et al., 2000; Klánova et al., 2003; Matykiewiczová et al., 2007]. Organic chromophores can account for 50% of the overall absorption coefficient (for λ ≥ 280 nm) of polar snow [Anastasio and Robles, 2007], while the rest is contributed by NO$_3^-$ and H$_2$O$_2$. NO$_3$ and H$_2$O$_2$ act as condensed-phase OH precursors [Chu and Anastasio, 2003; 2005] through the following reactions:

\[
\begin{align*}
\text{NO}_3^- + \text{hv} & \rightarrow \text{NO}_2 - \text{O}^- \text{ or } \text{NO}_2^- + \text{O} \\
\text{NO}_2^- + \text{hv} & \rightarrow \text{NO} + \text{O}^- \\
\text{O}^- + \text{H}^+ & \rightarrow \text{OH} \\
\text{O}^- + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{OH}^- \\
\text{H}_2\text{O}_2 & \rightarrow \text{OH} + \text{OH}^- 
\end{align*}
\]

[5] H$_2$O$_2$ has been suggested to be the dominant source of OH radicals within the snowpack as it has a much larger quantum yield than NO$_3^-$. However, there is a potential for differences in snow composition. The difference in emissions (both in terms of quantity and identity) from different snow samples could potentially dominate over direct photolysis in the presence of OH precursors [Matykiewiczová et al., 2007]. Currently, the relative contributions of direct and indirect photochemistry are still not fully understood. [6] The objective of this investigation was to evaluate the role of the snowpack as a photochemical source of VOCs using direct online measurements, and to reconcile emissions with snowpack composition. Chemical species may be incorporated into snow via snow crystal formation, scavenging during precipitation, and deposition on the snowpack through wet or dry processes [Houdier et al., 2002; Ferrier et al., 2002; Sokolov and Abbatt, 2002; Wanja et al., 1999]. Following deposition, changes to snow morphology due to temperature fluctuations (e.g., evaporation and condensation) can further alter the chemical composition of the snowpack [Grannas et al., 2007]. With this study, we attempted to address: (1) Can similar VOCs be produced from natural snow samples in a constant temperature laboratory setting using an artificial light source as can be observed in the field, thus confirming a photochemical source? (2) Can the differences in emissions (both in terms of quantity and identity) from different snow samples be accounted for by differences in snow composition? (3) Do midlatitude snows produce VOCs as observed previously for Arctic samples, and if so, in what relative proportion?

2. Experimental Setup

2.1. Barrow Measurements

[7] Measurements were made between 8 and 14 April 2009 in trailers near the Barrow Arctic Research Center (BARC), located 6.5 km northeast of the town of Barrow, Alaska. Real-time measurements of selected VOCs were made using an Ionicon High Sensitivity PTR-MS [de Gouw and Warneke, 2007]. The PTR-MS employs a soft ionization technique and is suited for measurements of VOCs with higher proton affinity than water, such as oxygenated VOCs. Species undergo the following reaction and are commonly detected at a m/z ratio of 1 larger than their molar mass.

\[
\text{H}_2\text{O}^+ + \text{R} \rightarrow \text{RH}^+ + \text{H}_2\text{O}
\]

[8] Measurements were collected at 3 sampling heights (18, 6, and 0 m above ground level). The ground level inlet line was Teflon and was covered by blowing snow (burial depth varied, roughly 15 cm of snow cover) for the measurements reported here, allowing for measurements of interstitial air. The other 2 inlet lines were constructed of stainless steel and were heated. Valves allowed for switching between measurements at different inlet heights. The total flow from the two stainless steel inlets was 100 slpm. A 3 slpm sample was brought into the trailer, from which 200 sccm of ambient air was sampled by the PTR-MS. The interstitial air was sampled through a Teflon line at 3 slpm, and 200 sccm was then drawn off by the PTR-MS.

[9] Identification and calibration of some species were completed through the use of 2 gas cylinders of VOC standards from Apel-Reimer (500 ppb in N$_2$ of methanol, acetone, and toluene in one and 500 ppb of benzene, acetaldehyde, and isoprene in the other). Formic and acetic acid, detected at m/z 47 and m/z 61, were calibrated at a later date at the University of Toronto using permeation tubes (VICI Metronics Dynacal Permeation Device) and a permeation oven (Dynacalibrator Model 120, VICI Metronics Inc.). The permeation tube emission rates were first calibrated using ion chromatography. In particular, the permeation oven was allowed to equilibrate for 2 days at 40°C, then a 200 sccm flow was bubbled through 2 glass bubblers connected in series, both filled with deionized water (18 MΩ), for a period of 1 week.

[10] Measurements for m/z ratios which were not calibrated are expressed in terms of normalized signal. The counts/sec at these masses are normalized to the reagent ion, H$_2$O$^+$ (average count/sec = 1.4 × 10$^6$ cps) to account for changes in reagent ion signal.

[11] A Charged-coupled device Actinic Flux Spectroradiometer (CAFS) [Shetter and Muller, 1999] measured spectrally resolved downwelling actinic flux at 0.1 Hz. The upwelling flux was estimated as a function of solar zenith angle using the Tropospheric Ultraviolet and Visible (TUV) radiative transfer model [Madronich and Flocke, 1999] under clear sky conditions. The sum of up- and downwelling
actinic fluxes was used to calculate total photolysis frequencies.

2.2. Laboratory Measurements

2.2.1. Sample Collection

[12] Snow samples were obtained from 3 types of locations (high Arctic, rural, and urban). Samples of high latitude snow from a remote region were collected on 25 April 2011, 200 m from the Global Atmospheric Watch Laboratory in Alert (82° N, 62.3° W), Nunavut, Canada. The samples used within this work only consist of top layer snow. Rural samples were collected on 4 February 2011 at the Environment Canada site in Egbert (44°14′N, 79°47′W), Ontario, Canada 1 day after fresh snow fall (Egbert is located approximately 85 km north of Toronto). Fresh (collected during a precipitation event, 12 January 2011) and aged (collected 5 days following fresh snow fall, 11 February 2011) urban samples were collected on St. George campus of the University of Toronto. Snow was only collected from the top 20 cm of the snowpack. Samples were collected in 1 L glass bottles, which had been rinsed with deionized water and allowed to air dry, and then were packed in dry ice during transport to minimize melting. The snow was stored in a −20°C chest freezer and kept in the dark until used for analysis and photolysis experiments. Extreme care was taken to reduce potential for contamination, and the experimental protocol was identical for each photolysis experiment and chemical analysis.

2.2.2. VOC Measurements

[13] Small amounts of snow (10 to 20 g) were weighed out prior to experimentation in a clean and dry glass jar and kept in the dark in dry ice until transferred to the cooled reaction cell. The photolysis experiment setup has previously been described in detail [Gao and Abbatt, 2011]. The temperature was measured inside the innermost sleeve of the reaction cell to be −20°C using a thermistor. The snow sample filled up 1/3 of the innermost sleeve of the reaction cell. The entire system was allowed to equilibrate in the dark with a constant flow of 150 sccm of compressed air (Linde, Grade 0.1) passing first through a humidifying flow tube (cooled to −18°C, containing ice made from deionized water) to prevent evaporation of the snow sample, then through the sample and finally to the PTR-MS, until a stable background signal was achieved for the m/z ratios monitored by the PTR-MS. The measurements were made in selected ion mode. The m/z ratios monitored were selected from preliminary photolysis experiments conducted with the PTR-MS in scan mode (from m/z 21 to 150).

[14] The snow sample within the reaction cell was photolyzed using a 1000-W Xe arc lamp. A longpass filter eliminating all light with wavelengths below 295 nm was used to simulate solar actinic radiation, which at ground level cuts off below 300 nm. Measurements were made initially with the reaction cell covered to represent dark conditions where no photochemistry would be occurring. The measurements began with 30 min under dark conditions, the cell was then uncovered and photolysis was allowed to occur for 30 min before another 30 min of dark measurements were made. The PTR-MS sampled 100 sccm of the carrier gas flow coming out of the reaction cell, carrying the volatile products present in the interstitial air of the snow sample. Photolysis experiments were conducted with an empty cell on some days to serve as a control. Several aliquots of the snow samples from each location were irradiated to evaluate reproducibility.

[15] Calibrations were conducted each day with a standard gas cylinder containing 500 ppb of methanol, acetone, and toluene in N₂. A calibration of m/z 47 and 61 was conducted at a later date using permeation tubes (described above).

[16] The output of the lamp between 295 and 400 nm was measured with a Scientech 372 Power and Energy Meter, using a 250 to 400 nm detector head and a 295 nm longpass filter. The measured quantity (in watts) was used to calculate the photon flux of the lamp.

2.2.3. Snow Composition

[17] Snow samples were melted, and anion and cation compositions were analyzed using two ion chromatography systems (IC; Dionex ICS-2000) each operating with a conductivity suppressor (ASRS 300 for anion and CSRS 300 for cation), a DS6 heated conductivity cell, an IonPac ion concentrator column (TAC-ULP1 5 × 23 mm for anion and TCC-ULP1 5 × 23 mm for cation), a guard column, and an AS40 automated sampler. Anion separation was conducted using gradient elution, with eluent generated from a KOH Eluent Generator Cartridge, on an IonPac AS11-HC 4 × 250 mm hydroxide-selective anion-exchange column. The KOH was held at 2 mM initially, ramped up linearly to 4 mM over 6 min, to 10 mM over the next 10 min, to 25 mM in the next 7 min, then equilibrated back to 2 mM over the 25 min run time at a flow rate of 1.2 mL/min at 30°C. Cation separation was conducted using gradient elution, with eluent generated from a methanesulfonic acid (MSA) Eluent Generator Cartridge, on an IonPac CS17 4 × 250 mm cation-exchange column. The MSA was held at 3 mM initially, ramped up linearly to 10 mM over 11 min, to 15 mM in the next 9 min, then equilibrated back to 4 mM over the 25 min run time at a flow rate of 1.0 mL/min at 30°C.

[18] IC measurements were calibrated with standards of nitrate, chloride, sulphate, sodium, ammonium, potassium, magnesium, and calcium, prepared fresh during the week of the analysis. Standards were run prior to every snow sample analysis. Deionized water sample blanks were run between every sample and standard to prevent carryover of species from previous samples.

[19] Total organic carbon (TOC) analysis of melted snow samples was conducted using a Shimadzu TOC-VCPN TOC analyzer using a nonpurgable organic carbon (NPOC) method due to the low TOC nature of samples. Samples were first acidified to pH 2 to 3 and sparged to eliminate the inorganic carbon (IC; including CO₂ and CO₃²⁻) component (believed to be negligible compared to the organic carbon component of our samples). The remaining TC was measured through combustion at 680°C in an oxidation catalyst filled combustion tube where all carbon was fully converted to CO₂ and detected by a nondispersive infrared (NDIR) gas analyzer. TC could be equated to TOC as loss of the IC component was minor. TOC measurements were calibrated using potassium hydrogen phthalate standards prepared in deionized water. TOC measurements were conducted on 3 separate snow samples (from each location), with multiple injections each time. Reported TOC content is the average TOC content of 3 aliquots. Deionized water samples were analyzed as blanks.
The concentration of H$_2$O$_2$ within snow samples was analyzed using fluorometry (Vernier SpectroVis Plus Spectrophotometer + Fluorometer) [Bartosz, 2006; Venkatachari et al., 2005]. First, 0.5 mL of 1 mM 2'-7''-dichlorofluorescin diacetate (Sigma, 97.0%) in methanol (Fisher, 99.0%) was mixed with 2 mL of 0.01 N NaOH (ACP, 97.0%) and left in the dark for 30 min. Two mL of the mixture were neutralized with phosphate buffer (pH 7.4, made of potassium phosphate monobasic [EM, 99.0%] and sodium phosphate dibasic [ACP, 99.0%]) in a 50 mL volumetric flask and placed on ice, covered to prevent exposure to light. To this mixture, 2 mg of peroxidase, type 1 from horseradish (Sigma) were added. This final solution was used to dilute samples and H$_2$O$_2$ standards (Sigma-Aldrich, 30 wt % solution in water) so that the final H$_2$O$_2$ signal fell within the linear portion of the calibration curve (in the range of 10$^{-7}$ M H$_2$O$_2$), then the entire mixture was allowed to react for 30 min. Dichlorofluorescin was used as a probe for H$_2$O$_2$, and it was assumed that all of the signal arises from H$_2$O$_2$. Samples were loaded into 1 cm x 1 cm cuvettes and placed within the fluorometer. The excitation wavelength was set to 405 nm, and the emission wavelength was at 520 nm. The fluorescence of the samples was read 3 times and averaged. Results from measurements made on different days for the same type of snow were averaged.

3. Results and Discussion

3.1. Barrow Measurements

Throughout much of the sampling period in Barrow (all measurements made after 9 April 2009), Alaska, snowdrift covered the ground level inlet (0 m), effectively giving a measurement of VOC mixing ratios within the interstitial air (see Figure 1). PTR-MS measurements showed snowpack enhancements (i.e., higher measured mixing ratios within the interstitial snow than in the ambient atmosphere) and daytime enhancement of VOC mixing ratios within the snowpack for some m/z ratios compared to ambient VOC levels (measurements taken at 6 m), but no enhancements were seen for other m/z ratios. The enhancement and resulting gradient observed between the snowpack and ambient VOC levels appeared to be due to the snow coverage of the 0 m inlet as VOC levels sampled at 0 m and 6 m were quite similar in measurements made prior to 9th of April (data not shown). The measured mixing ratios of selected m/z ratios are shown in Figure 1 for the period during which the 0 m inlet was covered by snow.

For m/z 59 (most likely acetone but potentially propenal or glyoxal), diel cycles were observed. Enhancements of m/z 59 tracked well with the level of actinic radiation available (as indicated by $J_{1202}$, measured in the gas phase 3.5 m above ground and suggested that a gradient existed during sunlit periods (likely a result of snowpack production of this species) which could result in a flux of this VOC to the atmosphere. These observations agree with previous measurements of acetone within the snowpack [Boudries et al., 2002; Grannas et al., 2002; Guimbaud et al., 2002], where it was suggested that acetone and other small carbonyl species could be produced from oxidation of organic matter (e.g., humic substances present within the snowpack), perhaps by photolytically produced, condensed-phase OH radicals. However, we note that snowpack levels could also be affected by temperature-dependent, physical release of VOCs. The largest difference between nighttime and daytime temperatures were observed during the first half of the data collection period shown in Figure 1, coinciding with the largest observed enhancements of m/z 59. In contrast, the latter half of the measurement period had less variable temperatures and saw smaller VOC enhancements. In general, it is hard to decouple light-driven effects from those associated with temperature change from field measurements of this type.

Snowpack enhancements were also observed for m/z 31 (potentially formaldehyde), 47 (likely formic acid), and 61 (likely acetic acid). M/z 31 showed possibly a weak photochemical source for the enhancement, with the maximum mixing ratios occurring at the same time as the radiation maximum for some days but not others. It was likely that temperature-dependent physical processes such as desorption may have played a role in affecting the snowpack mixing ratios [Hutterli et al., 1999; Perrier et al., 2002, 2003]. Photochemical production of formaldehyde has been observed previously during several previous studies [Grannas et al., 2002; Sumner and Shepson, 1999] and was believed to stem from oxidation of organics. Diel cycles for m/z 47 and 61 were not observed during this study. Snowpack enhancements for formic and acetic acids have been previously observed in polar regions [Dibb and Arsenault, 2002], and similar to our measurements, no significant drops in the mixing ratios of these species were observed during the night. These species were believed to be produced through oxidation of organics (e.g., carboxyls and alkenes) within the interstitial air and on snow grains and may build up within the interstitial air due to poor removal to acidic snow surfaces [Legrand and De Angelis, 1995].

In contrast, m/z 33 (likely methanol) and 79 (likely benzene) did not show snowpack or photochemical enhancement. Mixing ratios measured at ground level (within snow) and above the ground at 6 m remained similar throughout the sampling period. Neither showed a relationship with the level of actinic radiation. These observations agreed well with previous work [Boudries et al., 2002] and suggest that the enhancements observed at the other m/z mentioned previously are not a sampling artifact.

3.2. Laboratory Measurements

3.2.1. VOC Production

Snow samples collected from three different locations (remote – Alert, rural – Egbert, urban – fresh and aged Toronto snow) were irradiated in a controlled laboratory setting. As was observed in Barrow, enhancements were observed for some species but not others (Figure 2). This production of VOCs may have resulted from oxidation of organic species present within the snow samples by condensed-phase OH, produced from H$_2$O$_2$ or NO$_3$ through photolysis, or through direct photolysis. While experiments were conducted with a 295 nm longpass filter, we could not fully disregard the contribution of direct phototransformation of organics within the snow samples on the observed VOC products. The degree of enhancement varied depending on the location from where the sample was taken (Figure 3). Some species were enhanced for some samples but not for others. This was likely a result of differing composition of organics and oxidants within the samples.
Enhancements were not observed when an empty reaction cell was irradiated. Enhancement (or production of VOCs) was calculated by taking the difference between the average signal when irradiated and the average signal in the dark. In general, the largest enhancements (or production of VOCs) were observed during irradiation of aged Toronto snow samples, and the smallest enhancements were observed from irradiation of Alert snow samples. Somewhat surprisingly, however, the absolute magnitudes of the enhancements were relatively similar to each other, differing by no more than a factor of five.

For species of m/z ratios 31, 45 (likely acetaldehyde), 55 (protonated butanal - water), 57 (likely C4 hydrocarbon species), and 59, signal levels rose when the Xe arc lamp was turned on, and levels of these species remained enhanced until the lamp was turned off. In the dark, the signals fell back to their original levels. As the temperature of the reaction cell remained constant through the photolysis experiment, the enhancement of these species suggest a photochemical production of VOCs with minimal effects from physical, temperature-dependent processes. This release likely occurred as a result of photooxidation of organic substances present [Grannas et al., 2007; Sumner and Shepson, 1999]. Photochemical production and a snowpack source of m/z 59 and 31 (likely acetone, propanal, or glyoxal, and formaldehyde, respectively) agreed well with our Barrow observations and with literature reports. Also in agreement with our Barrow results, no photochemical enhancement was observed for m/z 33, 47, and 61 for any of our samples upon irradiation. However, a direct quantitative comparison

Figure 1. VOCs monitored at specific PTR-MS mass-to-charge ratios in Barrow, Alaska (blue trace – 0 m, interstitial air; red trace – 6 m, ambient air; black trace – $J_{H_2O}$; gray trace – air temperature at 2 m) (NOAA, Continuous one minute average meteorological data from the NOAA/ESRL/GMD observatory at Point Barrow, Alaska, 2009, ftp://ftp.cmdl.noaa.gov/met/BRW/2009). Mixing ratios are included for m/z 33, 47, 59, 61 and 79 assuming they arise from methanol, formic acid, acetone, acetic acid, and benzene. Normalized signal is indicated for m/z 31, likely due to formaldehyde.
of mixing ratios measured in Barrow with those measured within the laboratory could not be conducted as we were investigating concentration of VOCs in Barrow, with no measure of snowpack ventilation rates, and flux of VOCs within the laboratory.

[27] The photon flux of the lamp between 300 to 400 nm was determined to be $3.3 \times 10^{17}$ photons $\text{cm}^{-2} \text{s}^{-1}$ (with $\pm 50\%$ uncertainty), approximately 13 times higher than that of the solar flux found at the surface of the Earth, $2.5 \times 10^{16}$ photons $\text{cm}^{-2} \text{s}^{-1}$ (assuming a constant photon flux of $2.5 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ between 300 and 400 nm [Brasseur et al., 1999]). We assume the photochemistry is driven by this UV radiation, and not by visible radiation. For this UV flux, which is spread across 3 cm$^2$ snow area, total fluxes of acetone observed from each of the 4 snow samples were $4.8 \pm 0.9 \times 10^9$, $8 \pm 1 \times 10^9$, $8.7 \pm 0.3 \times 10^9$, and $1.1 \pm 0.2 \times 10^{10}$ molecules s$^{-1}$ for Alert, Egbert, fresh and aged Toronto samples respectively. When normalized to surface area and light intensity, our estimated flux for acetone from Alert snow samples was on the same order of magnitude as the flux of acetone from a snowpack measured in situ during an Alert field study (approximately $6.2 \pm 4.2 \times 10^9$ molecules cm$^{-2} \text{s}^{-1}$ at 253 K) [Guimbaud et al., 2002], from eddy diffusivity and vertical profile measurements.

3.2.2. Snow Composition

[28] The snow samples from the three locations showed similar levels of organic carbon content from TOC measurements (Table 1). Aged Toronto snow contained the highest amount of organic carbon ($3.04 \pm 0.06$ ppm), likely due to deposition of organics onto the snowpack in the days following precipitation, prior to collection of the snow sample. The similar levels of organics found within the Alert, Egbert, and fresh Toronto samples could suggest that post-precipitation deposition of organics was a more important

Figure 2. Time series of selected m/z showing effect of irradiation during a laboratory experiment ($-20^\circ\text{C}$) using aged Toronto snow (gray regions – lamp on; white regions – lamp off). Normalized signal is included for m/z 31, 33, 45, 55, and 57. Mixing ratios are included for m/z 47, 59, and 61.

Figure 3. Average enhancement at selected m/z for laboratory experiments as a result of irradiation (error bars show standard error calculated from 3 experiments); A = Alert, E = Egbert, FT = Fresh Toronto, AT = Aged Toronto.
source of organics than scavenging and incorporation of organic species during formation of snow and precipitation.

[29] It is important to note that our limited number of snow samples may not be representative of all snow found at these locations. Rather the goal was to collect four different snow samples from different locations. Previous measurements of TOC for remote samples (i.e., Greenland, Arctic, and Antarctic snow) range from 0.021 to 0.70 mg C L\(^{-1}\) (or ppm) [Grannas et al., 2004; Lyons et al., 2007; Twickler et al., 1986]. We note that the 0.70 mg C L\(^{-1}\) value in the literature, which is only a factor of three different from our measurement, is also for the Alert site in springtime [Grannas et al., 2004]. We do not believe contamination or method limitations affect our measurements because deionized water on average gave a much lower value for TOC (0.7 ± 0.1 ppm) than the sample measurements. In addition, the empty glass bottles were rinsed repeatedly with deionized water, and their extracts showed no significant TOC levels. Our urban sample TOC values for fresh and aged Toronto snow (2.20 ± 0.03 and 3.04 ± 0.06 ppm) are similar to previous TOC values measured from snow with more polluted sources of 1.2 to 2.5 mg C L\(^{-1}\) (or ppm) [Haan et al., 2001].

[30] Production of VOCs through indirect photochemistry will be dependent on both the concentration of organics and oxidants present. Though the relative contributions of direct and indirect photochemical processes are unknown, all indirect processes would likely stem from photolysis of precursors, most likely NO\(_3^−\) and H\(_2\)O\(_2\). OH is an important oxidant due to its high reactivity. H\(_2\)O\(_2\) and NO\(_3^−\) are common trace contaminants found within the snowpack. Due to having a much larger quantum yield, H\(_2\)O\(_2\) would likely be the dominant condensed-phase OH precursor unless concentrations of NO\(_3^−\) are high. Rate constants for OH production from photolysis of H\(_2\)O\(_2\) have been calculated to be 9–22 times higher than rate constants for NO\(_3^−\) [Chu and Anastasio, 2005]. In addition, as the two oxidants have different molar absorptivities and physical properties (H\(_2\)O\(_2\) concentrations in snow are strongly affected by temperature-dependent physical processes [Hutterli et al., 2001; McConnell et al., 1997]), the contribution of each precursor to OH radical formation will be also affected by temperature and actinic flux [Chu and Anastasio, 2005].

[31] Concentrations of NO\(_3^−\) and H\(_2\)O\(_2\) within snow samples have been previously investigated in other studies. Measurements of NO\(_3^−\) and H\(_2\)O\(_2\) concentration made for this work are listed within Table 1. Levels of NO\(_3^−\) range from 0.2 to 34 μM at the upper limit [Burkhart et al., 2004; Dibb et al., 2007; Lyons et al., 1990] in remote regions (i.e., locations of high altitude or latitude). They are generally higher in snow in more polluted regions (7.7 to 48.7 μM [Dasch, 1987; Topol, 1986]). Within our Alert samples, the average concentration of NO\(_3^−\) (37 ± 1 μM) was lower than values for the Egbert, fresh Toronto and aged Toronto samples (44.4 ± 0.9, 39 ± 2, and 63 ± 2 μM, respectively) but not by as much as expected. We do not know if there was some degree of contamination of the local environment at Alert given that surface snow was collected 200 m from the laboratory. Surface snow concentrations of H\(_2\)O\(_2\) have been measured to be 2.5 to 18 μM in remote regions [Bales et al., 1995; Jacob and Klockow, 1993]. H\(_2\)O\(_2\) concentration within our Alert sample was measured to be 4.5 ± 0.6 μM. Our Egbert, fresh and aged Toronto samples contained much smaller quantities of H\(_2\)O\(_2\), perhaps because of the higher levels of NO\(_x\) (0.21 ± 0.01, 0.3 ± 0.1, 0.08 ± 0.05 μM, respectively).

[32] Within our samples, the concentrations of NO\(_3^−\) at each site were at least an order of magnitude higher than measured concentrations of H\(_2\)O\(_2\), suggesting that NO\(_3^−\) may be the more important OH precursor. In addition, the amount of H\(_2\)O\(_2\) was highest, by far, in the Alert snow and yet it had the lowest VOC emissions fluxes despite having similar

Table 1. Snow Sample Composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>NO(_3^−) (μM)</th>
<th>SO(_4^{2−}) (μM)</th>
<th>Cl(^−) (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>37 ± 1</td>
<td>7.2 ± 0.1</td>
<td>88.5 ± 0.2</td>
</tr>
<tr>
<td>Egbert</td>
<td>44.4 ± 0.9</td>
<td>9.0 ± 0.2</td>
<td>27.2 ± 0.4</td>
</tr>
<tr>
<td>Fresh Toronto</td>
<td>39 ± 2</td>
<td>14.3 ± 0.8</td>
<td>233 ± 8</td>
</tr>
<tr>
<td>Aged Toronto</td>
<td>63 ± 2</td>
<td>48 ± 1</td>
<td>397 ± 12</td>
</tr>
<tr>
<td>DIW</td>
<td>0.30 ± 0.09</td>
<td>1.2 ± 0.4</td>
<td>0.5 ± 0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cations (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>--------------</td>
</tr>
<tr>
<td>Alert</td>
</tr>
<tr>
<td>Egbert</td>
</tr>
<tr>
<td>Fresh Toronto</td>
</tr>
<tr>
<td>Aged Toronto</td>
</tr>
<tr>
<td>DIW</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>H(_2)O(_2) Concentration (μM)</th>
<th>TOC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alert</td>
<td>4.5 ± 0.6</td>
<td>2.40 ± 0.08</td>
</tr>
<tr>
<td>Egbert</td>
<td>0.21 ± 0.01</td>
<td>2.20 ± 0.04</td>
</tr>
<tr>
<td>Fresh Toronto</td>
<td>0.3 ± 0.1</td>
<td>2.20 ± 0.03</td>
</tr>
<tr>
<td>Aged Toronto</td>
<td>0.08 ± 0.05</td>
<td>3.04 ± 0.06</td>
</tr>
<tr>
<td>DIW</td>
<td>N/A</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

*Errors represent standard error calculated for 3 measurements.*
TOC levels. Measured NO$_3^-$ concentration was found to be highest within our aged Toronto snow sample, with similar levels of NO$_3^-$ observed in the Alert, Egbert, and fresh Toronto snow samples. Taking into consideration the similar levels of organics and OH precursors found in Alert, Egbert, and fresh Toronto samples, these measurements could explain quite well our observed formation of VOCs, quite similar for these three samples. In addition, the largest production of VOCs was observed from irradiation of aged Toronto snow, a sample which contained the highest concentrations of organics and nitrate among our samples. While our snow samples may not be representative of all snow of the three different locations, our results suggest that production of VOCs may be dependent upon concentrations of oxidants and organics available.

From IC analysis of common anions and cations (Table 1), it was found that our Toronto snow samples, especially the aged Toronto sample, generally showed higher concentrations of these trace contaminants, likely due to urban pollution and scavenging as well as deposition of these species to the snowpack from the atmosphere or surroundings. In particular, extremely high levels of Cl$^-$ and Na$^+$ within our Toronto samples could easily be explained by the laying down of road salt during the winter. Our aged Toronto snow sample typically contained higher levels of contaminants than freshly fallen Toronto snow, suggesting that deposition following precipitation could be an important method for incorporation of chemical species into the snowpack. Snow metamorphism could also have led to the higher concentrations of ions found within our aged Toronto snow samples as sublimation reduces the size of snow crystals and enhances the apparent concentrations of ions within the snow; also, the surface concentrations of those ions might have increased.

Concentrations of selected common ions within high Arctic snowfall have previously been studied [Toom-Sauntry and Barrie, 2002]. Our measurements for certain ions (such as sulphate, calcium and magnesium) fall within the ranges previously found within falling Arctic snow, whereas other measurements within our samples were higher, possibly due to deposition from the atmosphere following precipitation.

4. Conclusions

Both the Barrow field results and our laboratory measurements indicate a photo-enhanced release of VOCs from snow to the gas phase. Measured mixing ratios of certain VOCs (e.g., m/z 59 and 31, likely acetone and formaldehyde) showed a snowpack enhancement in Barrow, Alaska, with mixing ratios in interstitial air higher than observed in the overlying atmosphere. This enhancement along with observed diel cycles suggests that snow can be a photochemical source for specific VOCs, in agreement with measurements from previous studies [Guimbaud et al., 2002; Sumner and Shepson, 1999]. The laboratory experiments showed similar VOC emissions to those in the field, when snow samples were irradiated using a Xe arc lamp. Fluxes of certain VOCs (measured at m/z 31, 45, 55, 57, and 59) were observed from snow samples collected from remote, rural, and urban locations (Alert, Egbert, and Toronto respectively).

Snowpack enhancements of m/z 47 and 61 (likely formic and acetic acid) were observed in Barrow as well but very little variation in the mixing ratio was seen throughout the measurement period, similar to previous field work [Dibb and Arsenault, 2002]. In the laboratory, m/z 47 and 61 similarly did not change during irradiation. Other VOCs (at m/z 33 and 69, likely methanol and benzene) did not show snowpack enhancements or evidence of photochemical production in Barrow or the laboratory. The enhancement of certain VOCs but not others suggests that our measurements in both Barrow and the laboratory were significant and not an artifact of the sampling technique. We conclude that VOCs can be photochemically produced from midlatitude snows as well as polar snows.

The production of VOCs from our collected snow samples indicated a relationship to the concentrations of organics and OH precursors present. Fresh Alert, Egbert, and Toronto snow produced similar amounts of VOCs when irradiated by the Xe arc lamp. These results agreed with previous work which hypothesized that the production of VOCs within polar snowpacks arose from both direct and indirect (through the photolytic production of OH radicals) photooxidation of organic matter present within snow [Sumner and Shepson, 1999]. Our analysis of snow composition found similar levels of organic content in freshly fallen snow from Alert, Egbert, and Toronto and slightly elevated levels of organics within the aged Toronto sample, believed to have resulted from deposition following precipitation. Despite H$_2$O$_2$ being described by previous work as the dominant OH precursor [Chu and Anastasio, 2005], NO$_3^-$ might have been the more important oxidant within our samples as we found concentrations of NO$_3^-$ to be more than an order of magnitude higher than those of H$_2$O$_2$. Concentrations of NO$_3^-$ were highest in our aged urban samples which matches our observation of more VOCs being produced from aged Toronto snow than the other three samples.

Although not surprising, our laboratory experiments show that photo-enhanced VOC release can occur from midlatitude snows in a manner similar to that observed with polar snow. While previous studies have illustrated that VOCs can be emitted from midlatitude snows through physical mechanisms [Couch et al., 2000; Hutterli et al., 2002], we believe that the fluxes observed during our laboratory experiments were influenced only by photochemistry because temperature was controlled.

Acknowledgments. The authors acknowledge support for the OASIS work came from Jan Bottenheim, Environment Canada, NSF Office of Polar Programs and Atmospheric and Geospace Science for lodgings, and NCAR Atmospheric Chemistry Division for providing infrastructure. We would also like to thank Desiree Toom-Sauntry and Environment Canada for the collection of Alert snow samples and Alex Petroff and Milos Markovic for help with the IC. Other financial support came from NSERC.

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J. P. D. Abbatt, S. S. Gao, and S. J. Sjostedt, Department of Chemistry, University of Toronto, 80 St. George St., Toronto, ON M5S 3H6, Canada. (shawna.gao@utoronto.ca; jabbatt@chem.utoronto.ca)

S. R. Hall and K. Ullmann, Atmospheric Chemistry Division, National Center for Atmospheric Research, 3090 Center Green Dr., Boulder, CO 80301, USA.

S. Sharma, Climate Chemistry Measurements and Research, Environment Canada, 4905 Dufferin St., Toronto, ON M3H 5T4, Canada.