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Snowpack processing of acetaldehyde and acetone in the Arctic atmospheric boundary layer

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Abstract

Acetaldehyde (CH_3CHO) and acetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$) concentrations in ambient air, in snowpack air, and bulk snow were determined at Alert, Nunavut, Canada, as a part of the Polar Sunrise Experiment (PSE): ALERT 2000. During the period of continuous sunlight, vertical profiles of ambient and snowpack air exhibited large concentration gradients through the top ~ 10 cm of the snowpack, implying a flux of carbonyl compounds from the surface to the atmosphere. From vertical profile and eddy diffusivity measurements made simultaneously on 22 April, acetaldehyde and acetone fluxes of $4.2(\pm 2.1) \times 10^8$ and $6.2(\pm 4.2) \times 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$ were derived, respectively. For this day, the sources and sinks of CH_3CHO from gas phase chemistry were estimated. The result showed that the snowpack flux of CH_3CHO to the atmosphere was as large as the calculated CH_3CHO loss rate from known atmospheric gas phase reactions, and at least 40 times larger (in the surface layer) than the volumetric rate of acetaldehyde produced from the assumed main atmospheric gas phase reaction, i.e. reaction of ethane with hydroxyl radicals. In addition, acetaldehyde bulk snow phase measurements showed that acetaldehyde was produced in or on the snow phase, likely from a photochemical origin. The time series for the observed $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, ozone (O_3), and propane during PSE 1995, PSE 1998, and ALERT 2000 showed a consistent anti-correlation between acetone and O_3 and between acetone and propane. However, our data and model simulations showed that the acetone increase during ozone depletion events cannot be explained by gas phase chemistry involving propane oxidation. These results suggest that the snowpack is a significant source of acetaldehyde and acetone to the Arctic boundary layer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acetaldehyde; Acetone; Arctic chemistry; Snowpack; Polar Sunrise Experiment 2000

1. Introduction

Recently, it has been found that snow can serve as a significant source of various chemical species such as

nitrogen oxides (NO_x = nitric oxide (NO) plus nitrogen dioxide (NO_2); Honrath et al., 1999), nitrous acid (HONO ; Zhou et al., 2001) and carbonyl compounds (Sumner and Shepson, 1999; Hutterli et al., 1999; Couch et al., 2000) to the lower atmosphere. It has been proposed that there is a photochemical component to the release of carbonyl compounds (Honrath et al., 1999; Sumner and Shepson, 1999), although physical

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processes can contribute as well (Hutterli et al., 1999; Couch et al., 2000).

Carbonyl compounds play an important role in tropospheric chemistry. HCHO is a significant source of HO_x in the Arctic (Sumner and Shepson, 1999), and aldehydes are significant Br atom sinks (Shepson et al., 1996). In the upper troposphere, CH₃CHO photolysis contributes significantly to HO_x production (Lary and Shallcross, 2000). CH₃CHO is an important NO_x sink in the Arctic (Shepson et al., 1996; Grannas et al., 2002), and thus it is important that the acetaldehyde sources and sinks are quantified. Acetone is a useful indicator of the relative importance of Cl atom chemistry (Shepson et al., 1996) and the major ketone observed in the Arctic (Yokouchi et al., 1994). CH₃C(O)CH₃ photolysis is an important source of HO_x in the upper troposphere (Folkins and Chatfield, 2000), and thus an indirect source of HOBr, via the reaction of HO₂ with BrO (Li et al., 1997). To investigate atmosphere–snowpack interactions of carbonyl compounds, we studied CH₃CHO and CH₃C(O)CH₃ during ALERT 2000 at Canadian Forces Station Alert (Nunavut, Canada, 82.5°N, 62.3°W). We report here vertical profiles of ambient and snowpack air acetaldehyde and acetone concentration, and fluxes of those compounds from the snowpack to the atmosphere. We discuss the importance of a snowpack source of acetaldehyde and acetone, and possible chemical origins within the snowpack.

2. Experimental methods

2.1. Analytical methods

Measurements were conducted ~6 km southwest of the Canadian Forces Station Alert. Acetaldehyde and acetone in the ambient and snowpack interstitial air were measured using a gas chromatography/ion trap mass spectrometry (GC-ITMS, Thermoquest Finnigan) system operating in electron impact mode. Acetaldehyde and acetone were detected as their CH₃CO⁺ ion fragment (43 amu). Ambient air was drawn continuously at a flow rate of 700 sccm through ~30 m of heated (to ~20°C) 1/4" OD PFA-Teflon tubing. A 200 sccm portion of this air was pumped (using a mass flow controller) through a 2 cm³ sample loop immersed in liquid nitrogen, quantitatively trapping the analyte carbonyl compounds. The total air sample volume was typically 2 l. After cryotrapping, the helium carrier gas was diverted through the sample loop to a vent, to remove air from the sample, and to protect the GC-ITMS filament. Then, a valve was switched on allowing carrier gas flow through the loop into the GC column, at which time the loop was heated to ~90°C, effectively transferring the analytes to the head of the column.

Chromatographic separation was achieved using a PoraplotQ analytical column (0.32 mm OD, 30 m; Hewlett Packard, Palo Alto, CA). The column temperature was maintained for 2 min at 35°C, thereafter increasing at 15°C min⁻¹ to 220°C, and then maintained at this temperature for 5 min. A double dilution calibration system was used to calibrate at concentrations typical of ambient or snowpack air. Frequent calibrations at the inlet line were conducted during the sunlit period (March–April). A known concentration of trichloroethylene used as an internal standard was injected (from a ~3 ppm cylinder standard, at ~5 sccm) with each sample to monitor the overall sensitivity of the GC-ITMS system between acetaldehyde and acetone calibrations. Calibrations were conducted using permeation sources (VICI, Dynacal), housed inside a thermostated oven maintained at 30 ± 1°C. Acetaldehyde and acetone permeation rates were determined via the DNPH-derivatization technique (Sirju and Shepson, 1995). The permeation rates measured over a 6-month period showed that the permeation source emission rates were stable, at 0.053 ± 0.003 (1 s) nmol min⁻¹ for acetaldehyde and 0.068 ± 0.010 nmol min⁻¹ for acetone.

The precision (1 s) of the measurements over a 6-h period (the time typically required to conduct a depth profile) was determined to be 9% on 11 April and 13% on 1 May for acetaldehyde and 6% on 11 April and 13% on 1 May for acetone. The average acetaldehyde and acetone instrument sensitivities measured from 25 March to 2 May were used to derive the concentration of each sample. A variability of 36% and 35% (1 s) for the acetaldehyde and acetone calibration sensitivities, respectively, was determined during that period. Those sensitivities were used to quantify acetaldehyde and acetone during the February–March period, because the trichloroethylene sensitivity was observed to remain constant from February to May. Limits of detection of 40 parts per trillion (ppt) and 130 ppt were calculated (in April) for acetaldehyde and acetone, respectively. The limit of detection was influenced in part by desorption of carbonyl compounds from the long inlet line. Frequent injections of zero air at the inlet line were performed to quantify the carbonyl compound blanks. The detection limit was defined as 3s_{blank}/K, where s_{blank} is the standard deviation of the carbonyl compound blank signal and K is the calibration sensitivity. The uncertainty of the determination of carbonyl compound concentrations depended largely on the variability of the calibration sensitivity, and to a minor extent on the uncertainty on the blank subtraction and on the uncertainty of the measured chromatographic peak area. The uncertainties in the determined concentrations for acetaldehyde and acetone are estimated as ±37% for both, for concentrations 5 times or more than their detection limits.

2.2. Air sampling protocols

To conduct measurements of carbonyl compound concentration within the snowpack, a hole was bored in the snowpack with a clean 25 mm OD stainless steel pipe. A 25 mm ID all Teflon snow probe was then inserted to the depth of the bored hole. The probe was connected at the end of a 30 m heated (20°C) sample line. To utilize identical sampling conditions for air and snowpack interstitial air sampling, the snow probe remained connected at the end of the sample line when sampling ambient air. Given the significant diel cycle of carbonyl compound concentrations (Grannas et al., 2002), depth profile measurements were obtained by alternating between snowpack air and ambient air (sampled at 1 m above the snowpack), to enable meaningful comparison between snowpack and ambient air.

Fluxes determined here made use of eddy diffusivities obtained from eddy covariance measurements. These measurements were accomplished with a 3-D sonic anemometer (model CSAT3, Campbell Scientific, Logan, UT) which was placed at 2 m above the snowpack surface at the SST site. The sonic anemometer sampled wind speed at the frequency of 10 Hz.

3. Results

Two individual depth profiles obtained on 16 February and on 22 April are presented in Fig. 1. In February, the CH_3CHO concentration decreases with depth in the snowpack, indicating that the snowpack could serve as an overall sink of CH_3CHO in the dark period. The data obtained on 16 February are characterized by relatively low carbonyl blank values, yielding a better detection limit for that specific day, compared with the average for the study. For the air samples, the concentrations were statistically significantly above the blank values, whereas in the snowpack interstitial air, this was not the case; for the latter we simply report the calculated values. This apparent snowpack sink could be explained by the fact that the snow temperature was typically lower by 4°C, on average, during the dark period, than the air temperature. In contrast, the CH_3CHO concentration increased with depth for the first few centimeters in the snow in April, during continuous sunlit conditions, as shown in Fig. 1. The same general behavior was observed for acetone although to a lesser extent.

Depth profiles were obtained during four periods, from darkness to the continuous sunlit period. In Fig. 2 we present the average profiles for each period, shown as the snowpack air concentration relative to that at 1 m above the snowpack surface. The average depth profiles show that the snow was a net sink for acetaldehyde

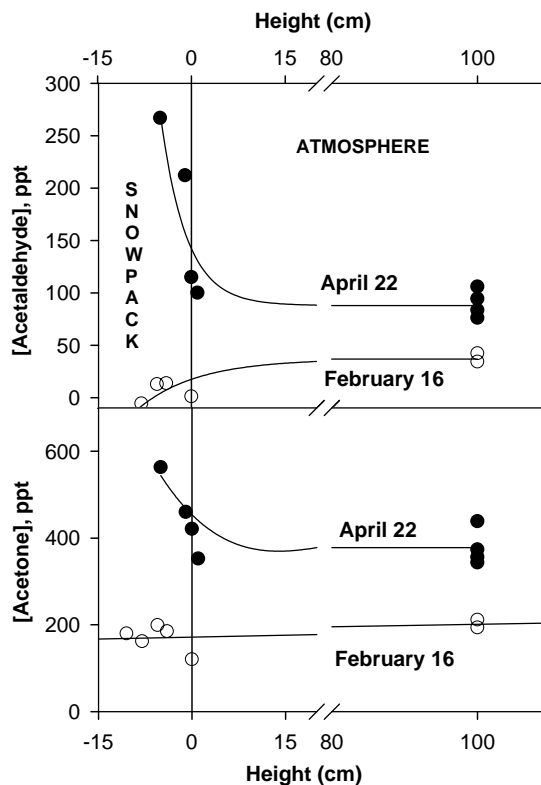


Fig. 1. Individual acetaldehyde and acetone depth profiles obtained on 16 February (open circles) and 22 April (filled circles).

during the dark period (for the period 16 February–9 March) and a net source of acetaldehyde during the sunlit period (experiments conducted from 20 to 23 April and from 1 to 2 May). Interestingly, the CH_3CHO snowpack interstitial air concentration at a snowpack depth of 6 cm was 2 times greater than at 1 m above the snowpack during the (sunlit) period of normal ozone concentrations (20–23 April, $\text{O}_3 \sim 40$ ppb), but became 9 times greater (i.e. ~ 1 ppb) than at +1 m during the period of low ozone (1–2 May, $\text{O}_3 = 0.5\text{--}3$ ppb). This may imply a more photolytically active snowpack during O_3 depletion conditions. It is known that BrCl in the snowpack air is inversely correlated with O_3 (Foster et al., 2001), and thus snowpack Cl atom concentrations (a presumed CH_3CHO precursor; Grannas et al., this issue) will increase during O_3 depletion events. We note also that the steady state CH_3CHO snow phase concentration in layers close to the surface was 3–4 times higher in spring than in winter. These two observations would suggest that CH_3CHO was produced in the snowpack during the sunlit period. A similar temporal trend was observed with the acetone average depth profiles, but was not as pronounced as that for acetaldehyde (Fig. 2). The snowpack air acetone

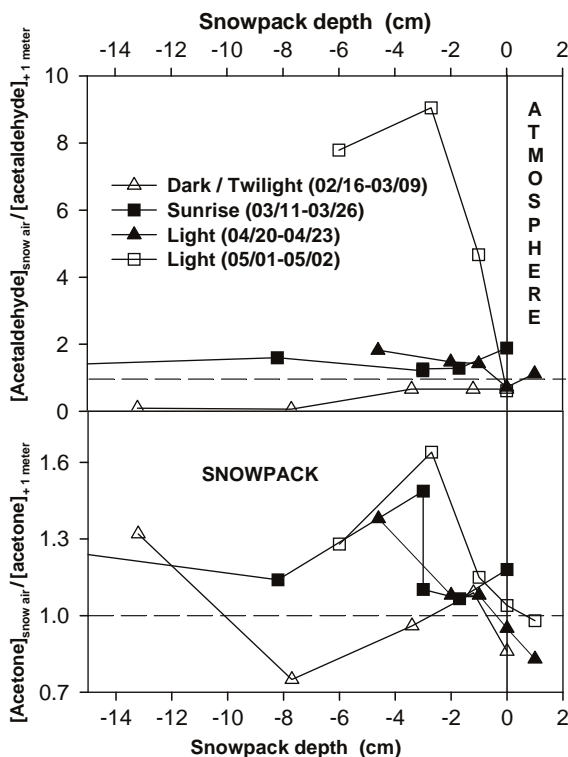


Fig. 2. Average acetaldehyde and acetone depth profiles at different periods during ALERT 2000.

concentration systematically increased with depth to –5 cm in April and May, to ~ 1.5 times than at +1 m.

4. Discussion

4.1. Estimation of acetaldehyde and acetone fluxes from the snowpack

To determine the rate of emission of carbonyl compounds to the local Arctic boundary layer, the gradient diffusion approach was employed as shown in Eq. (I) (Fuentes et al., 1996):

$$\text{Flux} = -K_C \frac{\partial C}{\partial Z} = -\frac{ku*(C_2 - C_1)}{\ln(Z_2/Z_1) + \Psi_{C_1} - \Psi_{C_2}} \quad (\text{I})$$

Here K_C is the atmospheric eddy diffusivity, k is von Karman's constant (0.4), Z_2 and Z_1 denote the upper and lower heights, respectively, at which carbonyl compound concentration determinations (C_2 and C_1) were made. The Ψ_{C_1} and Ψ_{C_2} denote the non-dimensional diabatic correction functions for scalar C . The friction velocity was derived from eddy covariance flux measurements. The 10 Hz sonic anemometer wind data were reduced to derive 0.5 h averages of momentum ($\tau = -\rho u'w' = -\rho u_*^2$, ρ is the air density) and virtual

sensible heat (H_V) fluxes. The H_V data permitted us to calculate the Monin–Obukhov length scale (L) required to estimate Ψ (see Fuentes et al., 1996 for further details).

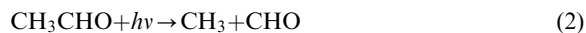
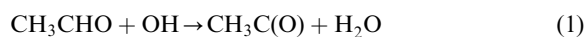
To estimate acetaldehyde and acetone fluxes, we used the 22 April depth profile since gas phase halogen atom chemistry is assumed to be relatively unimportant for this day. Indeed, under O_3 depletion conditions, gas phase production of those carbonyl compounds could be very active, and the gas phase could be out of equilibrium with the snowpack.

The 22 April concentration depth profiles were obtained between 11 a.m. and 4 p.m. Atlantic standard time (AST), simultaneous with eddy covariance measurements. An average temperature of 253 ± 1 K and a surface pressure of 1001.5 ± 0.1 hPa were measured. Eddy diffusivities for the atmospheric layer from 5 to 100 cm were derived from eddy covariance measurements. We note that the computed atmospheric eddy diffusivities were both lower (by almost an order of magnitude) than values derived for mid-latitude regions, and highly variable. This was the result of highly weak and intermittent turbulence observed throughout the atmospheric surface layer, which for the measurement period remained statically stable. During 22 April, the calculated eddy diffusivities averaged (normalized against height) $1.00 \text{ cm}^2 \text{ s}^{-1}$. Uncertainties in the individual calculated eddy diffusivities were $\pm 10\%$ (1 s), but the variability during the period of the flux measurement ranged from 0 to $3.1 \text{ cm}^2 \text{ s}^{-1}$. From the depth profiles, gradients of $0.16 (\pm 0.08)$ and $0.22 (\pm 0.15) \text{ ppt cm}^{-1}$ for CH_3CHO and $\text{CH}_3\text{C(O)CH}_3$ were estimated between intakes Z_2 and Z_1 representing the 5–100 cm atmospheric layer. Thus, the average calculated fluxes of acetaldehyde and acetone from the snow surface are $4.2 (\pm 2.1) \times 10^8$ and $6.2 (\pm 4.2) \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$, respectively, where the uncertainty in the final result is dominated by the uncertainty in the measured gradient. As the carbonyl compound concentration gradient was greatest near the snow surface, an eddy diffusivity average value of $0.49 \text{ cm}^2 \text{ s}^{-1}$ was also derived for the atmospheric layer from 1 to 100 cm. Within this layer, gradients of $0.40 (\pm 0.11)$ and $0.37 (\pm 0.20) \text{ ppt cm}^{-1}$ were estimated for acetaldehyde and acetone, respectively, leading to average fluxes of $5.6 (\pm 1.6) \times 10^8$ and $5.2 (\pm 2.8) \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$, in close agreement with the estimates discussed above. We note that in the flux estimation provided above, the influence of chemical processing on the carbonyl vertical distribution was not included. Nonetheless, these flux estimates compare favorably to those ($1.3 (\pm 0.6) \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ for CH_3CHO and $5.1 (\pm 1.2) \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$ for CH_3COCH_3) derived using the independent method described by Boudries et al. (2002), which involved use of a quartz flow-through flux chamber.

4.2. Impact of the snowpack on CH₃CHO and CH₃C(O)CH₃ boundary layer chemistry

On 22 April, normal background ozone concentrations were observed (~40 ppb). Under this atmospheric condition, OH is believed to be the predominant alkane oxidant (Jobson et al., 1994; Boudries and Bottenheim, 2000). During the period of 21–23 April, the isobutane/*n*-butane ratio was constant (Bottenheim et al., 2002) showing that Cl atom chemistry was insignificant compared to OH chemistry. Grannas et al. (2002) produced an updated photochemical model that incorporates diurnally varying fluxes (following radiation) of NO_x and HONO to simulate the observations for those species (Beine et al., 2002; Zhou et al., 2001). As discussed in Grannas et al. (this issue), HONO and HCHO photolysis are the main sources of HO_x, contributing 61% and 15% of production, respectively, in the Arctic boundary layer. From this model an average mid-day OH concentration in the atmospheric surface layer was estimated to be ~7 × 10⁵ molecules cm⁻³, on 22 April. The lifetime of acetaldehyde calculated (based on photolysis and OH reaction) for 22 April (<1 day) was much smaller than the average air mass residence time estimated for the Arctic of 20 days (Hopper and Hart, 1994). This implies that for our measurement period, long-range transport was an insignificant source of acetaldehyde at Alert. As a consequence, acetaldehyde sources in the ambient air were defined only by both local chemistry and local sources (snowpack).

Under non-ozone depletion conditions, such as 22 April, Cl and Br atoms were assumed to be in a low enough concentration that acetaldehyde mainly reacted via reactions (1) and (2):



To address the significance of the snowpack fluxes relative to the atmospheric chemical production rate, we can to a first approximation assume that CH₃CHO is at photochemical steady state in the gas phase, i.e. assuming that the photochemical production (or input) rates equal the removal rates. With this assumption then an imbalance between calculated production and loss implies missing sources and/or sinks.

To estimate volumetric CH₃CHO and CH₃C(O)CH₃ fluxes from the snowpack, it is necessary to estimate both the volume into which these carbonyl compounds mix and associated lifetime (τ). Acetaldehyde is consumed in reactions (1) and (2) where k_1 (245 K) = 2.0(+2.5/-10) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 1999) and $J_2 = 1.0 \times 10^{-6}$ s⁻¹ at Alert on 22 April, averaged from 11 a.m. to 4 p.m. AST (W. Simpson, personal communication). The CH₃CHO

lifetime can then be expressed as $\tau = (k_1[\text{OH}] + J_2)^{-1}$, or 19(+21/-10) h under these conditions, assuming an average OH concentration of 7 × 10⁵ cm⁻³. According to the atmospheric potential temperature profile obtained on 22 April, the lower atmosphere (from the surface to 5 km) remained statically stable, with the potential temperature increasing from 251 to ~263 K at 1 km altitude. Thus, in the absence of a convective atmosphere, we define an “effective mixing height” Z^* for CH₃CHO as the vertical distance traveled by molecules during one lifetime, τ. Thus, for the atmospheric surface layer, it can be shown from Eq. (I) that Z^* can be calculated from in situ eddy covariance measurements as described by Eq. (II) (see also Lenschow, 1995, pp. 137):

$$Z^* = \sqrt{K_C \tau} \quad (\text{II})$$

The K_C is the regular, average atmospheric eddy diffusivity (95 cm² s⁻¹) derived for the periods when concentration gradients were made. Thus, for CH₃CHO we estimated a Z^* value of 25(+12/-7) m. Applying a similar analysis for acetone, we derived a Z^* value of 320(+155/-105) m. For acetone we assumed that the main gas phase sink was reaction with OH and the estimated lifetime was more than 4 months, using a rate coefficient 1.3(+1.6/-0.7) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 1999).

With the values for Z^* calculated above, we can estimate the volumetric fluxes for acetaldehyde and acetone into the atmospheric surface layer defined by their respective lifetimes. Thus, using the acetaldehyde and acetone fluxes of 4.2(±2.1) × 10⁸ and 6.2(±4.2) × 10⁸ molecules cm⁻² s⁻¹ the corresponding volumetric fluxes from the snowpack to the atmosphere are 1.7(±1.1) × 10⁵ and 1.9(±1.4) × 10⁴ molecules cm⁻³ s⁻¹ for acetaldehyde and acetone, respectively. These results indicate our best estimates of the number of molecules emitted from the snowpack surface into each cubic centimeter of air within the effective mixing height Z^* for these two species. Because we characterized the temporal variation ($\partial C/\partial t$) of carbonyl compounds, the fidelity of these calculations can be verified if we apply the conservation of mass principle as shown in Eq. (III), where P is the gas phase chemical production rate, and in which we ignore the affect of advection:

$$\partial C/\partial t = P + (\text{volumetric flux}) - \{k_1[\text{OH}] + J_2\}[\text{CH}_3\text{CHO}] \quad (\text{III})$$

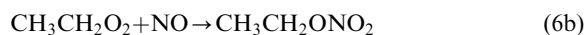
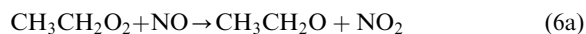
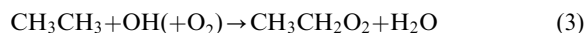
Below we quantify and discuss these terms.

4.3. CH₃CHO chemistry

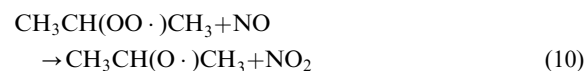
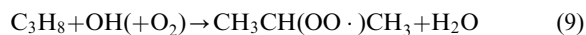
For 22 April, the average CH₃CHO concentration (at +1 m) was 90(±13) ppt, or 2.6 × 10⁹ molecules cm⁻³. We then calculate the removal rate for CH₃CHO as

$(k_1[\text{OH}] + J_2)[\text{CH}_3\text{CHO}] = 3.7 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$. This value is only 22% that of the calculated volumetric flux from the snowpack, implying that the snowpack flux term is much greater than P , at least for the lowest 25 m (we note that this result is not impacted by the k_1 uncertainty). This result is consistent with the diel cycles of acetaldehyde concentration in ambient air and snow, discussed by Grannas et al. (this issue), for late April. Indeed, the enhancement of the snowpack interstitial air concentration relative to the ambient air concentration follows radiation, implying then a strong diel cycle of the acetaldehyde flux. The ambient acetaldehyde concentration increases with the solar flux, because the acetaldehyde source from the snowpack increases faster than the acetaldehyde sinks from OH reaction and photolysis. In the evening, it is likely that CH_3CHO decreases due in part to uptake into the snowpack (Grannas et al., this issue). These results are very important with respect to attempts to understand the Arctic atmospheric boundary layer chemistry from measurements made within this layer.

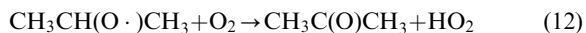
To confirm the conclusion drawn above, we can also compare the snowpack source with the calculated local gas phase chemical production rate, P . The previously assumed dominant mechanism for CH_3CHO formation is oxidation of ethane with OH or Cl as shown in the reactions given below:



Of importance is the fact that reaction (5) producing ethyl hydroperoxide competes with acetaldehyde production at low NO_x concentrations. An alternative mechanism for CH_3CHO production involves alkoxy radical decomposition (Atkinson et al., 1999), through scission of the α - β carbon-carbon bond of an appropriate secondary alkoxy radical. For example, it can be produced from the OH radical oxidation of propane as follows:



However, the unimolecular decomposition reactions are highly temperature dependent and, at 253 K, reaction (11) does not compete with the reaction given below:



Thus, under normal ozone concentration conditions, gas phase photochemistry produces acetaldehyde mainly from the OH radical oxidation of ethane. Using $k_3 = 1.2(+0.6/-0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and assuming an average $[\text{OH}] = 7 \times 10^5 \text{ molecules cm}^{-3}$, the calculated maximum (assuming all $\text{CH}_3\text{CH}_2\text{O}_2$ radicals react as in reaction (6a)) rate for acetaldehyde production is then $3.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$, given an average measured ethane concentration of $4.4 \pm 0.4 \times 10^{10} \text{ molecules cm}^{-3}$ (corresponding to an average mole fraction of 1531 ppt; Bottenheim et al., 2002). This is then only $\sim 10\%$ as large as the calculated CH_3CHO destruction rate, and $\sim 2\%$ of the calculated volumetric snowpack flux. Thus, it is clear that known gas phase chemistry cannot account for the observed CH_3CHO concentrations, and it is likely that most of the observed 1-m data represent the impact of the snowpack flux.

4.4. $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ chemistry

As discussed above, if we assume a mixing height for acetone of 320 m, our estimated acetone flux corresponds to a volumetric input rate of $1.9 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$, or 55 ppt day^{-1} . This represents a significant fraction of the observed gas phase concentration, which typically varies between 300 and 1000 ppt at Alert. This input from the surface would then be balanced by dilution from mixing from aloft, advection, photochemical destruction, and nighttime uptake into the snowpack. For acetone, we cannot conduct a meaningful comparison of its destruction rates with this input rate, as its photochemical lifetime is on the order of 4 months, and long-range transport processes will play a large role in its variability, as measured at Alert. However, we can assess the extent to which acetone concentrations can be accounted for from propane chemistry, its assumed atmospheric precursor. In Fig. 3 we present the measured acetone, ozone, and propane concentrations obtained during three field campaigns at Alert, in the winter/spring periods of 1995, 1998, and 2000. All data showed consistently that during ozone depletion events, acetone concentrations increased (as previously reported by Yokouchi et al., 1994) with a concomitant decrease in propane concentrations. For example, during the last ozone depletion period occurring at ALERT 2000 on 26 April (day 117), the propane concentration dropped from ~ 350 to ~ 100 ppt. During the same time, acetone increased by ~ 400 ppt. Similarly, the ozone depletion event occurring over days 108–109 of 1998 shows a decrease in the propane concentration

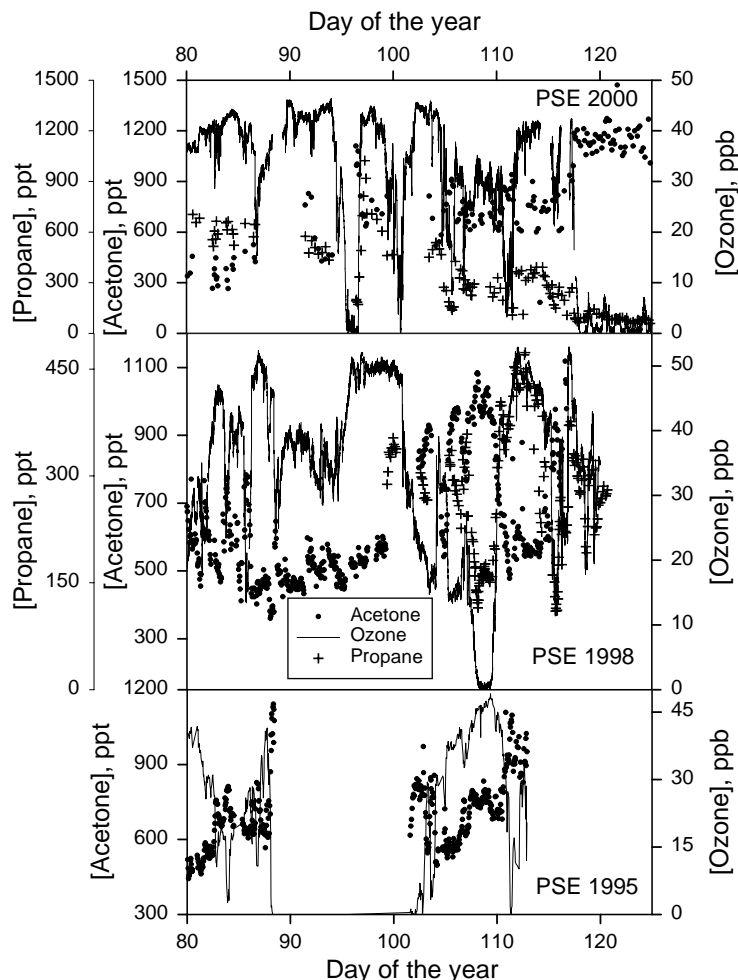
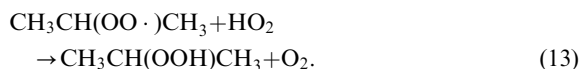


Fig. 3. Ambient acetone (filled circle symbols), ozone (thin solid line) and propane concentrations (crosses) during three different PSE studies.

of ~ 200 ppt, while the acetone concentration increased by ~ 500 ppt. The 1995 data show a 500 ppt increase in acetone on day 88–89 during an ozone depletion event. Yokouchi et al. (1994) observed a similar large (~ 600 ppt) increase in acetone during the complete O_3 depletion event of 9 April 1992.

It is generally believed that the principal hydrocarbon precursor for acetone is propane, initiated by reaction with either OH or Cl atoms (Singh et al., 1994). From Fig. 3 it can be seen that the amount of acetone produced was typically 2 times greater than the decrease in propane. In addition, because of the low NO_x concentrations, the estimated potential production of acetone from propane is much less than the estimated propane consumption. To examine this, we utilized the model described above and in Grannas et al. (2002) to investigate the production of acetone during ozone depletion events. We conducted model runs that

included a flux of halogens to simulate the halogen levels present during ozone depletion events as estimated by Boudries and Bottenheim (2000). The modeled concentrations of acetone, propane, ozone and halogen atoms simulated over a 10-day period is shown in Fig. 4. The results in this figure indicate that the decrease of propane concentration from 350 to almost 0 ppt, due to Cl chemistry, leads to a gas phase production of 175 ppt acetone, or only 50% of the propane consumed. This results largely from the importance of the reaction given below:



Given the discussion above, from the 250 ppt propane consumption during the 26 April 2000 ozone depletion event, we would expect an increase in acetone of

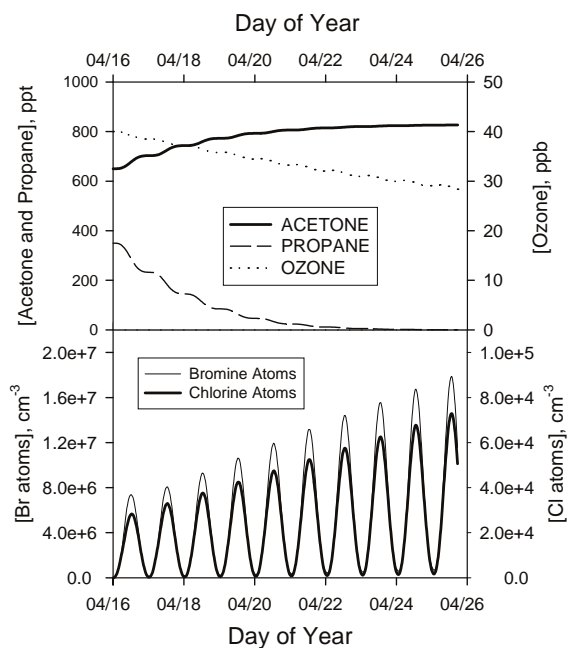


Fig. 4. Modeled acetone, propane, and ozone concentrations.

~125 ppt, or ~1/3 of the observed acetone concentration increase of ~350 ppt. The results discussed here make it clear that known gas phase chemistry cannot account for the change in acetone concentrations during ozone depletion events, and imply that it is likely that the snowpack is an important source of acetone to the Arctic boundary layer. The fact that acetone concentrations are significantly higher in the boundary layer air during O₃ depletion events may imply more active snowpack photochemistry (e.g., because of higher concentrations of Cl radicals) in the Arctic Ocean boundary layer surface, involving then a larger acetone flux from the Arctic Ocean surface. However, it is conceivable that the organic hydroperoxides such as that produced in reaction (13) could be oxidized in the snowpack (after dry deposition) to produce acetone. We also cannot rule out biological production in the Arctic surface snow, e.g. from ice algae.

4.5. Snowpack physical vs. photochemical processes

It has been proposed that physical processes, including bulk surface water loss during metamorphosis (Domine et al., 2001; Couch et al., 2000) and temperature dependent desorption (Hutterli et al., 1999) could account for release of species from bulk snow. During the metamorphosis of snow grains, species absorbed in bulk snow could be released, mostly just after snowfall, as discussed in Houdier et al. (2002). As discussed in Houdier et al. (2002), although there was substantial loss

of CH₃CHO from the snowpack surface after an 13/14 April snowfall, the metamorphosis-related loss of this species appeared to have stopped by 22 April, the day of one of the sunlit vertical profiles.

A simple calculation can allow us to examine the feasibility of physical processes explaining the emission of carbonyl compounds from the snowpack during the sunlit period. If we assume no carbonyl compound chemical production in the snowpack, the time scale (t) to release all carbonyl compound from the condensed phase can be estimated as $t = Q/F$, where Q is the column concentration (molecules cm⁻²) of carbonyl compound present in the snowpack, and F (molecules cm⁻²s⁻¹) is our estimated flux from the snowpack, as measured from the 22 April vertical profile data. Q is equal to $HN\rho X/M$, where H is the snowpack column height (10 cm), N is Avogadro's number, ρ is the density of the snow (~0.2 g cm⁻³), X is the determined mass fraction of the carbonyl compound in the condensed phase (grams of carbonyl/gram of snow) and M is the carbonyl compound molecular weight. The calculated removal time t for acetaldehyde and acetone is 3.7 and 1.2 days, respectively, using fluxes for acetaldehyde and acetone of 4.2×10^8 and 6.2×10^8 molecules cm⁻²s⁻¹, respectively. However, since significant snow phase concentrations were observed for weeks after a fresh snow fall (Houdier et al., this issue), it can be assumed that acetaldehyde and acetone must be produced within the snowpack, if our flux estimates apply over this time scale.

Hutterli et al. (1999) have discussed that HCHO and other partially water soluble species can efflux from a snowpack that contains winter snow (i.e. snow precipitated at colder temperatures) with HCHO concentrations in excess of the warmer spring snowpack equilibrium concentrations (i.e. assuming an equilibrium between condensed and gas phase concentrations). However, in this study, Houdier et al. (2002) found a steady state acetaldehyde snow phase concentration 3–4 times higher in spring than in winter, despite a significant snowpack temperature increase from winter to spring. In the absence of production, the snowpack warming should lead to decreasing snow phase acetaldehyde concentrations via desorption. Thus, Houdier et al. (2002) also suggest that the snowpack source of acetaldehyde is likely of photochemical origin.

Our data support the hypothesis that carbonyl compounds are generated in the snowpack, likely through a photochemical process. It has been suggested (Sumner and Shepson, 1999) that carbonyl compounds may be generated by reactions of dissolved organic matter (DOM) with condensed phase OH radicals. Honrath et al. (2000) discuss that NO_x, HONO and OH(aq) can be produced in the snowpack from the photolysis of nitrate ions. Since there is vegetation at the base of the Alert snowpack, it seems plausible that

the humic material present may be a reactive substrate for the OH radicals that are produced in the snowpack condensed phase. It has recently been shown that direct photochemical transformation (295–340 nm) of DOM present in seawater results in the production of carbonyl compounds and alkenes, which are then released to the atmosphere (Riemer et al., 2000). If this chemistry also occurs in the snowpack, photooxidation of DOM could serve as a source of carbonyl compounds in the Arctic snowpack. Li et al. (2000) reported total organic carbon concentrations from melted snow samples that are much in excess of what can be explained from dissolved carbonyl compounds and carboxylic acids. We note that Warneke et al. (1999) have shown that, in mid-latitudes, the production of acetone from the decay of dead plant matter is significant in comparison to the estimated atmospheric losses, and that acetaldehyde and methanol are also emitted in this process.

5. Summary and conclusions

Acetaldehyde and acetone vertical profiles measured at Alert during springtime showed significantly higher acetaldehyde and acetone concentrations in the snowpack air relative to the ambient air. Acetaldehyde and acetone vertical fluxes from the snowpack to the atmosphere were derived, with estimated values of $4.2(\pm 2.1) \times 10^8$ and $6.2(\pm 4.2) \times 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$, respectively. According to our carbonyl flux data and snow phase acetaldehyde measurements, the main source of the surface layer gas phase atmospheric acetaldehyde is the snowpack, and this source is likely of a photochemical origin. Acetone is also suggested to have a snowpack source, though quantification of the relative importance of the snowpack vs. transport is difficult. It is clear that biological and/or oxidative decay of the snowpack organic matter needs to be much better understood. These data suggest that surface layer atmospheric measurements are significantly impacted by the snowpack surface. Because of the extreme static stability of the Arctic boundary layer atmosphere, this could be further tested by measurement of the vertical profile of these gases through the full extent of the boundary layer.

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