



# A study of photochemical and physical processes affecting carbonyl compounds in the Arctic atmospheric boundary layer

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## Abstract

Experiments were conducted during the ALERT 2000 field campaign aimed at understanding the role of air–snow interactions in carbonyl compound chemistry and the associated ozone depletion in the atmospheric boundary layer. Under sunlit conditions, we find that formaldehyde, acetaldehyde and acetone exhibit a significant diel cycle with average ambient air concentrations of 166, 53 and 385 ppt, respectively. A box model of Arctic surface layer chemistry was used to understand the diel behavior of carbonyl compound concentrations at Alert, Nunavut, Canada, with a focus on the chemical and physical processes that affect carbonyl compounds. Results of the study showed that the measured carbonyl compound concentrations can only be simulated when a radiation-dependent snowpack source term (possibly photochemistry) and a temperature-dependent sink (physical uptake on snow grains) of carbonyl compounds were added to the model. We are able to simulate the concentration and amplitude of the observed diel cycle, but not the phase of the cycle. These results help confirm the importance of snowpack chemistry and physical processes with respect to carbonyl compound concentrations in the Arctic surface boundary layer, and reveal weakness in the details of our understanding. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Snow chemistry; Polar Sunrise Experiment 2000; Formaldehyde; Acetaldehyde; Acetone

## 1. Introduction

The study of the Arctic atmospheric surface boundary layer (SBL) has led to a number of fascinating findings, including the discovery of rapid springtime ozone and mercury consumption within the SBL (Bottenheim et al.,

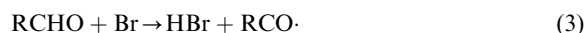
1986; Barrie et al., 1988; Schroeder et al., 1998) and snowpack chemistry and production/destruction of various photochemically active species such as NO<sub>x</sub>, HONO, HCHO and ozone (Honrath et al., 1999, 2000; Sumner and Shepson, 1999; Ridley et al., 2000; Peterson and Honrath, 2001; Zhou et al., 2001).

Springtime ozone depletion in the Arctic SBL has been attributed to chemistry occurring in aerosols and the snowpack, leading to the release of molecular

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halogens that can photolyze to produce halogen atoms (Vogt et al., 1996; Tang and McConnell, 1996; Impey et al., 1999; Foster et al., 2001). Bromine atoms can catalytically destroy ozone via reactions 1 and 2. However, this process can be terminated through reaction of bromine atoms with aldehydes as shown in reaction 3.



Since aldehydes such as formaldehyde (HCHO) and acetaldehyde ( $\text{CH}_3\text{CHO}$ ) can effectively terminate the chain, it is important to understand their sources and sinks. As discussed in Shepson et al. (1996) and Sumner and Shepson (1999), their chemistry remains poorly understood.

Sumner and Shepson (1999) reported that HCHO is likely emitted from the snowpack, significantly impacting the gas-phase HCHO concentration and, thus,  $\text{HO}_x$  production and Br loss. During the ALERT 2000 study, measurements of carbonyl compound fluxes from the snowpack were conducted (Boudries et al., 2002;

Guimbaud et al., 2002). We focus here on the observation of a large diel variation in the gas-phase carbonyl compound concentrations, particularly for HCHO and  $\text{CH}_3\text{CHO}$ , as shown in Fig. 1. We applied a modified/updated gas-phase model based on that described by Michalowski et al. (2000) to investigate our understanding of the factors that influence the gas-phase carbonyl compound concentrations and observed diel cycle. This study also examines the relative importance of OH and Cl atom chemistry on aldehyde production in the Arctic and the extent to which gas-phase chemistry alone can explain the observations for the aldehydes. The impact of a snowpack source and sink of carbonyl compounds on the observed gas-phase carbonyl compound concentrations is discussed.

## 2. Experimental methods

Measurements of HCHO,  $\text{CH}_3\text{CHO}$  and acetone ( $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ) were obtained in both ambient and snowpack interstitial air. Snowpack air samples were obtained using an all-Teflon snow probe that was inserted into a hole bored in the snowpack, as described by Sumner et al. (2002). Measurement methods for HCHO are described in Sumner et al. (2002) and measurement methods for  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  are described in Guimbaud et al. (2002) and Boudries et al. (2002). Additional measurements obtained during ALERT 2000, including HONO fluxes from the snowpack (Zhou et al., 2001), ambient air photolysis rates (Simpson et al., 2002), along with gas- and snow-phase measurements of a suite of other species, have been used to update and improve the model originally developed by Michalowski et al. (2000).

## 3. Model description

To investigate the behavior of carbonyl compounds in the Arctic SBL, four different versions of the modified Michalowski et al. (2000) model were utilized. We have utilized all of the gas-phase reactions originally used by Michalowski et al. (2000). In addition, we have made several updates to the gas phase and flux portions of the original Michalowski model, as outlined below.

### 3.1. Model updates

The diurnally varying photodissociation rate coefficients for several key species have been updated using spectral irradiance measurements obtained during the ALERT 2000 field campaign (Simpson et al., 2002). Photolysis rates of BrO,  $\text{NO}_2$ , HONO,  $\text{BrONO}_2$ , HCHO,  $\text{CH}_3\text{CHO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  and  $\text{CH}_3\text{Br}$  were fit to

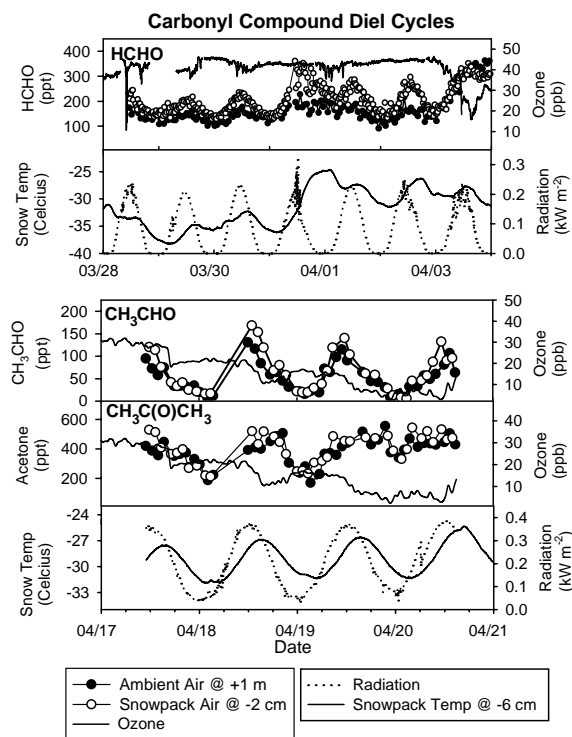


Fig. 1. Carbonyl compound concentrations in ambient air (filled circles), snowpack interstitial air (open circles), with snowpack temperature (solid line) and radiation (dotted line).

Eq. (I):

$$J(\text{s}^{-1}) = K_0 e^{\{K_1(1 - \cos(K_2(Q)))^{-1}\}}, \quad (\text{I})$$

where  $Q$  is the solar zenith angle in radians and  $K_0$ ,  $K_1$  and  $K_2$  are scaling parameters related to the maximum photolysis rate of a particular species and scattering and absorbance of radiation within an airmass. The calculated  $J$  values are typically at least 100% larger than those used in Michalowski et al. (2000), which did not consider the impact of the large surface albedo at Alert.

Measurements of HONO and HO<sub>2</sub>NO<sub>2</sub> during ALERT 2000 indicate that these species are present in large enough concentrations to substantially impact the local chemistry, and that HONO (Zhou et al., 2001) and NO<sub>x</sub> (Beine et al., 2002) are photochemically produced in the snowpack. Consequently, we have added HONO and NO<sub>x</sub> fluxes from the snowpack that are proportional to radiation (i.e. varying from the maximum flux when radiation maximizes to zero when radiation minimizes). HONO photolysis and dry deposition of HO<sub>2</sub>NO<sub>2</sub> (using a first order  $k = 2.5 \times 10^{-3} \text{ s}^{-1}$ ) have also been added to the model.

Laboratory studies have led to updated rate constants for the reaction 4 of aldehydes with BrO (reaction 3). Orlando et al. (2000) approximate that an upper-limit



rate coefficient for this reaction is  $4.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\sim 4$  times lower than the number used by Michalowski et al., 2000). Using the updated upper-limit rate constant, we find that BrO + aldehyde reaction produces only  $\sim 1\%$  of the simulated HOBr. Thus, reaction 4 is not an important route for HOBr generation in this environment (in contrast to the original findings of Michalowski et al., 2000).

With these improvements, we used the gas phase and zero-order flux components of the original Michalowski et al. (2000) model to investigate the behavior of carbonyl compounds in the Arctic SBL. The details of the four models utilized are described below.

### 3.2. Model A

A 0-D gas phase only version of the model was run to determine whether known gas-phase chemistry (no halogen chemistry) can account for the carbonyl compound observations. Model A included all of the gas-phase chemistry present in the Michalowski et al. (2000) model (with the additional reactions mentioned above). A flux of HONO and NO<sub>x</sub> was used to approximate the measured HONO and NO<sub>x</sub> concentrations, and varied from zero at midnight to  $5 \times 10^5$  and  $1 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$  at noon, respectively.

### 3.3. Model B

For Model B, we added a diurnally varying source (proportional to radiation) of bromine and chlorine atoms to yield maximum levels comparable to those estimated by Boudries and Bottenheim (2000). The average noontime simulated  $[\text{Br}] = 1.5 \times 10^7$  and  $[\text{Cl}] = 7 \times 10^4 \text{ molecules cm}^{-3}$ . Inclusion of halogen atoms at these concentrations leads to a simulated partial ozone depletion event (simulated O<sub>3</sub> decreases to 25 ppb over 8 days). This model allows for investigation of carbonyl compound behavior due only to gas-phase chemistry representative of partial ozone-depleted conditions (a condition during which carbonyl compound chemistry is not well understood (Sumner et al., 2002)).

### 3.4. Model C

Gradient and flux chamber measurements indicate that the snowpack is a major source of carbonyl compounds in the Arctic surface layer (Sumner and Shepson, 1999; Guimbaud et al., 2002; Boudries et al., 2002). To examine the effect of a snowpack source of carbonyl compounds on the simulated SBL carbonyl compound concentrations, we used Model A and added a diurnally varying source (proportional to radiation) of HCHO, CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>. Guimbaud et al. (2002) measured fluxes of acetaldehyde and acetone (impacting 25 and 320 m, respectively, due to their different lifetimes) from the Alert snowpack corresponding to  $1.7 \times 10^5$  and  $1.9 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ , (expressed as a volumetric input), respectively. A snowpack HCHO flux was not measured for the period of time shown in Fig. 1, so Model C included a diurnally varying volumetric source of HCHO with a maximum at noon of  $2.4 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ , which approximately simulated the concentrations shown in Fig. 1. We then compare this flux to data available for different time periods, as discussed below.

As discussed in Perrier et al. (2002), Sumner and Shepson (1999), Guimbaud et al. (2002), and Sumner et al. (2002), it is likely that HCHO and CH<sub>3</sub>CHO are produced photochemically in the snowpack. Given this, and the data shown in Fig. 2, we assume the fluxes varied diurnally from the maximum fluxes reported in Guimbaud et al. (2002) at noon, to zero at midnight. These source components of the model simulate the combined effect of a chemical production mechanism present in the snowpack and physical processes (e.g. desorption) that release carbonyl compounds from snow grains.

### 3.5. Model D

To investigate the possible impact of a temperature-dependent sink of carbonyl compounds in the snowpack

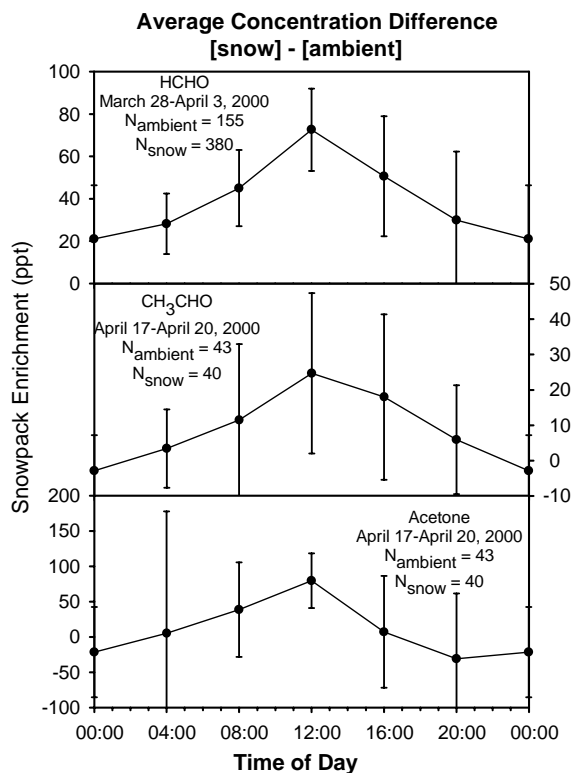


Fig. 2. Average difference between the snowpack interstitial air concentration and the ambient air concentration for formaldehyde, acetaldehyde and acetone from the data shown in Fig. 1 (error bars shown =  $S_N/\sqrt{N}$ ).

(e.g. physical uptake on snow grains), Model D included temperature-dependent loss terms for HCHO, CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>, which were added to Model C. In very stable conditions, the dry deposition velocity ( $V_D$ ) will be dominated by the aerodynamic resistance ( $r_a$ ) (Wesely and Hicks, 2000), as shown in Eq. (II).

$$V_D = 1/r_a. \quad (\text{II})$$

From Eq. (III), we calculate a resistance of  $21 \text{ s cm}^{-1}$ , using an eddy diffusivity coefficient ( $K_z$ ) estimated as  $95 \text{ cm}^2 \text{ s}^{-1}$  from the data in Fuentes et al. (1996),

$$r_a = z/K_z \quad (\text{III})$$

and a scale height ( $z$ ) of 20 m based on a calculated atmospheric thickness impacted by dry deposition, assuming it occurs during stable nighttime conditions. The deposition velocity calculated from the aerodynamic resistance (Eq. (II)) is  $0.05 \text{ cm s}^{-1}$  (corresponding to a first-order loss rate constant of  $2.5 \times 10^{-5} \text{ s}^{-1}$ ), which we apply to all three carbonyl compounds. This value is in the range reported for O<sub>3</sub> deposition to snow (Gong et al., 1997) and consistent with the value of  $0.06 \text{ cm s}^{-1}$  reported by Galbally and Roy (1980). In

Fig. 1, we present the snowpack temperature data (at a depth of 6 cm), which exhibits a maximum about 2–3 h later than the radiation maximum for the Alert snowpack. Consequently, in Model D we varied the simulated deposition rate from zero at 1400 to the calculated maximum rate at 0200.

## 4. Results and discussion

### 4.1. Diel cycles of carbonyl compounds

Fig. 1 shows a series of simultaneous measurements of ambient air and snowpack interstitial air concentrations of HCHO, CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>. Note that the time series measurements for HCHO were conducted ~2 weeks earlier than for the other species. These data represent periods during full or near full-sunlight conditions when high temporal resolution sampling was conducted for both snowpack and ambient air. The data in Fig. 1 indicate a significant diel cycle for all three carbonyl compounds in both the ambient and snowpack interstitial air.

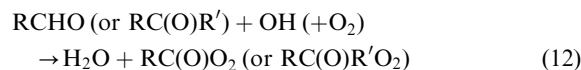
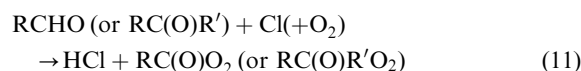
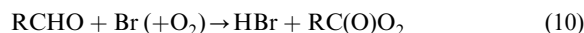
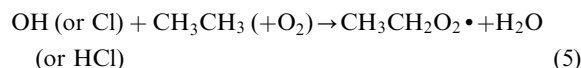
It can be seen that as radiation and snowpack temperature maximize, so does the enrichment of the snowpack air relative to ambient air concentrations, particularly for the aldehydes. To demonstrate this more clearly, in Fig. 2 we present plots of the average (using 4 h bins) difference between the snowpack air and ambient air concentrations for all three compounds. These data indicate that a flux of these species from the snowpack exists and will vary diurnally, with a larger efflux from the snowpack at noon than at midnight.

The large diel variability of these carbonyl compounds is an intriguing discovery, as it has not been previously observed for CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>, and previous models failed to predict this behavior with chemistry known to occur in this environment. This indicates that there are chemical and/or physical processes occurring that we do not understand or have not identified. Of interest is not only that the average concentrations are higher than have been predicted (Shepson et al., 1996), but also that they exhibit a significant diel cycle.

### 4.2. Gas-phase photochemistry

The first question we wish to address is whether the diel variations can be explained from the diel cycle in gas-phase radical chemistry. Carbonyl compounds can be formed from the oxidation of hydrocarbons via OH or Cl in the presence of NO, as shown in reactions 5–7, using ethane as an example. However, HO<sub>2</sub> can compete with this process in this low NO<sub>x</sub> environment, lowering the efficiency of carbonyl compound formation, via reaction 8. Carbonyl compounds can be

destroyed via photolysis and reaction with Br (aldehydes only), Cl atoms and OH, as shown in reactions 9–12. Thus, it is important that we treat HO<sub>x</sub>, NO<sub>x</sub>, Cl, and Br concentrations correctly in the model to properly simulate carbonyl compound chemistry.



To examine this issue, we employed model A to isolate the influence of the gas-phase chemistry, and to establish accurate free radical concentrations in the model, with respect to measurement data. Fig. 3 shows the simulated and measured concentrations of HONO and NO<sub>x</sub> for an 8-day period in April. The HONO and NO<sub>x</sub> measurement data have been screened for local pollution episodes, and thus only periods of “clean” data are shown in Fig. 3. As shown in Fig. 3, without a flux of HONO and NO<sub>x</sub> in the model, simulated NO<sub>x</sub>

concentrations drop to near zero in about 8 h, indicating the importance of the snowpack flux of NO<sub>x</sub> (effectively in the form of HONO) to Arctic SBL chemistry.

Given the discovery of the significant HONO flux, we need to re-evaluate the importance of gas-phase OH chemistry (e.g. with respect to carbonyl compound production) in this environment, given that HONO will serve as a significant HO<sub>x</sub> source through its photolysis via reaction 13. Models A and B were used to determine

$$\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \quad (13)$$

the relative importance (i.e. relative to halogen atoms) of HONO as a gas-phase OH source. By artificially adding halogens to the model to simulate the levels estimated for partial ozone depletion events (Jobson et al., 1994; Ramacher et al., 1999; Boudries and Bottenheim, 2000; Sumner et al., 2002), we are also able to determine how gas-phase chemistry changes in the presence of halogen atoms.

Using Models A and B, it was determined that HONO is the dominant HO<sub>x</sub> source, followed by HCHO photolysis, both in the presence and absence of halogen atoms, while HO<sub>2</sub>NO<sub>2</sub> formation serves as the main HO<sub>x</sub> sink (see Table 1). Due to the low absolute humidity in the Arctic, O<sub>3</sub> photolysis (followed by O(<sup>1</sup>D) reaction with H<sub>2</sub>O) is a negligible source of HO<sub>x</sub>. The models simulate HONO in reasonable agreement with the measured concentrations (Fig. 3), particularly at noon when OH formation via photolysis will be most active. In the evening, simulated HONO drops, as photolytic loss dominates the emission term. Thus, it is likely that we have constrained the simulated OH levels to the best of our ability, given current measurements and determinations of the most significant HO<sub>x</sub> sources

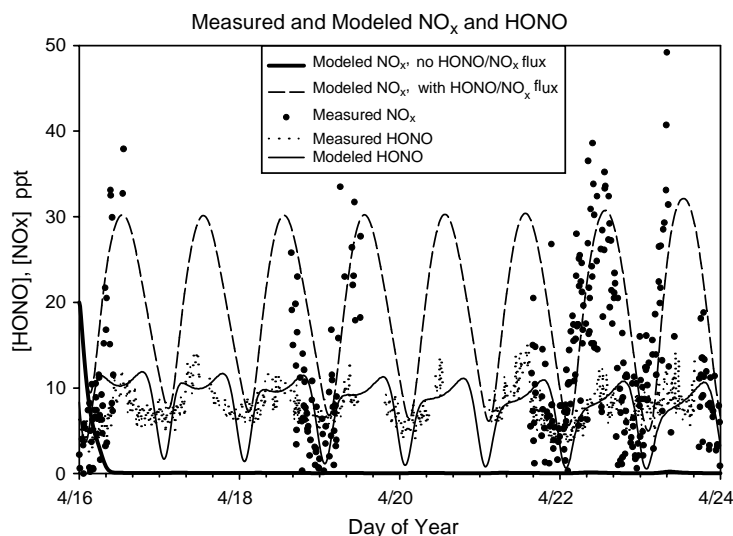


Fig. 3. Measured and modeled NO<sub>x</sub> and HONO concentrations for an 8-day period in April.

Table 1  
Summary of gas-phase HO<sub>x</sub> production and destruction pathways

Reaction	% of HO <sub>x</sub> production Model A	% of HO <sub>x</sub> production Model B	% of HO <sub>x</sub> destruction Model A	% of HO <sub>x</sub> destruction Model B
O <sub>3</sub> + hν → OH	<2	<1		
HONO + hν → OH + NO	64	32		
HCHO + hν → HO <sub>2</sub>	25	13		
HOBr + hν → OH	5	33		
Cl + Hydrocarbons → HO <sub>2</sub>	<1	19		
HO <sub>2</sub> + NO <sub>2</sub> → HO <sub>2</sub> NO <sub>2</sub>			81	40
OH + NO <sub>2</sub> → HNO <sub>3</sub>			8	4
HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub>			5	5
HO <sub>2</sub> + BrO → HOBr			5	45
HO <sub>2</sub> + Br → HBr			<1	<1
HO <sub>2</sub> + ClO → HOCl			<1	5

and sinks in the Arctic. The simulated OH levels reached  $1 \times 10^6$  molecules cm<sup>-3</sup> at noon in Model A (in agreement with Zhou et al., 2001), and  $7 \times 10^5$  molecules cm<sup>-3</sup> at noon in Model B.

#### 4.3. Simulations of carbonyl compound diel cycles

Fig. 4a shows simulated carbonyl compound concentrations for Model A. HCHO and CH<sub>3</sub>CHO achieve steady state concentrations in the 50–75 ppt range, which is lower than the measured concentrations shown in Fig. 1 and reported by Sumner et al. (2002) for HCHO and reported by Boudries et al. (2002) for CH<sub>3</sub>CHO. More importantly, the model-simulated amplitude of the diel cycle is small for HCHO compared to the data in Fig. 1, and non-existent for CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>. CH<sub>3</sub>C(O)CH<sub>3</sub> concentrations increase by ~7 ppt per day. For HCHO, loss by photolysis is much faster than for CH<sub>3</sub>CHO and CH<sub>3</sub>C(O)CH<sub>3</sub>, and this leads to the small simulated diel cycle for HCHO.

Rudolph et al. (1999) discuss the role of chlorine atoms in HCHO formation and propose that, at halogen levels typical of partial ozone depletion events, HCHO concentrations between 100–300 ppt can be maintained by gas-phase chemistry alone. To investigate this we used Model B, which produced HCHO concentrations between 100 and 130 ppt, as shown in Fig. 4b. This is, however, significantly lower than typical observed HCHO concentrations during partial ozone depletion events (~300 ppt), as discussed in Sumner et al. (2002). Thus we conclude, consistent with the conclusions of Sumner et al. (2002), that Cl atom chemistry cannot account for the observed HCHO concentrations during partial ozone depletion events, i.e. when [Cl] is expected to be high, and the [Br]/[Cl] ratio is relatively low (Ramacher et al., 1999).

CH<sub>3</sub>CHO drops significantly over the course of the 8-day simulation with Model B, to a final concentration of

#### Modeled Carbonyl Compound Concentrations

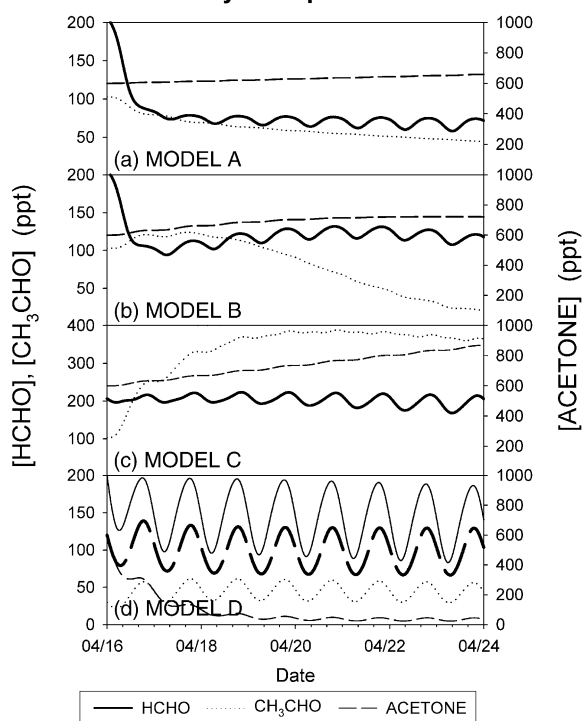


Fig. 4. Modeled carbonyl compound concentrations for models containing: (a) gas-phase chemistry only, (b) gas-phase chemistry with a flux of halogen atoms, (c) gas-phase chemistry with a flux of carbonyl compounds, (d) gas-phase chemistry with a flux of carbonyl compounds and temperature-dependent deposition of carbonyl compounds. (Bold dashed line represents simulated acetone using a 20 m layer; thin dashed line represents simulated acetone using a 320 m layer).

about 20 ppt, again in contrast to the observations shown in Fig. 1 and reported by Boudries et al. (2002). The data in Fig. 1 show that the ozone concentration

decreases from 17 April to 21 April to below 10 ppb, indicating that halogen chemistry was becoming more active. However, while observed  $\text{CH}_3\text{CHO}$  concentrations remained consistent across this period, Model B indicates gas-phase chemistry (in the presence of halogens) would dictate a significant  $\text{CH}_3\text{CHO}$  concentration decrease. Model B simulates  $\text{CH}_3\text{C(O)CH}_3$  concentrations increasing by  $\sim 20$  ppt per day, but with little diel variation. Consequently, in both the presence and absence of halogen atoms (Figs. 4a and b), it is difficult to explain the high concentrations of the aldehydes and the diel cycle of aldehydes and acetone measured in the Arctic SBL via gas-phase chemistry alone.

#### 4.4. Snowpack interactions

The HCHO source used in Model C ( $2.4 \times 10^5$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) simulated HCHO concentrations near those shown in Fig. 1, as shown in Fig. 4c. For comparison, a HCHO flux of  $2 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  (or  $1 \times 10^6$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  in a 20 m layer) was measured on 18 April 2000 at Alert. The source used in Model C is 4 times smaller than this measured flux, but is 3 times larger than the flux estimated by Sumner and Shepson (1999) for Alert snow in 1998 (assuming that the calculated surface flux mixed into a 20 m layer above the snowpack Guimbaud et al. (2002)).

As discussed in Fuhrer et al. (1996) and Hutterli et al. (1999), HCHO can undergo temperature-dependent uptake/release from snow. Burkhart et al. (2002) determined the temperature-dependent equilibrium con-

stant for exchange of HCHO between air and snow. We can calculate the equilibrium snowpack air [HCHO], using Eq. (IV), derived from the Burkhart et al. (2002) data.

$$P_{\text{HCHO}} = [\text{HCHO}]_{\text{aq}} / e^{(2036/T - 3.478)} \quad (\text{IV})$$

Using the available snowpack temperature data and the average snowpack aqueous phase [HCHO] of  $2.3 \times 10^{-7}$  M (Perrier et al., 2002), we obtain the snowpack air HCHO concentrations shown in Fig. 5. As shown in the figure, these calculated concentrations are  $\sim 5$  times larger than those observed, but have features similar to the measurement data. A correlation of the calculated snowpack interstitial air concentration and the measured snowpack interstitial air concentration led to a correlation coefficient of 0.33. However, as discussed by Albert et al. (2002) significant dilution of the snowpack air from ambient air aloft is expected due to the sampling method, and thus the snowpack air HCHO will be influenced by the atmospheric HCHO. We note also that for the Burkhart et al. (2002) experiments, the ice did not reach complete equilibrium with the gas phase, and the partition coefficients were somewhat underestimated. This would lead us to overestimate the snowpack air concentrations. It is also likely that HCHO partitioning to snow in the Arctic will also involve partitioning to crustal material and organic substances (e.g. humic substances) present in the snow. This will lead to an effectively larger equilibrium constant, and consequently lower interstitial air [HCHO]. It is nonetheless instructive to use the Burkhart et al. (2002) data to estimate an upper-limit

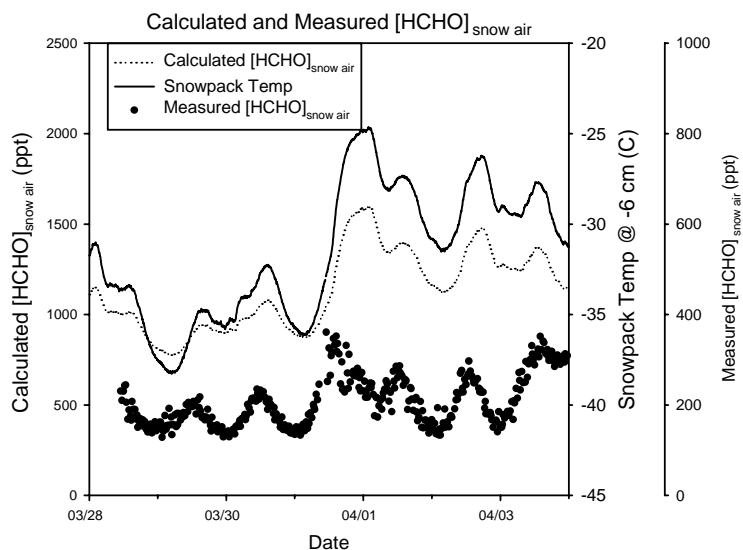


Fig. 5. Measured and calculated [HCHO] in snowpack interstitial air. Snowpack temperature at a depth of 6 cm is shown as the solid line.

flux of HCHO due to temperature-driven desorption from snow.

Given the calculated temperature-dependent snowpack interstitial air HCHO concentration, it is possible to calculate a flux of HCHO from the snowpack, due only to temperature-dependent desorption, followed by ventilation out of the snowpack. The flux can be calculated according to Eq. (V), where  $k$  is a transfer velocity determined by the ventilation and diffusion coefficients (see below),  $C_{\text{snow}}$  is the snowpack interstitial air concentration of HCHO, and  $C_{\text{air}}$  is the ambient air concentration of HCHO. The transfer velocity can be determined using a resistance model for diffusion out of the snowpack and mixing in the surface layer of the atmosphere, from Eqs. (VI) and (VII), where  $r_{\text{snow}}$  represents the resistance to transport within the snowpack air and  $r_a$  represents the resistance to vertical mixing in the lower atmosphere.

$$\text{Flux} = k(C_{\text{snow}} - C_{\text{air}}), \quad (\text{V})$$

$$k = 1/(r_{\text{snow}} + r_a), \quad (\text{VI})$$

$$r = z/K_z. \quad (\text{VII})$$

In the case of  $r_{\text{snow}}$ ,  $z$  is the depth of the Alert snowpack (40 cm) and  $K_z$  is the ventilation coefficient as determined by Albert et al. (2002) averaged over the 40 cm depth of the snowpack ( $0.05 \text{ cm}^2 \text{ s}^{-1}$ ), while  $r_a$  is  $21 \text{ s cm}^{-1}$ , as discussed above. The transfer velocity ( $k$ ) used in Eq. (V) is then  $0.0012 \text{ cm s}^{-1}$ , as the  $r_{\text{snow}}$  term limits the transfer velocity. The average upper-limit flux of HCHO from the snowpack for 28 March–4 April 2000 (due to temperature-dependent exchange of HCHO with snow) was then determined to be  $6 \times 10^7 \text{ molecules cm}^{-2} \text{ s}^{-1}$ , or a volumetric source of  $3 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$  in 20 m. This is  $\sim 10$  times smaller than the source required in the model to simulate gas-phase HCHO concentrations measured from 28 March to 4 April 2000 ( $2.4 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ ). The calculated flux is over 30 times smaller than the flux of HCHO measured on 18 April 2000 at Alert ( $2 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ ). This indicates that temperature-dependent desorption alone cannot explain the HCHO concentrations observed at Alert in spring, and supports the possible role of photochemical production at the snowpack surface.

While temperature-driven processes can act as a source of species from the snowpack, they can also act as a sink. Fig. 4c shows the simulated carbonyl compound concentrations for Model C. HCHO concentrations are maintained at about 200 ppt and show a slight diel cycle. However, the simulated amplitude ( $\sim 40$  ppt) is  $\sim 60$  ppt smaller than that shown in Fig. 1.  $\text{CH}_3\text{CHO}$  increases to  $\sim 380$  ppt over the first 3 days, while  $\text{CH}_3\text{C(O)CH}_3$  increases by  $\sim 100$  ppt over the course of the 8-day model. For both species, the

simulated diel variation is weak. However, from the measurements in Fig. 1, we see that, even though acetone has a calculated lifetime of months, it exhibits a significant diel cycle. This implies not only significant daytime production (or input), but also a physical removal mechanism (since chemical removal is too slow). We hypothesize that this removal mechanism is adsorption to the snowpack. In fact, Houdier et al. (2002) found 40% higher  $\text{CH}_3\text{C(O)CH}_3$  in the condensed snow phase at midnight than at noon and found that adsorption is also likely to be important for  $\text{CH}_3\text{CHO}$ . In addition, Jacobi (2002) measured a daytime emission and nighttime deposition of HCHO at Summit, Greenland. Although no diel cycle was observed in the snow phase [HCHO] reported by Perrier et al. (2002), our hypothesis of nighttime snowpack uptake is not inconsistent with their results. For the 20 m atmospheric depth affected by deposition,  $>99.5\%$  of HCHO is present in the snowpack condensed phase. Deposition to the snowpack of all the gas-phase HCHO from a 20 m height would result in a snow phase [HCHO] increase of  $<1 \times 10^{-8} \text{ M}$ , which would be undetectable by the measurement methods of Perrier et al. (2002). Thus, we hypothesize that nighttime deposition of carbonyl compounds to the snowpack could serve as an important temporary sink for the gas-phase species, and that successful simulation of carbonyl compound concentrations in the Arctic SBL requires the use of a temperature-dependent deposition term. Model D incorporates such a deposition term (as derived above), representing a sink of carbonyl compounds caused by physical uptake onto snow grains.

Fig. 4d shows the simulated carbonyl compound concentrations for Model D. It is clear that these conditions more closely simulate the measured concentrations and behavior of the carbonyl compounds than the previous models. HCHO is simulated at near the concentrations shown in Fig. 1 and the amplitude of the diel cycle is near that measured ( $\sim 100$  ppt). The simulated (Model D) concentration of  $\text{CH}_3\text{CHO}$  is larger than that shown in Fig. 1 (and is also larger than the concentrations measured for the same period of time by Boudries et al. (2002), while the amplitude of the cycle is in approximate agreement. However,  $\text{CH}_3\text{C(O)CH}_3$  (thin dashed line) decreases to  $<50$  ppt and shows little diel variability. Guimbaud et al. (2002) estimate that the snowpack source of  $\text{CH}_3\text{C(O)CH}_3$  impacts the lowest 320 m of the atmosphere, given the long chemical lifetime of  $\text{CH}_3\text{C(O)CH}_3$ . However, the increased stability of the lower atmosphere at night suggests that the use of a 320 m effective mixing height for acetone (which corresponds to an effective mixing time of 4 months) is not appropriate, with respect to the physical processes that impact its surface layer behavior. If we apply an effective mixing height of 20 m (the scale height affected by dry deposition), this increases the

maximum of the volumetric source of acetone to  $3.4 \times 10^5$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Fig. 4d shows that the simulated acetone concentrations using the larger volumetric source term and a nighttime sink varied between 400 and 650 ppt (bold dashed line). This simulation more closely approximates the measurements shown in Fig. 1. These results imply a strong dependence of carbonyl compound concentrations (and their diel cycles) with height over the lowest  $\sim 100$  m. This should be further investigated with vertical profile measurements.

The results in Fig. 4d (compared to the data in Fig. 1) indicate that in each case where a diel cycle is apparent, the phase of the cycle is not properly simulated. For the carbonyl compounds, the simulated concentration maximum occurs near 1800, while the measured concentration maximum occurs near noontime. The nature of the diel cycle results from the convolution of the emission, chemistry, deposition and vertical mixing cycles; in the case of the latter, we have not incorporated a diurnally varying mixing rate, which may significantly impact the phase of the cycle. Nonetheless, the results shown in Fig. 4 indicate the likely importance of both chemical and physical processes in this environment, involving photochemistry and temperature-dependent uptake and release of carbonyl compounds from the surface of snow.

## 5. Conclusions

Our measurements have shown that a significant diel cycle exists for carbonyl compounds in the surface layer at Alert, Nunavut, Canada, even for acetone, which has a long gas-phase chemical lifetime. The aldehydes, because of their short lifetime, must be locally produced. The acetone concentrations are also impacted by local chemistry, snowpack exchange, as well as long-range transport. This snowpack exchange may help explain the apparent relatively large acetone concentrations over the Arctic Ocean surface (Yokouchi et al., 1994; Guimbaud et al., 2002). The measurement data suggest a significant impact of snowpack emissions and nighttime adsorptive uptake for all three carbonyl compounds, which can be simulated by including these processes in the model. However, we estimate that this is likely to impact only the lowest  $\sim 20$  m of the surface layer. This could be tested through measurements of vertical profiles of these species over the lowest  $\sim 100$  m of the boundary layer.

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