PERGAMON

Atmospheric Environment 36 (2002) 2573–2583

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Distribution and trends of oxygenated hydrocarbons in the high Arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the ALERT2000 field campaign

H. Boudries[a,1], J.W. Bottenheim[a,*], C. Guimbaud[b], A.M. Grannas[b], P.B. Shepson[b], S. Houdier[c], S. Perrier[c], F. Dominé[c]

[a] Meteorological Service of Canada, 4905 Dufferin Street, Toronto, Ont., Canada M3H 5T4
[b] Departments of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN, USA
[c] CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement, BP 96, 54 rue Molière, 38042 Saint Martin d'Hères Cédex, France

Received 4 June 2001; received in revised form 17 October 2001; accepted 11 January 2002

Abstract

Oxygenated hydrocarbons, including for the first time alcohols, in the atmosphere and snow-pack interstitial air were measured at Alert, Nunavut, Canada from 15 February to 5 May 2000. Unexpectedly high concentrations of oxygenated hydrocarbons were observed. Acetone, acetaldehyde and methanol represent about 90% of all oxygenated hydrocarbons measured in this work, and together with formaldehyde their total concentration was higher than the sum of measured NMHCs. During sunlit hours, concentrations in the snow-pack interstitial air were higher than those measured in the gas-phase, implying a positive flux from the snow-pack to the Arctic boundary layer. Fluxes of acetaldehyde, acetone and methanol at that time were estimated to be 26, 7.5 and 3.2×10^8 molecules cm^{-2} s^{-1}, respectively. These rates would deplete the local snow of acetaldehyde and acetone in about 2 days if degassing was driving the flux. Additional evidence suggests that photochemical production in the snow-pack could explain these fluxes, especially for acetaldehyde. Diel variations were observed at Alert after polar sunrise in the snow-pack interstitial air and in ambient air. During decreasing O_3 conditions, positive correlation with acetaldehyde was observed which is interpreted as implying local Br driven chemistry, but acetone mixing ratios showed a strong negative correlation. Crown Copyright © 2002 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Oxygenated hydrocarbons; Alcohols; Snow-pack interstitial air chemistry; ALERT2000

1. Introduction

Recent studies at Alert, Nunavut, Canada and Summit, Greenland have shown that formaldehyde concentrations (HCHO) in snow-pack interstitial air and firn are often much higher than those measured in the atmospheric boundary layer, suggesting that surface snow is a HCHO source (Sumner and Shepson, 1999; Hutterli et al., 1999). These observations may explain why the observed HCHO concentrations in the Arctic are generally much higher than can be explained with conventional gas-phase chemistry models (Shepson et al., 1996). Concentrations of acetone have also been observed to be surprisingly high (Yokouchi et al., 1994; Biesenthal, 1997) but the only information on acetone in snow-pack interstitial air reported to date is for winter snow in Northern Michigan (Couch et al.,

---

*Corresponding author.
E-mail address: jan.bottenheim@ec.gc.ca (J.W. Bottenheim).

[1] Now at Aerodyne Research Inc., MA, USA.

PII: S1352-2310(02)00122-X

2000). High levels of these compounds may have a significant impact on radical chemistry in the boundary layer air, since they will constitute an important source of HO_x radicals through photolysis by natural sunlight, and sink of species such as Br.

In this paper, we present measurements of several oxygenated hydrocarbons including, for the first time, methanol and ethanol in the Arctic atmosphere and in the snow-pack interstitial air at Alert, Nunavut, Canada (82.5°N, 62.3°W). The measurements were made as part of the ALERT2000 campaign from 15 February to 5 May 2000 and are analyzed to determine the potential for the snow-pack to be a source of these compounds. In companion papers we report on the concentrations in the snow (Houdier et al., 2002), focus on the mechanistic details of the exchange between snow-pack interstitial air and the overlaying boundary layer (Guimbaud et al., 2002), and present a box model study to explore the implications for the chemistry in the surface boundary layer air (Grannas et al., 2002).

2. Experimental

2.1. Sampling and analysis

Oxygenated hydrocarbon concentrations were determined in situ and in real time using a Tekmar model 6000 preconcentration system and a Hewlett-Packard GC-MS-FID analysis system (HP5890 and HP5972). Ambient air was collected at 2 m above the surface through an unheated 25 m Teflon tube at a flow rate of $3\,\mathrm{dm^3\,min^{-1}}$; $1\,\mathrm{dm^3}$ of air was sampled from this high flow sampling line at a rate of $100\,\mathrm{cm^3\,min^{-1}}$ by the preconcentration system. Standard mixtures (Section 2.2) were sampled through equal length PFA Teflon tubing both inside and outside the trailer that housed the analysis system to ascertain that no line losses occurred (the actual sample line was not used for these tests to prevent potential contamination by the higher than ambient concentrations in these test mixtures). We note that no condensation effects were observed by the sampling procedure, nor were they expected in view of the low humidity of ambient air at –20°C to –40°C).

The air sample was preconcentrated in a SS tube (15 cm long, 2.5 mm i.d., 3 mm o.d.) filled with three adsorbents (115 mg 20–40 mesh Carbotrap C, 85 mg 20–40 mesh Carbotrap; 102 mg 60–80 mesh Carbosieve SIII), cooled to a temperature of –20°C. Trapped components were desorbed by heating the SS tube to 250°C for 5 min and then transferred to the head of the analytical column cooled at –150°C by the Helium carrier gas at a flow of $2\,\mathrm{ml\,min^{-1}}$. The head of the analytical column was then flash heated to + 150°C, and chromatographic separation was performed on a $60\,\mathrm{m} \times 0.32\,\mathrm{mm}$ i.d. capillary column (DB-Wax, $0.5\,\mu\mathrm{m}$ film, J&W, Ranch Cordoba, CA, USA). UHP helium was used as carrier gas and the flow rate was set by maintaining a constant pressure of 14 psi at the head of the analytical column. The temperature program was as follows: 30°C for 20 min, increased at $3^\circ\mathrm{C\,min^{-1}}$ until 120°C, then $5^\circ\mathrm{C\,min^{-1}}$ to 150°C and held at this temperature for 15 min. Flame ionization detection (FID) was used for quantitative analysis, and mass spectrometry (MSD), operated in electron impact ionization mode (70 eV) (scanning m/z 29–250) was used for qualitative analysis.

2.2. Calibration, reproducibility and detection limits

Quantitative calibration of the system was performed using two different techniques. Static dilution involved the introduction of a small amount of a standard gas mixture (10 ppmv ± 10% of acetaldehyde, propanal and butanal, Scott Specialty Gases, USA) in a large glass vessel, followed by several dilution steps with pure nitrogen to mixing ratios <1 ppbv. In a dynamic dilution system the flow from commercial diffusion tubes (VICI Metronics Inc., Santa Clara, USA) was diluted in two stages to yield mixing ratios of 5–26 ppbv (Table 1). All calibrations were carried out within the linear range of the FID. The long-term stability of the FID was followed during the field campaign by analyzing a standard mixture under identical conditions of sampling and analysis. Results from these experiments, based on benzene, showed a precision $\leqslant 2\%$. The limit of detection for a $1\,\mathrm{dm^3}$ sample volume was determined as three times the standard deviation of the blank value and is included in Table 1.

3. Results and discussion

3.1. Gas-phase distributions

Table 2 summarizes the average mixing ratios and standard deviation of gas-phase mixing ratios of the oxygenated hydrocarbons measured during the campaign. Data that might have been biased by local sources have been excluded from the final dataset. The results are divided into three categories: dark period (15 February–10 March 2000), when the sun was virtually always below the horizon; transition period (10–31 March 2000) when a clear difference was observed between total darkness and day light; and finally, light period (1 April–4 May 2000) when the sun was always above the horizon. Time series of aldehydes, ketones and alcohols as well as ozone from 15 February–5 May are presented in Fig. 1. Little linear correlation was apparent: the best correlation was between acetaldehyde and propanal ($R = 0.50$), acetaldehyde and methanol

Table 1
Experimental permeation rates in μg min^{-1}, precision, reproducibility and detection limits for some primary oxygenated standards

	Emission rate in μg min^{-1} (std. dev.)	Final concentration and precision[a] ppbv (% std. dev.)	Reproducibility[b] std. dev. (%), ($n = 7$)	Detection limits 3 σ (pptv)
Methanol	29.8 (7.7)	15.7 (27)	10.5	11
Ethanol	29.8 (2.9)	10.9 (12)	12.1	8
MEK	54.7 (7.1)	12.8 (15)	12.1	2
Acetaldehyde	69.6 (5.7)	26.7 (10)	5.4	8
Propanal	39.8 (4.8)	11.6 (14)	6.3	7
Butanal	19.9 (2.0)	4.66 (12)	28.9	29
Acetone	69.6 (8.1)	20.2 (13)	4.8	1

[a] Final concentration and precision after two stage dilutions of primary gas standard.

[b] Reproducibility of the system, determined from two successive samplings of the same mixture.

Table 2
Average and standard deviation of oxygenated hydrocarbon mixing ratios observed at Alert during PSE2000 during the dark (14 February–10 March), transition (10–31 March) and 24 h light period (1 April–4 May)

	Dark			Transition			24 h light		
	Data range (min–max)	Average (pptv)	Std. dev. ($\pm 1\,\sigma$)	Data range (min–max)	Average (pptv)	Std. dev. ($\pm 1\,\sigma$)	Data range (min–max)	Average (pptv)	Std. dev. ($\pm 1\,\sigma$)
Methanol	41–424	200	125	42–571	269	118	34–594	256	136
Ethanol	19–464	99	91	d.l.–282	75	54	d.l.–236	36	31
Acetone	18–776	200	174	265–945	479	142	183–1470	871	234
MEK	d.l.–116	47	33	d.l.–194	54	40	d.l.–442	54	44
Acetaldehyde	42–452	134	92	68–552	202	90	26–459	166	79
Propanal	d.l.–31	11	9	6–28	13	5	d.l.–56	11	5
Butanal	<d.l.	……	…..	<d.l.	……	…	d.l.–54	7	8

($R = 0.46$) and methyl-ethyl-ketone (MEK) and methanol ($R = 0.44$)

3.1.1. Aldehydes

Acetaldehyde mixing ratios were found in a range 26–550 pptv, with an average value of 170 pptv and a standard deviation of 88 pptv. Propanal mixing ratios were measured close to the detection limit, whereas butanal mixing ratios were below the detection limit most of the time. Acetaldehyde and formaldehyde (Sumner et al., 2002) represent more than 90% of all aldehydes observed in the lower Arctic boundary layer; acetaldehyde alone comprises roughly half of the total. As can be seen from Table 2 and Fig. 1, little variation between February and May was observed.

High mixing ratios of acetaldehyde observed in the dark period can be attributed to long range transport originating from an area of anthropogenic sources (Worthy et al., 1994), however after polar sunrise the atmospheric lifetime of acetaldehyde decreases substantially due to photolysis and reaction with OH radicals. Its lifetime due to reaction with OH alone is lower than that of pentane (Atkinson et al., 1992). Pentane shows a drastic decrease in mixing ratio between February and May (Bottenheim et al., 2002a), ascribed to increasing OH concentrations over this period (Rasmussen and Khalil, 1983; Jobson et al., 1994). Hence even more substantial decreases of the acetaldehyde mixing ratio would be expected if long range transport was its only source. Guimbaud et al. (2002) show that production from reactions involving hydrocarbon precursors such as ethane with OH and Cl cannot compensate for this discrepancy between observations and gas-phase chemistry.

3.1.2. Ketones

Acetone and MEK represent the major ketones measured at Alert. Uniquely amongst all organic gases observed at Alert, acetone showed an increase in mixing ratio with time. About 150 pptv of acetone was observed early in February, increasing to >1 ppbv in May. Mixing ratios of this magnitude are in agreement with previous reports except for the very low levels in early February (Yokouchi et al., 1994; Biesenthal, 1997; Splawn et al., 1998). No seasonal trend could be discerned in the mixing ratios of MEK (see Table 2),

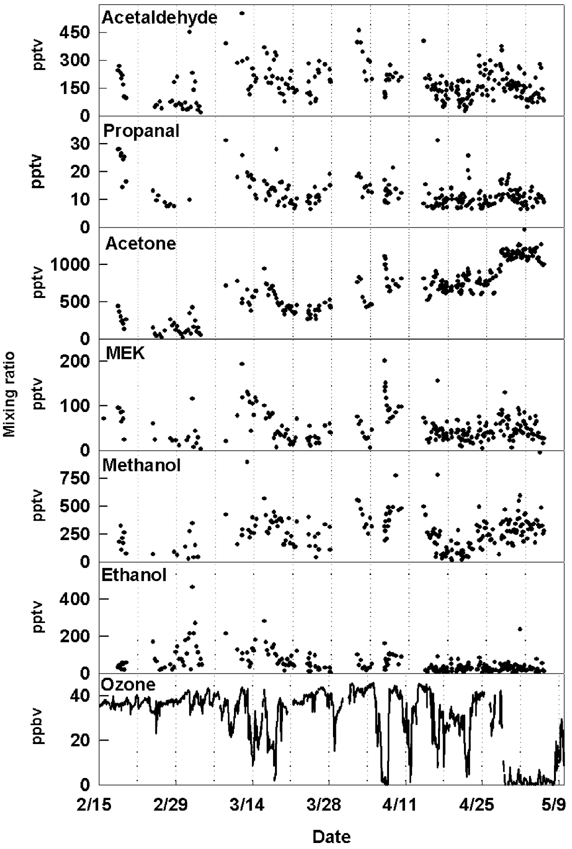

Fig. 1. Time series of the mixing ratios (pptv) of aldehydes, ketones and alcohols at Alert during PSE2000. Also shown is the concurrent trend in ozone (ppbv).

and they were substantially lower than for acetone. While the average mixing ratio of 53 ($\pm$42) pptv is somewhat lower than the 86 ($\pm$24) pptv observed by (Biesenthal, 1997) in 1995, both datasets show only a weak correlation between the two ketones ($R = 0.41$ in 1995, $R = 0.36$ in 2000). The difference in the seasonal trend and weak correlation between acetone and MEK suggests that different physical and chemical processes control their abundance.

The acetone lifetime due to OH radical chemistry is comparable to ethane, which is known to decrease with season (Jobson et al., 1994). Similar to acetaldehyde, a decrease of acetone mixing ratio (albeit much less pronounced) might be expected between February and May if no other processes than long range transport were important. Box model calculations suggested an upper limit for a local production rate from NMHC oxidation of ca. 7 pptv d^{-1} in a shallow boundary layer above the surface under full sunlight conditions in late April (Grannas et al., 2002). Average production rates are expected to be much lower and hence gas-phase oxidation processes can be ruled out as the explanation for the observed temporal trend. The global source strength for acetone (from terrestrial and photochemical processes only) is estimated to be larger than for ethane (60 Tg yr^{-1}, in Singh et al., (2000), and 15.5 Tg yr^{-1}, in Rudolph (1995)). It is therefore conceivable that the temporal trend observed from February to May is due to increasing importance of biogenic sources in the Arctic but an exploratory effort to compare the acetone data with concurrent CH_4 measurements showed no correlation ($R<0.1$), seemingly excluding a stronger biogenic source far upwind from Alert. Increased photochemical and/or abiotic production from decay of humic material in the snow-pack, which would increase as T increases could be another possibility (Warneke et al., 1999).

3.1.3. Alcohols

Data for the high latitudinal distribution of alcohols are reported here for the first time. While the analytical method could quantify all linear and branched alcohols from C_1 to C_8 at Alert, only two compounds were mostly found above the detection limit; methanol and ethanol. Mixing ratios of methanol and ethanol varied between 35 and 350 pptv and <8 (detection limit)–200 pptv, respectively. These levels are compare well with observed values for free tropospheric air (5–10 km, between 400 and 900 pptv (32N–38N) and 40–120 pptv (45N–65N), respectively (Singh et al., 1995, 2000). The atmospheric lifetime of methanol with respect to OH is comparable to that of propane (DeMore et al., 1990; Atkinson et al., 1992) but no seasonal trend was observed for methanol, in contrast with propane (Bottenheim et al., 2002a) and once more long range transport can be ruled out as the only determinant of the alcohol concentrations. As for acetone, methanol has both natural and anthropogenic sources (Goldan et al., 1995; Grosjean et al., 1998) and an increasing importance of the former could explain the absence of a long-term trend in our data. Production of alcohols from gas-phase photochemical oxidation of NMHCs is too slow to explain the trend.

Even though methanol and ethanol mixing ratios in general compare well with the free troposphere values, the large variability of their mixing ratios in the Arctic boundary layer is puzzling. The weak correlation between methanol and acetaldehyde might suggest similar sources for these compounds. However, as will be shown below, acetaldehyde was emitted from the snow-pack while methanol appeared mostly to be taken up. If the affinity of alcohols for the surface of ice and snow-crystals is much greater than that of the carbonyl compounds, then it is conceivable that they were efficiently removed from the air by ice crystal showers that occurred frequently at Alert. We are not aware of affinity data that may shed light on this hypothesis. While a comparison of Henry's law constants (Sander,

1998) would support the argument, it is doubtful that Henry's law is applicable to ice and snow-crystal surfaces especially at the temperature regime during this study (−20 to –40°C).

3.2. *Vertical distribution between snow-pack interstitial air and the overlying boundary layer*

For the remainder of this paper we will primarily focus on the more abundant oxygenated hydrocarbons measured in this work, acetaldehyde, acetone, MEK and methanol. The existence of a vertical gradient between ambient air and snow-pack interstitial air was explored by sampling at different depths in the snow-pack and the air above. These experiments were conducted on 22–26 March, which corresponds to the transition period between 24 h dark and 24 h light at Alert, and 24–26 April during a period of 24 h sunlight. During both periods no O_3 depletion was apparent.

3.2.1. *Transition period, 22–26 March 2000*

A Teflon tube (snow-probe) (Sumner et al., 2002) was penetrated into an undisturbed snow layer and kept in the snow until equilibrated with the snow temperature. The inlet of the sampling line (with $3\,\mathrm{dm^3\,min^{-1}}$ sampling flow rate), was then connected to the snow-probe <1 min before the sampling started. Snow-pack interstitial air samples were collected at different depths in the snow varying from –1 to –26 cm, the total depth of the snow-pack. The results from these experiments are summarized in Table 3.

Acetaldehyde, acetone and MEK showed similar behavior. Diel variations were stronger in snow-pack interstitial air than in the air above. During the day there was little difference between snow-pack interstitial and boundary layer air; at night atmospheric levels became higher than those of snow-pack interstitial air. The opposite pattern was found for methanol. For comparison purposes we indicate that no variation was observed for benzene.

3.2.2. *24 h light period, 24–26 April 2000*

The sampling procedure from the snow-pack during the light period was modified to collect a larger interstitial air sample than was possible with the snow-probe. Two clean Teflon tubes (60 cm long, 6 mm o.d.) were buried horizontally in the snow-pack at two different depths, −6 cm and –12 cm, where they remained for the duration of the experiment. Small holes were made along the last 25 cm, allowing a large volume of air trapped in the snow-pack to be sampled before depleting the sample tube environment. The observed $C_{\mathrm{snow}}/C_{\mathrm{air}}$ ratios as function of C_{snow}, where C_{snow} denotes the mixing ratio in the snow-pack interstitial air measured at –6 cm and –12 cm, and C_{air} the mixing ratio in ambient air, are summarized in Table 4.

While different at the two depths, the acetaldehyde $C_{\mathrm{snow}}/C_{\mathrm{air}}$ ratios were always >1. During the day (defined as between 6 h and 18 h local time), snow-pack mixing ratios were 1.1–2.2 times higher than in ambient air, with highest ratios observed at –6 cm. Albert et al. (2002) report calculations showing that under the sampling procedures used here, most of the air at –6 cm is drawn from the surface of the snow-pack into the sampler. Hence the mixing ratio observed in the snow-pack interstitial air sampled at –6 cm could well be a lower limit of the true mixing ratio. Since the impact of

Table 4

Snow-to-air distributions of oxygenated hydrocarbons and benzene measured in late April (24 h light)

	$C_{\mathrm{snow}}/C_{\mathrm{air}}$ at –6 cm		$C_{\mathrm{snow}}/C_{\mathrm{air}}$ at –12 cm	
	Day	Night	Day	Night
Acetaldehyde	1.55–2.15	1.03–1.10	1.29–1.71	1.07–1.17
Propanal	0.91–4.13	1.67–2.50	1.09–2.38	1.00–1.50
Acetone	1.30–1.47	1.23–1.45	1.33–1.56	1.37–1.67
MEK	1.63–2.60	0.99–1.33	1.51–2.95	1.06–1.23
Methanol	0.06–0.86	0.10–0.41	0.21–0.77	0.41–0.82
Benzene	0.93–1.06	0.99–1.05	1.05–1.10	0.97–1.06

Table 3

Snow-to air-distributions of oxygenated hydrocarbons and benzene measured in late March (transition period)

	$C_{\mathrm{snow}}/C_{\mathrm{air}}$		$C_{\mathrm{day}}/C_{\mathrm{night}}$		Average conc. (pptv)		Std. dev.	
	Day	Night	Snow	Air	Day	Night	Day ($n=8$)	Night ($n=7$)
Acetaldehyde	1.19	0.71	2.92	1.75	323	111	145	29
Propanal	1.12	1.20	1.25	1.34	15	12	5	2
Acetone	1.19	0.86	2.05	1.47	586	286	220	49
MEK	1.03	0.46	2.97	1.33	36	12	10	9
Methanol	1.72	2.93	1.20	1.95	406	339	133	245
Benzene	0.89	0.94	1.09	1.16	68	63	9	3

sampling surface air decreases with depth of the probe in the snow-pack, our results suggest that the highest mixing ratios of acetaldehyde are in the top layer decreasing gradually with snow-depth, in agreement with Guimbaud et al. (this issue). During the "night" (between 18 h and 6 h local time, with reduced solar radiation), the vertical distribution changed dramatically, indicating little vertical variation similar to the daytime observations in March.

The vertical distribution of acetone exhibited a different behavior. Snow-pack mixing ratios were always higher than those of ambient air and the highest concentrations were always observed at the lower depth (–12 cm), suggesting that acetone fluxes from the snow were occurring all day long. Contrary to the observations by Grannas et al. (2001), the $C_{\mathrm{snow}}/C_{\mathrm{air}}$ ratios changed little between day and night

$C_{\mathrm{snow}}/C_{\mathrm{air}}$ ratios for methanol were always found to be substantially <1. In fact only during 24 April were the methanol mixing ratios higher than the detection limit of 34 pptv obtained at –6 cm. Thus it appears that the snow-pack was mostly a sink for methanol at this time of year.

3.3. The influence of solar radiation and temperature on acetaldehyde and acetone

In the previous sections we have shown that a similar gradient between snow-pack interstitial and boundary layer air is observed at Alert as for HCHO during sunlit hours. Both photochemical production and thermally driven degassing have been proposed to explain high levels of HCHO in ambient air in the Arctic (Sumner and Shepson, 1999; Hutterli et al., 1999). To investigate whether either of these processes could explain the gradients for other carbonyl compounds between snow-pack interstitial and boundary layer air, we compare in Figs. 2 and 3 the variation of acetaldehyde and acetone in the boundary layer air with total UV radiation (295–385 nm) in ambient air and temperature measured at –6 cm for the period between 22 April and 26 April. This period was selected since a high frequency of sampling took place, and the ozone mixing ratio was > 30 ppbv implying that the carbonyl concentration was unlikely to be substantially influenced by halogen atom chemistry. It is noteworthy that temperature and radiation in the snow were not in phase: a lag of almost 4 h was observed. Simpson and King (2002) report that while the intensity of UV radiation in the snow-pack reduces with depth, the temporal pattern of the diel cycle is not attenuated. A correlation between solar radiation and ambient temperature is expected, but it is well known that due to the insulating capacity of a snow-pack, changes in snow-pack temperature normally trail ambient temperature changes by several hours (Albert and McGilvary, 1992). It can be seen that acetaldehyde exhibited a strong diel variation with a maximum level during the day and minimum during the night. Fig. 2 shows that acetaldehyde mixing ratios correlate well with radiation (significant at the 95% level with $R = 0.88$, $n = 18$) but are out of phase with temperature in the snow-pack at –6 cm ($R = -0.03$, $n = 22$). In the case of acetone these effects are much less pronounced (Fig. 3). There is indication of a diel variation, but little correlation is evident either with radiation or snow-pack temperature (linear regressions show no significant correlations in either case ($R = -0.06$, $n = 16$ and $R = -0.05$, $n = 20$, respectively).

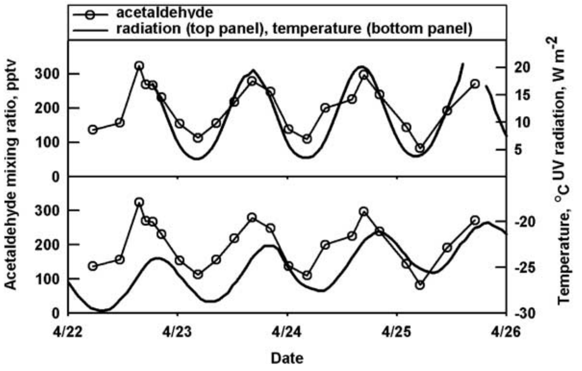

Fig. 2. A comparison of the time series of acetaldehyde (pptv) (circles) with ambient UV radiation (top panel, from Simpson and King, 2002), and with snow-pack temperature at –6 cm (bottom panel, from Sumner et al., 2002) at Alert from 22–26 April 2000.

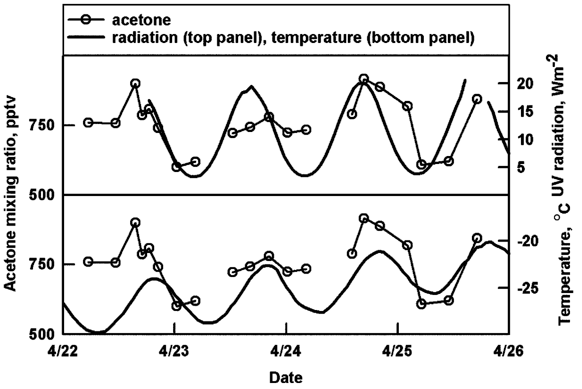

Fig. 3. Same as Fig. 2 but for the mixing ratio (pptv) of acetone.

The impact of radiation was studied further with a cylindrical quartz snow chamber (1 m long, 18 cm i.d., snow-volume 23.5 l, see Beine et al., 2002). Ambient air was sampled before and after passing through the chamber filled with snow, using a flow rate of about 12 dm^3 min^{-1}, which resulted in a residence time of

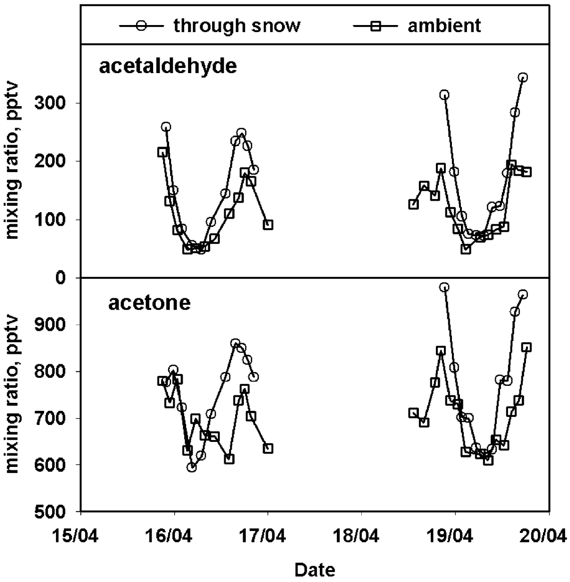

Fig. 4. Comparison of the mixing ratios (pptv) of acetaldehyde and acetone in ambient air, sampled directly, and through a quartz cylinder filled with fresh snow.

ambient air in the chamber of <2 min. Results from these experiments are presented in Fig. 4, revealing a diel cycle with a minimum at midnight and a maximum around noon. The $C_{\text{chamber}}/C_{\text{air}}$ ratios during the day differed by a factor of ca. 2 and 1.25 for acetaldehyde and acetone, respectively, while there was virtually no difference at midnight. Additional tests were conducted in the early afternoon when the $C_{\text{chamber}}/C_{\text{air}}$ ratio was near its maximum, by temporarily covering the quartz snow chamber with aluminum foil and immediately sampling the air exiting the chamber. A significant reduction of ca. 40% of the acetaldehyde mixing ratios was observed which could be reversed by uncovering the chamber. Acetone showed a similar behavior.

While these experiments clearly show that irradiation of the snow-pack by solar radiation leads to increased ambient carbonyl mixing ratios, they do not prove that photochemical production of these compounds in the snow-pack (in snow or interstitial air) is responsible. If the highest carbonyl mixing ratios are found in the surface snow rather than at –6 cm, then temperature-dependent degassing from the surface layer snow would be an alternative explanation since the ambient temperature correlates very well with the solar flux in contrast to the temperature at –6 cm in the snow-pack. A good correlation between ambient temperature and the carbonyl compounds would then be expected.

Linear regressions using all data-points collected between 15 February and 5 May when O_3 mixing ratios were >30 ppbv to exclude the impact of O_3 depletion chemistry, showed no correlation between ambient temperature and acetaldehyde but a statistically significant correlation (95% level) in the case of acetone ($R = 0.59$, $n = 122$) indicating that about 35% of the variance in acetone can be explained by variation in the ambient temperature. Below we show that other arguments argue against the hypothesis that simple degassing of the snow-pack explains our observations.

3.4. Estimation of acetaldehyde, acetone and methanol fluxes from the snow-pack

The previous sections suggested that the carbonyl compounds were emitted from the snow-pack. Snow chamber experiments were performed to obtain a quantitative estimate of the flux rate from the snow. A hemi-cylindrical quartz snow chamber (60 cm long, 20.5 cm wide and 10.5 cm high) open at the bottom was positioned on undisturbed fresh snow and its edges were pressed to a depth of −3 cm, to ensure that no boundary layer air could enter through the bottom. Ambient air was passed laterally through the chamber entering via a 6 mm diameter hole on one end and sampled at another 6 mm hole at the opposite end. Since the residence time of ambient air in the snow chamber was <3 min, changes in the mixing ratios due to photolysis and oxidation by OH can be neglected and assuming a steady-state condition, the flux from the snow-pack can be derived from the equation

$$Q_i(t) = (C_i - C_{io}) \times \frac{F}{L \times W}, \tag{1}$$

where $Q_i(t)$ is the flux in molecules cm^{-2} s^{-1}, F is the pumping speed in cm^3 s^{-1}, L is the length and W the width of the snow chamber at the snow surface in cm, and C_{io} and C_i are the concentrations at the entry and exit point of the chamber.

The average flux rates obtained from this experiment were $2.6\ (\pm 0.1) \times 10^9$, $7.5\ (\pm 1.8) \times 10^8$ and $3.2\ (\pm -0.9) \times 10^8$ molecules cm^{-2} s^{-1} for acetaldehyde, acetone and methanol, respectively (see Table 5). Guimbaud et al. (2002) obtained flux rates for acetaldehyde and acetone of ca. 5×10^8 molecules cm^{-2} s^{-1} using a gradient measurement technique. Those measurements were made on a day with little O_3 depletion and near the FTX building, ca. 500 m to the NW of the SST. Given these different conditions and overall uncertainties in the measurements we feel that the two results are compatible.

An additional experiment was performed by completely covering the flux chamber with aluminum foil to exclude direct solar radiation while the surface snow temperature in the chamber remained to within 0.5°C ± 1°C of the snow-pack temperature. In this experiment the acetaldehyde flux reduced by 50% reinforcing the notion that direct solar radiation is required. However,

Table 5
Mixing ratios (pptv) and standard deviations (1σ) of acetaldehyde, acetone and methanol measured at the exit of the quartz flux chamber (C_i) and in ambient air (C_{io}) and the resulting flux rate

	C_i (pptv) ($n = 4$)	C_{io} (pptv) ($n = 3$)	Flux (molecules $cm^{-2} s^{-1}$)
Acetaldehyde	2338 (±91)	178 (± 57)	$2.6 (\pm 0.1) \times 10^9$
Acetone	1773 (±141)	1160 (± 54)	$7.5 (\pm 1.8) \times 10^8$
Methanol	570 (±70)	306 (± 20)	$3.2 (\pm 0.9) \times 10^8$

Table 6
Results of linear correlations during periods of decreasing O_3 concentration

Date	O_3 vs. acetaldehyde R	O_3 vs. acetone R	O_3 vs. methanol R	Propane vs. acetone	
				R	Slope
13–14 April	+0.85 ($n = 7$)	−0.97 ($n = 7$)	+0.17 ($n = 7$)	−0.98 ($n = 7$)	−0.98 (±0.01)
19–20 April	+0.96 ($n = 7$)	−0.65 ($n = 7$)	No data	No data	No data
26 April	+0.65 ($n = 6$)	−0.81 ($n = 6$)	+0.50 ($n = 6$)	−0.88 ($n = 6$)	−1.4 (±0.4)

acetone and methanol mixing ratios did not show a significant change.

Using the observations on acetaldehyde and acetone in snow by Houdier et al. (2002), we can estimate whether these fluxes can be sustained by physical degassing of the snow only. These authors observed typical mixing ratios of 4 ppbw (acetaldehyde) and 2.5 ppbw (acetone) in the surface snow. Assuming a that the atmosphere exchanges reactive species with recent surface snow only, and placing an upper limit of 10 cm on the thickness of this snow layer (Dominé et al., 2002) with a mean density of $0.2\,g\,cm^{-3}$, this calculates to a total amount of 1.1×10^{14} and 5.2×10^{13} molecules cm^{-2}, respectively. Hence the snow would seem to be able to sustain the observed flux rates for ~1–2 days. For acetaldehyde Houdier et al. (2002) did not observe a continuous decrease in concentration with time, and hence we conclude that degassing of the snow only cannot explain the observed flux. The data for acetone reported by Houdier et al. (2002) are only preliminary; nevertheless our calculations do suggest that simple outgassing alone is incompatible with the measured flux rates.

3.5. Correlations with ozone

Ozone depletion in the Arctic boundary layer air due to reactions involving reactive halogen atoms is well documented (Bottenheim et al., 2002b). O_3 depletion is predominantly due to reaction with bromine atoms (Br), but concurrently chlorine atoms (Cl) have been shown to oxidize NMHCs (Jobson et al., 1994) which could lead to production of OVOCs. These products may react further via photolysis and reactions with the same halogen atoms. All OVOCs are known to react efficiently with Cl, but only aldehydes appear to react efficiently with Br. The overall chemistry is therefore complex and not well understood; for more details see Grannas et al. (2002).

Three depletion episodes occurred in April for which OVOC data were available to investigate their covariance with O_3. Results from linear regressions of O_3 against acetaldehyde, acetone and methanol during these episodes are presented in Table 6. Significant positive correlation between acetaldehyde and O_3 was apparent. The data were not filtered for the previously discussed effects of solar radiation or snow-pack temperature; hence we conclude that Br atom oxidation is the determining factor for the acetaldehyde variance during O_3 depletion episodes. A simple calculation shows that this is in agreement with estimates of the flux of acetaldehyde from the snow-pack. Assuming a Br atom concentration of about 5×10^7 molecules cm^{-3} (Boudries and Bottenheim, 2000), an average acetaldehyde mixing ratio of 150 pptv and $k_{Br+acetaldehyde} = 3 \times 10^{-12}$ at 248 K molecules $cm^{-3} s^{-1}$ (Atkinson et al., 1992) the rate of loss of acetaldehyde is 6.8×10^5 molecules $cm^{-3} s^{-1}$. Guimbaud et al. (2002) estimated a volumetric flux of acetaldehyde from the snow-pack of 1.7×10^5 molecules $cm^{-3} s^{-1}$ when no O_3 depletion was occurring.

A negative correlation between acetone and O_3 was observed, in agreement with previous studies (Yokouchi et al., 1994; Biesenthal, 1997). Enhanced production of acetone from gas-phase oxidation of propane by Cl atoms could be one viable explanation. Concurrent propane data were available for the 13–14 and 26 April episodes, and results of linear correlations between propane and acetone are included in Table 6. The slopes of these correlations (−0.98±0.01 and −1.4±0.4, respectively) indicate that all oxidized propane would have to lead to acetone production to explain the increase in acetone mixing ratios. However the rate coefficients of primary versus secondary H-abstraction from propane by Cl are virtually identical and with 6 primary and 2 secondary H-atoms in propane, only 25% of its reaction with Cl atoms should lead to acetone production. We conclude that other unidentified processes contribute to the increase in acetone during O_3 depletion episodes.

Little trend is observed between O_3 and methanol, in agreement with the expectation that the reaction between Br atoms and methanol is slow.

4. Conclusions

Our data show that acetaldehyde is emitted from the snow-pack. Calculations with the measured flux out of the snow-pack indicate that simple outgassing would deplete the snow of acetaldehyde in about 1–2 days, which is not supported by the snow-phase measurements of Houdier et al. (2002). A distinct diel variation was observed in April, which appeared to be driven by the change in solar zenith angle, even though the sun was 24 h above the horizon at that time. We therefore postulate that photolysis by solar UV radiation (which due to the low solar angle at Alert is highly variable) of organic matter in the snow-pack or organic aerosols, constitutes the origin of acetaldehyde. In support of this hypothesis we note that Leithead et al. (2000) reported substantial levels of total water soluble organic carbon material in Alert snow during April 2000 ($<$1–4 ppmv). The positive correlation between acetaldehyde and O_3 during apparently locally occurring O_3 depletion episodes puts an upper limit to the efficiency of this production process that is commensurate with the estimated flux rate.

Acetone showed an increasing trend with time, which correlated with temperature. This could imply thermally driven degassing of acetone from the snow-pack as the temperature rose from February–May. However, our calculations using late April observations of the flux rate from the snow and the measured acetone content of snow suggested that the snow would be exhausted in a few days. Frequent supply of fresh snow would be required which was not happening, and hence additional snow chemical processes seem to be required

Evidence for a direct solar radiation driven process was weak. The flux chamber experiment did not suggest a marked decrease in the flux rate when the chamber was covered by aluminum foil. Furthermore, a much weaker diel variation than for acetaldehyde was observed which might be due to the fact that acetone has a long atmospheric lifetime (Singh et al., 1994; Lee et al., 1995). A diel variation was more apparent in the snow-chamber experiment. We note that Grannas et al. (2002) observed a stronger diel cycle; we have no explanation for this discrepancy other than the fact that those measurements were made $\sim$200 m away from the SST. There were some notable differences between the two sites such as the thickness of the snow-pack and the amount of fresh snow on the top and this may have played a role.

Acetone showed a strong negative correlation with ozone during ozone depletion events in April. An explanation for this observation remains elusive: oxidation of propane by Cl atoms was shown to be able to explain at most 25% of the observed increase in acetone. During the large ozone depletion event starting on 26 April (Bottenheim et al., 2002b), a substantial increase in temperature was experienced, but during other events (13–14, 19 April) this was not the case.

Contrary to the carbonyl compounds, vertical gradient measurements, especially in April, showed that methanol was not emitted from the snow-pack but rather that it was taken up by the snow. Snow-chamber experiments were inconclusive although a positive flux was observed in the flux chamber experiment. The question remains whether the snow-pack actually accumulates methanol over the season. Since reaction of OH with methanol leads to the production of formaldehyde, this could be a (photochemistry driven) route to formaldehyde formation in the snow. Clearly, measurements of methanol in the snow are warranted to shed light on this interesting hypothesis. As expected, methanol did not show much correlation with O_3 during depletion episodes. Since the observed methanol levels were much higher than expected based on known gas phase chemical production we are left to speculate that entirely different processes determine the concentration of methanol compared to the carbonyls in the Arctic atmosphere and in the snow-pack air.

Acknowledgements

The help of Alan Gallant and Peter Brickell (MSC) in all aspects of this project is gratefully acknowledged. We also thank the other participants in the ALERT2000 project and the staff of CFS Alert for their support.

References

Albert, M.R., McGilvary, W.R., 1992. Thermal effects due to air flow and vapor transport in dry snow. Journal of Glaciology 38, 129.

Albert, M.R., Grannas, A.M., Bottenheim, J.W., Shepson, P.B., Perron Jr., F.E., 2002. Processes and properties of snow-air transfer in the high Arctic with application to interstitial ozone at Alert, Canada. Atmospheric Environment 36, 2779–2787.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson Jr., R.G., Kerr, J.A., Troe, J., 1992. Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement IV IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. Journal of Physical and Chemical Reference Data 21, 11245–11568.

Beine, H.J., Honrath, R.E., Dominé, F., Zhou, X., Simpson, W., 2002. Snow-pile and chamber experiments during the Polar Sunrise Experiment 'Alert 2000': exploration of nitrogen chemistry. Atmospheric Environment 36, 2707–2719.

Biesenthal, T.A., 1997. The role of carbonyl compounds in tropospheric ozone chemistry. Ph.D. Thesis, York University, Canada.

Bottenheim, J.W., Boudries, H., Brickell, P.C., Atlas, E., 2002a. Alkenes in the Arctic boundary layer at Alert, Nunavut, Canada. Atmospheric Environment 36, 2585–2594.

Bottenheim, J.W., Fuentes, J.D., Tarasick, D.W., Anlauf, K.G., 2002b. Ozone in the Arctic lower troposphere during winter and spring (ALERT2000). Atmospheric Environment 36, 2535–2544.

Boudries, H., Bottenheim, J.W., 2000. Cl and Br atom concentrations during a surface boundary layer ozone depletion event in the Canadian high Arctic. Geophysical Research Letters 27, 517–520.

Couch, T.L., Sumner, A.L., Dassau, T.M., Shepson, P.B., Honrath, R.E., 2000. An investigation of the interaction of carbonyl compounds with the snowpack. Geophysical Research Letters 27, 2241–2244.

Dominé, F., Cabanes, A., Legagneux, L., 2002. Structure, microphysics, and surface area of the Arctic snowpack near Alert during the ALERT2000 campaign. Atmospheric Environment 36, 2753–2765.

DeMore, W.B., Sander, S.P., Golden, D.M., Molina, M.J., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., 1990. Chemical kinetics and photochemical data use in stratospheric modeling. Evaluation number 9. J.P.L. publication 90-1, Pasadena, CA.

Goldan, P.D., Kuster, W.C., Fehsenfeld, F.C., 1995. Hydrocarbons measurements in the southeastern United States: the rural oxidants in the southern environment (rose) program 1990. Journal of Geophysical Research 102, 26795–26807.

Grannas, A.M., Shepson, P.B., Guimbaud, C., Sumner, A.L., Albert, M., Simpson, W., Dominé, F., Boudries, H., Bottenheim, J., Beine, H.J., Honrath, R., Zhou, X., 2002. A study of carbonyl compounds and photochemistry in the Arctic atmospheric boundary layer. Atmospheric Environment 36, 2733–2742.

Grosjean, E., Grosjean, D., Gunawardena, R., Rasmussen, R.A., 1998. Ambient concentrations of ethanol and methyl tert-butyl ether in Porto Alegre, Brazil, March 1996–April 1997. Environmental Science and Technology 32, 736–742.

Guimbaud, C., Grannas, A.M., Shepson, P.B., Boudries, H., Bottenheim, J., Fuentes, J.D., Dominé, F., Houdier, S., Perrier, S., Biesenthal, T.B., Splawn, B.G., 2002. Importance of the snow-pack inn processing acetaldehyde and acetone in the Arctic atmospheric boundary layer. Atmospheric Environment 36, 2743–2752.

Houdier, S., Perrier, S., Dominé, F., Grannas, A.M., Guimbaud, C., Shepson, P.B., Boudries, H., Bottenheim, J.W., 2002. Acetaldehyde and acetone in the snowpack near Alert during Polar Sunrise Experiment 2000. Snowpack composition, incorporation processes, and atmospheric impact. Atmospheric Environment 36, 2609–2618.

Hutterli, M., Rothlisberger, R., Bales, R.C., 1999. Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland. Geophysical Research Letters 26, 1691–1694.

Jobson, B.T., Niki, H., Yokouchi, Y., Bottenheim, J., Hopper, F., Leaitch, R., 1994. Measurements of C_2–C_6 hydrocarbons during the Polar Sunrise Experiment 1992: evidence for Cl atom and Br atom chemistry. Journal of Geophysical Research 99, 25355–25368.

Lee, Y., Zhou, X.K., Hallock, K., 1995. Atmospheric carbonyl compounds at a rural southeastern United States site. Journal of Geophysical Research 100, 25933–25944.

Leithead, A., Li, S.M., Toom-Sauntry, D., 2000. Water soluble organic carbon in fresh snow and snow-pack near Alert during the ALERT2000 experiment. Poster # A22C-15, Presented at the Annual Fall Meeting of the AGU, San Francisco, December.

Rasmussen, R.A., Khalil, M.A.K., 1983. Altitudinal and temporal variation of hydrocarbons and other traces of Arctic haze. Geophysical Research Letters 10, 144–147.

Rudolph, J., 1995. The tropospheric distribution and budget of ethane. Journal of Geophysical Research 100, 11369–11381.

Sander, R., 1998. Compilation of Henry's Law Constants for inorganic and organic species of potential importance in environmental chemistry. http://www.mpch-mainz.mpg.de/~sander/res/henry.html, p. 37.

Shepson, P.B., Sirju, A.P., Hopper, J.F., Barrie, L.A., Young, V., Niki, H., Dryfhout, H., 1996. Sources and sinks of carbonyls compounds in the Arctic Ocean boundary layer: polar Ice Flow Experiment. Journal of Geophysical Research 101, 21081–21089.

Simpson, W.R., King, M.D., 2002. Atmospheric photolysis rates during the Polar Sunrise Experiment ALERT2000 field campaign. Atmospheric Environment 36, 2471–2480.

Singh, H.B., O'Hara, D., Herlth, D., Sachse, W., Blake, D.R., Bradshaw, J.D., Kanakidou, M., Crutzen, P.J., 1994. Acetone distribution in the atmosphere: distribution, sources and sinks. Journal of Geophysical Research 99, 1805–1819.

Singh, H.B., Kanakidou, M., Crutzen, P.J., Jacob, D.J., 1995. High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere. Nature 378, 50–54.

Singh, H., Chen, Y., Taabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F., Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Saches, G., Vay, S., Kondo, Y., 2000. Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic. Journal of Geophysical Research 105, 3795–3805.

Splawn, B.G., Shepson, P.B., Ridley, B., Bottenheim, J., Barrie, L., Anlauf, K., 1998. A Study of carbonyl compound chemistry during the Polar Sunrise Experiment 1998. Poster #A11A-21 Presented at the Annual Fall Meeting of the AGU, San Francisco, December.

Sumner, A., Shepson, P., 1999. Snow-pack production of formaldehyde and its effect on the Arctic troposphere. Nature 398, 230–233.

Sumner, A.L., Shepson, P.B., Grannas, A.M., Bottenheim, J.W., Anlauf, K.G., Worthy, D.E.J., Dominé, F., Houdier, S., 2002. Atmospheric chemistry of formaldehyde in the Arctic troposphere at Polar Sunrise, and the influence of the snowpack. Atmospheric Environment 36, 2553–2562.

Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., Crutzen, P.J., 1999. Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by abiological processes: significance for atmospheric HO_x chemistry. Global Biogeochemical Cycles 13, 9–17.

Worthy, D.E.J., Trivett, N.B.A., Hopper, J.F., Bottenheim, J.W., Levin, I., 1994. Analysis of long-range transport events at Alert, northwest territories, during the Polar Sunrise Experiment. Journal of Geophysical Research 99, 25329–25344.

Yokouchi, Y., Akimoto, H., Barrie, L.A., Bottenheim, J.W., Anlauf, K., Jobson, B.T., 1994. Serial gas chromatographic/mass spectrometric measurements of some volatile organic compounds in the Arctic atmosphere during 1992 Polar Sunrise Experiment. Journal of Geophysical Research 99, 25379–25390.