Seasonal cycles of nonmethane hydrocarbons and methyl chloride, as derived from firn air from Dronning Maud Land, Antarctica

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[1] This paper presents atmospheric concentrations of ethane, propane, acetylene, and methyl chloride, inferred from firn air by using a numerical one-dimensional firn diffusion model. The firn air was collected on the Antarctic plateau in Dronning Maud Land during the Norwegian Antarctic Research Expedition (NARE) 2000/2001. The influences of seasonal variations in temperature and pressure and the variation in accumulation rate were studied and are not negligible, but appear to cancel each other out if all variability is taken into account. This paper also demonstrates that firn air from the uppermost firn layer (30 m) can be used to derive seasonal cycles of these trace gases, without needing a year-round facility. These cycles display higher atmospheric mixing ratios during the Antarctic winter and lower atmospheric mixing ratios in summer. The cycles for the year 2000 show amplitudes of 140 ± 25 ppt for ethane, 30 ± 10 ppt for propane, 24 ± 6 ppt for acetylene, and 40 ± 20 ppt for methyl chloride. For ethane and propane the amplitudes and months of maximum atmospheric concentration (phase) are in reasonable agreement with year-round measurements at the South Pole and Baring Head (New Zealand). The amplitudes for methyl chloride and acetylene are significantly greater than seen in year-round measurements at the South Pole and at Neumayer (Antarctica), although the phase is in line. While biomass burning and removal by OH radicals can partially explain these large amplitudes, the exact cause still remains unclear for methyl chloride and acetylene. INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: firn air, seasonal cycles, NMHC, methyl chloride


1. Introduction

[2] This paper shows that it is possible to infer seasonal trace gas cycles from firn air samples instead of direct atmospheric measurements. This eliminates the need for a year-round operating facility to carry out atmospheric measurements.

[3] Trace gas data from the Antarctic continent can help clarify the concentration variations of nonmethane hydrocarbons (NMHCs; in this paper, ethane (C2H6), propane (C3H8) and acetylene (C2H2)). NMHCs and methyl chloride play a major role in atmospheric photochemistry, which

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[5] The previous studies were all based on direct measurements, but air stored in Antarctic firn preserves a record of past atmospheric composition and can provide useful trace gas data as well. Air at the firn surface diffuses into this porous medium until the open pores are sealed off as a result of the increasing density of the firm with depth. Owing to the decreasing diffusion rate of the air with depth, seasonal variations can only be observed in the upper part of the firm. By using a one-dimensional (1-D) numerical firn diffusion model, we were able to derive the seasonal cycle for NMHCs and methyl chloride from firn air. We included an investigation into the effects of local meteorological variability on firn air diffusion, to make sure that the signal we observed in the firn air is not due to meteorological variations over a year.

[6] This paper is organized as follows. In the next section, we briefly describe the firn sampling procedure and firn air measurements, and then continue with a brief description of the diffusion model. In section 4, we discuss experiments to investigate the model’s sensitivity to seasonal variability in the meteorological parameters (temperature, pressure and accumulation). We then present the retrieved seasonal cycles for the NMHCs and methyl chloride.

2. Sampling and Analysis

[7] Firn air samples were all collected in January 2001 (all samples within 6 days) at site M (75.00°S, 15.00°E, 3453 m a.s.l.) on the Antarctic plateau in Dronning Maud Land during the NARE 2000/2001 expedition [Winther et al., 2002]. Owing to the low annual mean temperature (−51°C), pressure (615 hPa) and accumulation (5.0 cm w.e.a−1) at this site [Winther et al., 1997; van den Broeke et al., 1999], the density (ρ) of the firm increases only slowly with depth. Pore close-off, where ρ becomes 830 kg m−3, is located at 101 ± 1 m.

[8] We used a firm air pumping system [Bräunlich et al., 2001] to sample firn air after every 8 m of drilling until pore close-off. After 8 m of drilling, the drill was removed and a 5-m-long inflatable rubber bladder was inserted to seal the borehole and prevent contamination from the surface. Two 100-m-long 3/8-inch tubes made of perfluoroalkoxy alkane (PFA) penetrated through the bladder and connected the bottom of the borehole with the pumping system at the surface. Prior to the expedition, the complete system had been tested under laboratory conditions, while sampling pure nitrogen; the amount of contamination was below detection limits. Samples were collected in 1.5 L electro-polished stainless steel canisters that, prior to the expedition, had been precleaned and filled with pure nitrogen in order to prevent contamination during transport. On site, the flasks were flushed with 5 volumes of firm air to remove the pure nitrogen and then filled to a pressure of 2 bars, using the Parker two-stage metal bellows pump at a flow rate of 12 L/min. The sampling procedure of the stainless steel canisters took roughly 5 min, including flushing.

[9] Before sampling, we measured the difference in CO2 concentration between the firm air and the surface air with a LI-COR LI-6262 analyzer. The surface air was sampled approximately 10 m upwind from the drill tent via a 15-m-long 1/4-inch PFA tube, in order to prevent contamination from generators. We started collection of samples when the CO2 content of the firm air had stabilized.

[10] The samples were transported to the Netherlands; the time between sampling and analysis was 3 months. We conducted storage tests before the expedition, in which stainless steel canisters were filled with standard gases with known concentrations of chlorocarbons and NMHCs and stored those in a freezer at −20°C for 2 months. We observed no significant gas loss or production.

[11] The air in the stainless steel canisters was analyzed by gas chromatography for CO2, NMHCs, chlorocarbons, CFCs, and aromatic compounds (see Scheeren et al. [2002] for details). A flame ionization detector was used for NMHCs (ethane, propane and acetylene) and aromatic compounds (benzene and toluene), and an electron capture detector was used for chlorocarbons (including CH3Cl) and CFCs. The precision of the analyses (1σ) was 2% for CFC-12 and methyl chloride, and 5% for the NMHCs. Accuracies were 5% for the NMHCs (12% for ethane), methyl chloride and CFC-12, determined with standard commercial gas mixtures (PRAXAIR). The absolute concentrations in our PRAXAIR standards were checked by a comparison with NOAA/CMDL (S. A. Montzka; see Scheeren et al. [2002]). The detection limits for these gases are 15 ppt for methyl chloride and CFC-12 and 5 ppt for the NMHCs. At the detection limit, the precision (1σ) is 50%.

[12] Aromatic compounds such as benzene and toluene were measured to determine the degree of sample contamination by the pumping system and during transport by ship. The values for the aromatic compounds were around the detection limit (15 ppt for benzene and toluene, which is relatively high). We can therefore rule out a large degree of contamination, but some contamination of the samples could still have occurred. According to Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) data, the concentrations of benzene and toluene at the South Pole in the summer period are 5 to 10 ppt for benzene and less than 5 ppt for toluene.

[13] We measured the 29N2 profile with depth in order to constrain thermodiffusion as explained in section 3. The 29N2 of the firm air samples (from the stainless steel canisters) was obtained by correcting the measured nitrogen ratio with laboratory working 29N2 standards. The Centre for Isotope Research at Groningen, where the analyses were carried out, adapted the method of Bender et al. [1994] and used a dedicated dual-inlet isotope ratio mass spectrometer (Micromass Optima) for the analysis of 29N2 (as well as 34O2, 6Ar/N2 and 8O2/N2, simultaneously). The results are given on a per-mil scale relative to the uppermost sample of the profile.

[14] Outliers in the measured isotopic ratios relative to the model profile appear in the samples from 56 m and 80 m depth (Figure 1; the error bars represent the 1σ analytical error). We have been unable to find an analytical reason that would justify rejecting these outliers. Even though the analytical error in Figure 1 is small, there is some scatter in the 29N2 profile. This scatter can be a result of storage artifacts and transport contamination. These nonanalytical errors have only a small effect on the concentration profiles of the NMHCs and methyl chloride because larger differ-
from 48 m did not contain enough air to measure the NMHCs; the concentrations of benzene and toluene were below the detection limit for these depths. The sample from 56 and 80 m did not contain enough air to measure the 29N2 profile with depth. The error precision. We assumed 29N2 to be zero at the surface. The modeled result, with thermal diffusion included to take the effect of thermal changes in the firn layer into account, is shown as a solid line. From these analyses the temperature profile at site M was obtained (Figure 2).

3. Diffusion Model

3.1. Model Description

The basic equations for gas diffusion in the open channels of the firn layer are described in terms of the gas flux $J_{(z,t)}$ (where $z$ is the depth in the firn layer, and where $t$ is time; equation (1)), first introduced by Schwander et al. [1993]. From this equation, the concentration $C_{(z,t)}$ in the firn layer can be determined.

$$J_{(z,t)} = J_{\text{Molecular diffusion}} + J_{\text{Gravity}} = -D_{(z,t)} \left( \frac{\partial C_{(z,t)}}{\partial z} + \frac{M g C_{(z,t)}}{R T_{(z,t)}} \right)$$  

Here, $D_{(z,t)}$ is the total diffusion coefficient, $R$ is the gas constant, $g$ is the gravitational constant, $T$ is the temperature in K at a certain depth $z$ in time $t$, and $M$ is the molecular mass (g/mol). The first term between the brackets, $\partial C_{(z,t)}/\partial z$, is the variation of the time-dependent concentration $C_{(z,t)}$ with depth $z$; the second term, $M g C_{(z,t)}/R T_{(z,t)}$, describes the effect of gravity on the diffusion ($J_{(z,t)}$). The diffusion coefficient is based on the following equations:

$$D_{(z,t)} = \frac{D_{(z)} D_{\text{m,ref}}}{1 + 0.5 \gamma_{(z)} (1 - \pi_{\text{open}}(z))}$$  

$$D_{\text{m,ref}} = D_{\text{m,ref,P0}} \left( \frac{T_{(z)}}{T_0} \right)^{1.85}$$  

$$P_{(z)} = P_{(z=0)} \exp \left( \frac{M u g z}{R T_{(z)}} \right)$$  

The total diffusion coefficient $D_{(z,t)}$ is a function of the species-characteristic diffusion coefficient $D_{12}$ (relative to CO2), a correction term for atmospheric temperature and pressure $D_{\text{m,ref,P0}}$ (equation (3)), the open porosity profile $\pi_{\text{open}}(z)$ and the tortuosity function $\gamma_{(z)}$ [Schwander et al., 1993; Spahni et al., 2003; Fabre et al., 2000]. The open porosity profile is an inverse function of the density profile and was described by Schwander [1989] and Kaspers et al. [2004]. The 3-D structure of the porous firn layer is represented by $\gamma_{(z,t)}$, which is the main tuning parameter in the model, described for site M by Kaspers et al. [2004]. The diffusion coefficient $D_{\text{m,ref,P0}}$ is expressed in equation (3), where $D_{\text{m,ref,P0}}$ is a constant diffusion coefficient (12.2 $\times$ 10$^{-6}$ cm$^2$ s$^{-1}$: $T_0 = 253$ K, $P_0 = 1013$ hPa) and $P_{(z,t)}$ (equation (4)) is the pressure as function of depth and time, $P_{(z=0,t)}$ is the time-dependent surface pressure (obtained from an automatic weather station (AWS) located at site M [van den Broeke et al., 1999]). The temperature profile $T_{(z,t)}$ is derived from equation (5) [van der Veen, 1999] as described below.

$$T_{(z,t)} = T_{(z=0,t)} - \Delta T_{(t)} \exp (-\alpha z)$$  

Here, $T_{(z=0,t)}$ is the time-dependent surface temperature (obtained from an AWS located at site M [van den Broeke et al., 1999]), $\Delta T_{(t)}$ is the time-dependent temperature difference between the temperature in the firn layer and the mean temperature at 10 m depth, and $\alpha$ (5.0 $\times$ 10$^{-3}$) [Grew and Ibbs, 1952] is the thermal diffusion factor. $\Delta T_{(t)}$ follows from calibration of the model with $\delta^{29}$N2, as described below.

[15] To calibrate the diffusion model for site M, we used the measured CO2 concentration profile with depth in the firn layer and the concentration history of CO2 in the atmosphere, as determined from the Siple Dome ice core for the years 1750–1976 [Neftel et al., 1985; Stauffer et al., 1985] and from directly measured NOAA-CMDL South Pole data for 1976 to the present. The model was calibrated for site M by adjusting the tortuosity $\gamma_{(z)}$ to fit the modeled CO2 profile to the measured profile to within 1 ppm [Kaspers et al., 2004]. The model consists of 300 layers in the vertical; each layer contains the same amount of air, resulting in increasing layer thickness with increasing depth (0.5 m at pore close-off depth, 101 m). The age of CO2 at

![Figure 1. Measured $\delta^{29}$N2 profile with depth. The error band represents the 1σ precision. We assumed $\delta^{29}$N2 to be zero at the surface. The modeled result, with thermal diffusion included to take the effect of thermal changes in the firn layer into account, is shown as a solid line. From these analyses the temperature profile at site M was obtained (Figure 2).](image-url)
pore close-off was 28 ± 3 years. Note that each trace gas has a different pore close-off age because of its species-specific diffusion coefficient $D_{12}$.

[17] We included the effect of thermal changes in the firm layer during one year by means of a thermal diffusion term in the diffusion model, as proposed by Severinghaus et al. [2001] and rewrote equation (1) as

$$J_{(z,t)} = -D_{(z,t)} \left( \frac{\partial C_{(z,t)}}{\partial z} + \frac{MgC_{(z,t)}}{RT_{(z,t)}} + \Omega \frac{\partial T_{(z,t)}}{\partial z} \right).$$

According to Severinghaus et al. [2001], the thermal diffusion coefficient $\Omega$ for the South Pole is $4.5 \times 10^{-6} \% \, K^{-1}$.

[18] Figure 1 depicts the measured $^{39}N_2$ depth profile. Also shown are the model results, including thermal diffusion, using a $^{39}N_2$ ratio of zero at the surface and the temperature-depth profile of equation (5) as input parameters over 100 model years. The values for $\Delta T_{(t)}$ and $\Omega$ were calculated by minimizing the difference between the modeled $^{39}N_2$ profile and the measured profile. For site M, we calculated a value for $\Omega$ of $4.5 \times 10^{-6} \% \, K^{-1}$, which is equal to the value of Severinghaus et al. [2001] for the South Pole. The temperature profile in Figure 2 is asymmetric, because of the seasonally varying surface temperature ($T_{(z=0,t)}$, in equation (5)), which is typical for Antarctica [van den Broeke, 1998].

[19] We did not explicitly account for wind pumping in our model since the diffusion rate near the surface is already very high, which implies complete mixing above the first level of the measurements (8 m). This result is consistent with findings of Albert and Hawley [2002], who showed that wind pumping only influences the first 4 to 5 m of the firm layer.

3.2. Obtaining Time Series and Seasonal Cycles

[20] Our diffusion model is a numerical model working in the forward mode, creating therefore a concentration profile with depth. We calibrated the diffusion model for our specific site (site M) with the known CO$_2$ atmospheric history. Subsequently, we used an inverse method to obtain times series for the surface, from measured concentration profiles of NMHCs. This method was described in detail by Kaspers et al. [2004] and first used by Butler et al. [1999]. This procedure produces an error estimate based on the 1σ precision of the measured concentration profile.

[21] For the measured concentration profile of CFC-12 with depth (Figure 3a), we assumed that the temporal history of CFC-12 could be described by a Gaussian function:

$$C_{CFC-12,(0,t)} = \alpha \exp \left\{ -[\beta(t - \chi)]^2 \right\}$$

$C_{CFC-12,(0,t)}$ is the concentration of CFC-12 in the atmosphere over Dronning Maud Land as a function of time ($t$ in years). The constants $\alpha$, $\beta$ and $\chi$ were found through an iterative process by using the model in forward mode. With a least squares method the model performance was evaluated, such that the difference between modeled and measured CFC-12 profile with depth was minimized. All model results within the 1σ precision of the measured concentration profile (Figure 3a) were accepted as solutions for the CFC-12 atmospheric history (Figure 3b). Figure 3b shows the solution yielding the best fit. To indicate the accuracy of the method, we included the directly measured CFC-12 concentrations from Prinn et al. [2000] (solid circles) in Figure 3b. The derived CFC-12 time series displayed in Figure 3b (with $\alpha$, $\beta$ and $\chi$ of 536 ppt, $-1.6 \times 10^{-3}$ ppt yr$^{-1}$ and 1 year, respectively) was used to determine the influence of variations in meteorological parameters to the diffusion model in the sensitivity study (section 4).

[22] For the time series of ethane, propane, acetylene and methyl chloride, we used best fit functions, and linear time series instead of Gaussian functions (see Kaspers et al. [2004] for details). Such linear functions are more appropriate because previous studies with direct measurements by Khalil and Rasmussen [1999] and Clarkson et al. [1997] indicated a linear history for NMHCs and methyl chloride in the Southern Hemisphere. CFC-12 has a nonlinear history as a result of its anthropogenic origin and emission regulations [Prinn et al., 2000].

[23] We superimposed a sine function, as indicated in equation (8), on the linear time series for ethane, propane, acetylene and methyl chloride. The sine function represents the yearly variation in atmospheric concentration of the specific gas.

$$S_{(t)} = \epsilon \sin \left\{ \frac{1}{6} \pi \left( \phi + \pi_{(t)} \right) \right\}$$

Here, $S_{(t)}$ is the seasonal concentration difference from the annual mean concentration, $\epsilon$ is a constant representing the seasonal amplitude, $\phi$ is a constant representing the phase shift of the seasonal cycle, and $\pi_{(t)}$ is the number of months as function of time. We used a least squares method for
calculate values for \(e\) and \(f\), similar to how we obtained the constants for CFC-12. We studied the covariance between \(e\) and \(f\), and found that \(f\) could be determined with an error (1\(\sigma\)) of approximately 1 month; the error (1\(\sigma\)) in \(e\) is relatively large compared to the error in \(f\).

We superimposed equation (8) over all the model years for the NMHCs and methyl chloride (25 years). It should however be realized that the seasonal cycle arising from equation (8) will only be accurate for the year immediately preceding (in this study, the year 2000) because the firn air only preserves the seasonal cycle of the past year for these trace gases in the upper layer of the firn.

4. Influence of Meteorological Variability on the Diffusion Process

[25] Atmospheric temperature and surface pressure vary substantially during one year on the Antarctic plateau; they notably show the twice-yearly contraction and expansion of the circumpolar trough, known as the semiannual oscillation (SAO) [Schwerdtfeger, 1967]. We carried out a sensitivity experiment to study the contribution of meteorological variations to the model error for deriving time series of trace gas concentrations. It was not our intention to establish past meteorological conditions at the surface and we only accounted for the meteorological variability on seasonal timescales.

[26] Data from site M [Reijmer and Oerlemans, 2002] that were measured by an AWS placed at this site during the 1996/1997 NARE-EPICA expedition [Winther et al., 1997; Reijmer, 2001] covered temperature and surface pressure for the same two years (1999 and 2000) as for the obtained seasonal gas concentration cycles. From the two years of data, we constructed a mean annual cycle of temperature and surface pressure (indicated as monthly mean values in Figures 4a and 4b). The annual temperature cycle at site M (Figure 4a) is typical for the Antarctic plateau, in that it has a flat winter minimum (coreless winter) and a peaked summer maximum [van Loon, 1967; van den Broeke, 1998]. The air surface pressure (Figure 4b) shows a well-defined summer maximum in accordance with other observations [Parish and Bromwich, 1997]. On the basis of these general observations and on the basis of theory, we decided to describe the mean annual cycles of atmospheric temperature and surface pressure at site M by harmonic functions. Figures 4a and 4b display the harmonic functions for temperature and surface pressure for each of the two years. We incorporated the second harmonic functions of temperature and surface pressure one by one in the sensitivity experiment. To give an estimate of year-to-year variability, we first used the 1999 second harmonic function in the model (we used these functions over a model period of 25 years) and next, the 2000 second harmonic function for each parameter (temperature and pressure).

[27] L. Karlöf et al. (manuscript in preparation, 2004) derived the variation in accumulation over the past 8 years from the \(\delta^{18}O\) records of firn and the depth of the Pinatubo volcanic layer in 5 snow pits at and around site M. Snow pit M was located at the original site M location; the other four (Ma to Md) were located in a square of 8 by 8 km around site M [Winther et al., 2002]. The extracted accumulation variations (Figure 5) show large differences between years and sites. The average accumulation rate is 5.0 cm w.e.a\(^{-1}\) for the period 1992–2000, but the range is 2 to 8 cm w.e.a\(^{-1}\). Although there is no direct evidence for this, it is likely that the differences in the accumulation records between the different snow pits are due to snowdrift (L. Karlöf et al., manuscript in preparation, 2004). On the basis of these observations, we randomly varied the accumulation between 2 and 8 cm w.e.a\(^{-1}\) between 1975 and 1992 with a mean value of 5.0 cm w.e.a\(^{-1}\). For 1992 to 2001, we used the accumulation record of site M as input for the diffusion model.

[28] Finally, we considered the effect of the variability in temperature, surface pressure and accumulation on the diffusion of CFC-12 in the firn layer. CFC-12 is anthropo-
genic, very stable in the atmosphere (lifetime $\tau = 100$ years) [Seinfeld and Pandis, 1998] and has no seasonality. We used the CFC-12 time series of Kaspers et al. [2004] in these sensitivity experiments. Figure 3a shows the measured and modeled profiles with depth for CFC-12, with the modeled profile taken as reference, which was derived without any seasonality in the meteorological model parameters.

Figure 6 is intended to show small differences between the modeled concentration profiles of CFC-12 with meteorological variations and the reference modeled concentration profile of CFC-12 (Figure 3a, without any seasonality in the model) versus depth. In these modeled profiles, we have incorporated (seasonal) variations for only one term at a time (temperature, pressure or accumulation) and kept the others at their annual mean value. The effect of the incorporated (seasonal) variations is strongest for temperature and pressure and increases with depth. Variations in one of these parameters affect the diffusion in the firn layer significantly. In the winter, when the pressure is low, the diffusion rate is increased (see equation (3)), because of fewer collisions between molecules. The increased air flux in the upper layer influences the concentration gradient; this effect becomes more pronounced deeper in the firn, where diffusion depends only on molecular diffusion. Temperature variations in the summer lead to increased diffusion rates, whereas the diffusion rate is lower in the winter. The influence of temperature and pressure variations becomes negligibly low only very close to pore close-off, where diffusion approaches zero; here, gravitational effects and vertical movement due to snow accumulation become important. In Figure 6 the effect of accumulation variability is visible near pore close-off. The pressure and temperature variations are therefore the most important parameters in this study of the seasonal trace gas cycle. In general, the combined meteorological profiles in Figure 6 show that (seasonal) variations in meteorological parameters have only a minor influence on diffusion in the firn layer compared to decadal mean meteorological parameters. The small difference between the combined profile and the reference profile reflects that the effects of the seasonal variations of temperature, pressure and accumulation on the diffusion process cancel each other out. This is particularly true in the upper 40 m, from which seasonality of trace gases are primarily derived.

5. Results: Derived Seasonal Cycles of Methyl Chloride and NMHCs

Figure 7 presents the measured concentration profiles for methyl chloride, ethane, propane and acetylene. The 8 m
resolution equals approximately 0.3 years, according to the diffusion model, operating in forward mode; the sample from 32 m represents an age of 1.2 years. The strong decrease in concentration from a depth of 30 m toward the firn surface is due to diffusion during the summertime when the concentrations of methyl chloride and NMHCs are low [Sturges et al., 2001]. If the firn samples had been taken in the winter period, the concentrations in the firn air would have increased toward the surface. Rudolph et al. [1989] were the first to recognize the seasonal variation in trace gas concentration in the troposphere over Antarctica. Rudolph et al. [1992], Clarkson et al. [1997], and Khalil and Rasmussen [1999] observed the seasonality of trace gas concentrations over Antarctica in later studies as well. All these studies showed low NMHC and methyl chloride concentrations in the Antarctic summer (as in our surface measurements) and high concentrations in the Antarctic winter. Deeper in the firn layer, the seasonal information is lost because of diffusion, so these deeper measurements, from 40 m and beyond, represent the annual average concentration. At pore close-off, the age for NMHCs is 25 years [Kaspers et al., 2004]. For this reason, the seasonal information extracted from firn air only represents one year, the twelve months prior to sampling (in this study, the year 2000). Our main goal is to develop a method to derive seasonal information from firn air analyses. Only four measurements in the firn layer of site M contain the seasonal information of trace gas concentrations and we can therefore expect a large error in the derived seasonal cycles for NMHCs and methyl chloride from our data set.

Figure 6. Difference from the reference concentration profile (CFC-12 profile presented in Figure 3a) plotted versus depth. The circles represent profiles for which only the seasonality of temperature at the surface was used (other parameters at their annual mean value). The solid circles represent the profile for which the 1999 temperature fit was used, and the open circles represent the 2000 data of Figure 4a. The squares represent profiles for which the surface pressure seasonality of Figure 4b was included; the solid squares represent 1999 data, and the open squares indicate 2000 data. The profile due to the accumulation variability is presented by solid triangles. When all meteorological parameters (T, P, and A) are taken into account, one obtains the thick solid line.
measured period of 1984 to 1990. Our derived seasonal cycles are all within the concentration range of these extremes and the timing of the maximum concentration is in good agreement with the measured seasonal cycles.

The following three mechanisms can partially explain the somewhat large seasonal amplitude we found for NMHCs and methyl chloride.

5.1. Oxidation Chemistry

Seinfeld and Pandis [1998] described the tropospheric chemistry of NMHCs and methyl chloride with OH radicals and other oxidizing species. Because these species are formed by sunlight, the concentrations of these highly reactive oxidizing agents are highest in the summer (January and February) and lowest in the winter period (for Antarctica, even zero because of lack of sunlight). This in turn influences the NMHC and methyl chloride concentrations.

Dibb et al. [2002], Swanson et al. [2002], Sumner et al. [2002], and Honrath et al. [2002] showed that large ice caps (in their papers, Greenland) contribute to the formation of OH radicals and other oxidizing agents. These agents form in the snow pack, from which they are emitted into the atmospheric boundary layer. Note that this phenomenon does not affect the stability of NMHCs and methyl chloride deeper in the firn layer because the reactions with OH and other oxidizing species only take place in the upper 1 or 2 m of the snow pack [Swanson et al., 2002; Kaspers et al., 2004]. Although Greenland might have slightly different chemical conditions of snow air than Antarctica (for instance, with regard to formation of CH₃Br [Swanson et al., 2002]), formation of oxidizing agents can also be expected for Antarctica because the strong seasonal cycle in shortwave radiation.

The increased concentration of oxidizing agents in the boundary layer over Antarctica in the summer results in

![Figure 7](image-url) Concentration profiles with depth for methyl chloride, ethane, propane, and acetylene. The markers present the measured concentrations with 1σ precision. The solid line shows the model result, forced with a linear time series (derived from Kaspers et al. [2004]) with the optimal seasonal sine functions (presented in Figures 8a–8d) superimposed. The quality of the modeled profiles is indicated by the correlation coefficient: \( r^2 = 0.58 \) for methyl chloride, \( r^2 = 0.76 \) for ethane, \( r^2 = 0.87 \) for propane, and \( r^2 = 0.68 \) for acetylene.

### Table 1. Comparison of the Seasonal Cycle Information of Ethane (C₂H₆), Propane (C₃H₈), Acetylene (C₂H₂), and Methyl Chloride (CH₃Cl) as Derived From Firn Air With Information From Directly Measured Tropospheric Boundary Layer Air

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<td></td>
<td>C₂H₆</td>
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<td>Reference</td>
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*The error in ε and σ represents 1σ.

extra removal of NMHCs and methyl chloride. In the winter period, when no sunlight is present and therefore no oxidizing agents are formed, the NMHCs and methyl chloride concentrations can remain high.

The oxidation conditions over a large ice sheet in summer can partially explain large seasonal amplitudes. However, the methyl chloride record of the South Pole (Table 1) where the air is expected to undergo similar processes as in Dronning Maud Land indicates that oxidation alone is not enough to explain the large amplitudes that we found (particularly for acetylene and methyl chloride).

We can therefore acknowledge that the oxidation conditions in the summer time over a large ice sheet will influence the seasonal variation of trace gas concentration, but the importance of this mechanism relative to other mechanisms is hard to assess.

5.2. Source Contribution and Transport

The sources and transport mechanisms strongly influence the seasonality of NMHCs and methyl chloride. The main source for ethane and propane is the use of natural gas whereas biomass burning is the largest source of methyl chloride and acetylene. Both sources are strongest in the winter period [Cros et al., 1988]. Although the emission of NMHCs and methyl chloride can vary between years, as indicated in the records of Rudolph et al. [1992], Clarkson et al. [1997], and Khalil and Rasmussen [1999], we have no evidence of increased biomass burning activity in the year 2000 to explain the high seasonal amplitude of acetylene and methyl chloride in our results.

Transport to Antarctica also plays an important role for the NMHCs and methyl chloride because they have relatively short atmospheric lifetimes. Both the location of the sources (mostly Africa and Southern America for our part of Antarctica) and transport result in spatial variability. Khalil and Rasmussen [1999] found a 10 ppt difference in seasonal amplitude for methyl chloride between three measured records for the South Pole, Tasmania and Samoa Southern Hemisphere.

Although these mechanisms might give an explanation for the large seasonal amplitude we found for ethane and propane, they probably only partly explain the also relatively large seasonal amplitudes for acetylene and methyl chloride. The cause of the latter therefore remains partly unclear.

6. Summary and Conclusions

We have derived the seasonal variation in atmospheric concentration of ethane, propane, acetylene and methyl
chloride from firn air analyses in Dronning Maud Land Antarctica for the year 2000. To do so, we used sine functions superimposed on linear histories of atmospheric trace gases concentrations in a firm air diffusion model. [43] The period of maximum atmospheric concentrations (φ) of ethane, propane, acetylene and methyl chloride as derived from firn air is in good agreement with that obtained from direct atmospheric measurements. The derived seasonal amplitudes for ethane and propane in this study are in agreement, within the uncertainties, with earlier seasonal cycles, directly measured at the South Pole and Baring Head (New Zealand). The seasonal amplitude for methyl chloride seems enlarged compared to directly atmospheric measurement from the South Pole, in particular when the last 10 years (the period 1990–1997) is considered. Our acetylene data show a significantly higher seasonal amplitude than the seasonal amplitude in directly measured atmospheric records [Rudolph et al., 1992; Khalil and Rasmussen, 1999]. Although three factors (variations in oxidation chemistry, sources and transport) can offer some explanation for the greater seasonal amplitude of acetylene and methyl chloride than directly measured, the exact cause remains unclear. [45] We have also considered the influence of seasonal variability in meteorological parameters (surface temperature, pressure and the variability in accumulation) on diffusion in the firm layer and tested this in a sensitivity study. The concentration profile of CFC-12 differed by at most 20 ppt (just above pore close-off depth) from a reference concentration profile of CFC-12, when we only considered the seasonality in surface temperature. The effect of the combined meteorological parameters was most pronounced deeper in the firm layer with the maximum deviation from the reference concentration profile just above pore close-off. When taking the variability of the combined meteorological parameters (φsurface, Psurface and A) into account in the diffusion model, the deviation from the reference concentration profile of CFC-12 is only minor. Apparently, the deviations due to temperature and pressure (the two major parameters) cancel each other out. Nevertheless, we did include the seasonality of temperature and pressure in our diffusion model for deriving the seasonal cycles of NMHCs and methyl chloride; there was only a 10% increase of the 1σ error bar when the seasonality of temperature and pressure was not taken into account. [46] On the basis of this study, we can give the following recommendations: (1) Recognize the valuable information the air stores in the upper layer of the firm, with respect to seasonal variability of trace gases. (2) To assess the seasonal information stored in the upper layer, more samples should be taken in the upper part of the firm layer, to increase the accuracy of the obtained seasonal cycles of trace gases. [47] More information about seasonal variations of trace gases over Antarctic is needed as this information can be used in combination with sophisticated chemical transport models. With firm air analysis, the seasonal variations in trace gas concentrations over Antarctica can be obtained without the need for an all-year-round facility. 

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