Analyses of firn gas samples from Dronning Maud Land, Antarctica: Study of nonmethane hydrocarbons and methyl chloride


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[1] Firn air was sampled on the Antarctic plateau in Dronning Maud Land (DML), during the Norwegian Antarctic Research Expedition (NARE) 2000/2001. In this paper, we describe the analyses for methyl chloride and nonmethane hydrocarbons (NMHCs) in these firn air samples. For the first time, the NMHCs ethane, propane, and acetylene have been measured in Antarctic firn air, and concentration profiles for these gases have been derived. A one-dimensional numerical firn air diffusion model was used to interpret the measured profiles and to derive atmospheric concentrations as a function of time. The atmospheric trends we derived for the NMHC and methyl chloride at DML cover the period from 1975 to 2000. Methyl chloride shows a decreasing trend of 1.2 ± 0.6 ppt per year (annual mean concentration 548 ± 32 ppt). For ethane we found an increasing trend of 1.6 ± 0.6 ppt per year (annual mean concentration 241 ± 12 ppt). The concentrations of propane and acetylene appear to be constant over the period 1975–2000, with annual mean concentrations of 30 ± 4 ppt for propane and 24 ± 2 ppt for 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, NMH and methylchloride, atmospheric trends


1. Introduction

[2] Chemical analyses of air trapped in firn allow the reconstruction of the concentrations of atmospheric trace gases. Such a record can go back beyond the earliest direct measurements and can be obtained for remote locations [Schwander et al., 1993; Butler et al., 1999].

[3] This paper focuses on nonmethane hydrocarbons (NMHC) and methyl chloride. These gases play an important role in tropospheric chemistry on regional and global scales. The nonmethane hydrocarbons in this paper, ethane, propane and acetylene, react strongly with OH radicals, which are a major oxidizing agent of the atmosphere. Furthermore, NMHC are responsible for the formation of tropospheric ozone, which is a hazardous gas for the biosphere and acts as a greenhouse gas [Sillman et al., 1995].

[4] Methyl chloride is less reactive with OH radicals, but makes an important contribution to organic chlorine in the stratosphere [Khalil and Rasmussen, 1999]. This gas, which is emitted by biomass burning and natural sources, contributed approximately 15% of the total stratospheric organic chlorine in 1992 [Montzka et al., 1996]. Because of the emission reduction of anthropogenic halocarbons such as chlorofluorocarbons (CFCs), the relative importance of methyl chloride as a stratospheric chlorine source is slowly increasing [Khalil and Rasmussen, 1999]. In spite of numerous studies of the large-scale distribution of NMHC and methyl chloride, little is still known about their global trends [Clarkson et al., 1997; Khalil and Rasmussen, 1999].

[5] Biomass burning, natural emissions, and use of fossil fuels are the main sources of NMHC and methyl chloride in the atmosphere. The influence of biomass burning and use of fossil fuels can be estimated in Antarctica by use of methyl chloride and ethane, because the relatively long atmospheric lifetimes (τ) of methyl chloride (τ = 1.5 years) [Keene, 1999] and ethane (τ = 92 days) [Boïssard et al., 1996] permits long-range transport from anthropogenic sources to remote regions. Oceans contribute approximately 10% to the atmospheric NMHC concentrations [Clarkson et al., 1997] and significantly to the methyl chloride concentration [Keene, 1999]. This makes the oceans an important source of these gases, and for Antarctica the only local source. Background levels for propane and acetylene are therefore relatively undisturbed by local events in Antarctica.
Firm air analyses on NMHCs are presented for the first time in this paper, yielding the longest atmospheric record for ethane, propane and acetylene over Antarctica. The atmospheric seasonal cycle for the NMHCs and methyl chloride are obtained in an accompanying paper by K. A. Kaspers et al. (Analyses of firm gas samples from Dronning Maud Land, Antarctica: Derived seasonal variations of NMHCs and methyl chloride from firm air of the upper layer, submitted to Journal of Geophysical Research, 2003).

We sampled firm air at a remote location on the Antarctic plateau in Dronning Maud Land (DML) during the NARE 2000/2001 expedition [Winther et al., 2002]. We analyzed the observed concentration profiles and used a one-dimensional numerical firm diffusion model to explain the measured concentration profiles. In the section on the diffusion model we describe the method to obtain time series of concentrations at the surface from the analyzed gases, including an error estimate. This methodology is applied to obtain atmospheric records for methyl chloride, ethane, propane and acetylene over the period 1975–2000.

2. Sampling and Analyses

Firm air samples were collected at site M (75.00°S, 15.00°E, 3453 m a.s.l.) in DML during the NARE 2000/2001 expedition [Winther et al., 2002]. Because of the low annual temperature (−51°C) and accumulation (5.0 cm w.eq. a−1) at this site [Van den Broeke et al., 1999; Karlöf et al., Accumulation variability in a 8 by 8-km area, eastern Dronning Maud Land, Antarctica, as determined from shallow firm cores and snow pits: Some implications for ice core analysis, submitted to Journal of Glaciology, 2003], pore close-off (depth where the air is trapped in air bubbles) is located at a depth of 101 m (C. M. Hofstede et al., Firn accumulation records for the past 1000 years on the basis of dielectric profiling of six cores from Dronning Maud Land, Antarctica, submitted to Journal of Glaciology, 2003) (hereinafter referred to as C. M. Hofstede et al., submitted manuscript, 2003).

Samples were collected with a firm air pumping system [Bräunlich et al., 2001] (Figure 1) every 8 m 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. Two 100-m-long 3/8-inch perfluor alkoxy alkane (PFA) tubes went through the bladder and connected the bottom of the borehole with the pumping system at the surface. One of the tubes was used to pump firm air into the bladder at a flow rate of 0.4 L s−1. The other tube ended 10 cm lower, beneath an aluminum plate, and was used to sample the firm air at a flow rate of approximately 0.2 L s−1.

At the surface, the sample line was split into more PFA lines. The air was pumped directly into 5-L Tedlar sampling bags via a Teflon membrane pump (KNF Neuberger N840.3 FT.18). Precleaned electropolished stainless steel canisters of 1.5 L, filled with pure nitrogen in order to prevent contamination during transport, were used to sample firm air through a Parker two-stage metal bellow pump at a pressure of 2 bar. The metal pump was also used to pump the extracted firm air into a three-stage, oil-free, modified RIXSA 3 piston compressor [Mak and Breninkmeijer, 1994]. This compressor was used to fill high-volume air samples to ~120 bars in 5-L aluminum cylinders (Scott Marrin). All the samples were taken separately; the high-pressure samples were collected last.

Before sampling, we measured the difference in CO2 concentration of the firm air and surface air with a Lior Li6262 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 by generators. We started the collection of samples when the CO2 content of the firm air had stabilized.

The air in the stainless steel canisters was analyzed by gas chromatography (GC) for CO2, NMHCs, chlorocarbons, CFCs, and aromatic compounds (see Scheeren et al. [2002] for details). A flame ionization detector (FID) was used for NMHCs and aromatic compounds, and an electron capture detector (ECD) for chlorocarbons (including CH2Cl) and CFCs. The precision of the analyses (1σ) was 2% for CFC-12 and methyl chloride and 5% for the NMHCs. The detection limits for these gases are 15 ppt.

The Centre for Isotopic Research of the University of Groningen measured CO2 concentrations in the low-pressure samples (GC; Hewlett-Packard model 6890), expressed
on the WMO mole fraction scale and on the NOAA CMDL scale. CO₂ and CH₄ were separated on a 4-foot-long Haynes Q column. Methane was measured directly by FID. CO₂ was first converted into methane by a methanizer (nickel catalyst with hydrogen) and then measured on the same FID. The instrument’s precision, 1σ, for CO₂ was 0.1% [Ramonet et al., 2002].

Aromatic compounds such as benzene and toluene were measured in the low-pressure firm air samples to determine the amount of contamination. The values for the aromatic compounds were all around or below the detection limit (15 ppt for benzene and toluene) and we therefore concluded that none of the samples had been significantly contaminated.

3. Diffusion Model
3.1. Model Description
[15] Schwander et al. [1993] introduced the basic equations for gas diffusion in the open channels of the firn layer in terms of the gas flux J(z,t) (where z is the depth in the firn layer and t time, equation (1)). From this equation the concentration C(z,t) in the firn layer can be determined.

\[ J(z,t) = J_{\text{Molecular diffusion}} + J_{\text{Gravity}} = -D(z) \left( \frac{\partial C(z,t)}{\partial z} + \frac{MgC(z,t)}{RT} \right) \]  

(1)

Here, D(z) is the total diffusion coefficient, R the gas constant, g the gravitational constant, T the temperature in K at 10 m, and M the molecular mass (g/mol). The first term between the brackets represents the diffusion resulting from a concentration gradient and the second term the effect of gravity. The diffusion coefficient (D(z)) is based on the following equations:

\[ D(z) = \frac{D_{12}\, D_{m(z)}}{1 + 0.5(1 - \gamma_{\text{open}})} \gamma(z) \]  

(2a)

\[ D_{m(z)} = D_{T_0P_0} \left( \frac{T}{T_0} \right)^{1.85} \]  

(2b)

\[ P(z) = P_{\text{atm}} \cdot \exp \frac{-M_{\text{air}} g z}{RT} \]  

(2c)

The total diffusion coefficient D(z) is a function of the species characteristic diffusion coefficient D₁₂, the diffusion coefficient for standard temperature and pressure Dₘ₀(z) [Schwander et al., 1993; Spahni et al., 2003; Fabre et al., 2000], the open porosity profile γ₀(z) and the tortuosity function γ(z) (equation (3)). The diffusion coefficient Dₘ₀(z) is expressed in equation 2b by Dₜₒₚ₀ as the standard diffusion coefficient (12.2 × 10⁻⁶ cm s⁻¹; T₀ = 253 K, P₀ = 1013 hPa), Pₘ₀ is the pressure as a function of depth, annual surface pressure (Pₘ₀), γ₀(z) represents the three-dimensional pore structure of the firn and is used to optimize the diffusion model. Calibrating of the model yields values for γ₀ and γ(z) (J. Schwander, personal communications, 2001).

[18] The open porosity is determined from a semi empirical relation of Schwander [1989]. With this relation, the porosity can be calculated from the density profile. The density profile itself is obtained by a polynomial fit through the ice and by dielectrical profiler measurements (C. M. Hofstede et al., submitted manuscript, 2003). The resulting porosity and tortuosity profiles are shown in Figure 2, together with the measured density profile.

[19] The lower boundary condition to solve equation (1) is that \[ \frac{\partial C(z,t)}{\partial z} \] is constant. The upper boundary condition is the surface concentration as a function of time. The latter is the main output parameter of the model and was found iteratively by comparing measured and modeled concentration profiles for the different gases. The firn column was divided into 300 boxes, each containing the same amount of air, so that the firm density and porosity determine the size of the boxes. The model was calibrated with South Pole CO₂

![Figure 2. Measured density profile, indicated with dots, and the third-degree polynomial fit. Density was measured in a field lab at Site M [Winther et al., 2002]. The porosity profile indicated by black triangles (including the open porosity, open triangles) was extracted from the empirical relations by Schwander [1989]. The tortuosity profile (open circles) was obtained from the open porosity as indicated in equation (3). The horizontal dotted line indicates the pore close-off depth.](image-url)
ice core data [Siegenthaler et al., 1988] and NOAA-CMDL South Pole data (1976 to present) to simulate the measured CO$_2$ concentration profile (Figure 3). The model result yields a mean age of 28 ± 3 years at pore close-off for CO$_2$. This result was obtained with values for $\gamma_a$ and $\gamma_b$ being 0.98 and 3.2.

3.2. Obtaining Time Series

[20] The model we have used is a numerical model for diffusion in the forward mode, creating a concentration profile. We used the known CO$_2$ atmospheric history, to calibrate the diffusion model for our specific site (Site M). After we calibrated the diffusion model, an inverse method was used to obtain times series at the surface from the measured concentration profile. Here we describe the inverse method that is able to give an error estimate based on the 1σ precision of the measured concentration profile. We describe the inverse method based on CFC-12 measurements (Figure 4). CFC-12 is only emitted by anthropogenic sources [Butler et al., 1999], its lifetime in the atmosphere is 105 years and the gas is chemically inert. Therefore CFC-12 is a very useful gas to test the inverse method. First we adopt an optimal function that best describes the concentration history of CFC-12.

[21] CFC-12 appeared in the atmosphere in the early 1950s. The use and emission strongly increased over the years, until the recognition of its harmful effects on the environment. Emission regulations were agreed upon in the Montreal protocol of 1989, resulting in strongly reduced emissions and a stabilisation of the atmospheric concentration [Prinn et al., 2000]. We assume that the history of CFC-12 can be described by a Gaussian function:

$$C_{\text{CFC-12}}(t) = \alpha \cdot e^{-\left(\frac{t-\chi}{\beta}\right)^2}$$

$C_{\text{CFC-12}}(0,0)$ 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 derived from an iterative process using the model in forward mode. The model performance was evaluated with a least squares method, such that the difference between modelled and observed CFC-12 profile was minimized. All model results within the 1σ precision of the measured concentration profile were accepted as solutions for the CFC-12 atmospheric history. Taking the error in the diffusion coefficient into account (Table 1), we were able to derive an upper and lower limit for the derived time series (Figure 5 and Table 2). There is a good agreement with the directly measured data of Prinn et al. [2000] (Figure 5). Our results are furthermore in line with the firn air analyses in DML and at Dome Concordia by Sturges et al. [2001] analyses from Law Dome by Sturrock et al. [2002] and analyses from Butler et al. [1999].

[22] Here, we have indicated that the inverse modeling method yields good results to extract the atmospheric history of a gas over DML from firn air.

[23] Of course, one could argue that we should use other functions than the Gaussian functions. Tests do, however, show no significant improvements. In the next section, we use linear time series for ethane, propane, acetylene and methyl chloride (instead of Gaussian functions). Such functions are more appropriate because previous studies from direct measurements by Khalil and Rasmussen [1999] and Clarkson et al. [1997] indicate a linear history for NMHC and methyl chloride in the Southern Hemisphere. No maximum is to be expected like that of CFC-12, whose nonlinear history is the product of its anthropogenic origin and emission regulations.

4. Nonmethane Hydrocarbons and Methyl Chloride Analyses in Firn Air

[24] The concentration profiles for methyl chloride, ethane, propane and acetylene represent the period from
Table 2. Constants $\alpha$, $\beta$ and $\chi$ for the Anthropogenic Gas CFC-12, for a Gaussian Fit$^a$

<table>
<thead>
<tr>
<th>CFC-12 (CF$_2$Cl$_2$)</th>
<th>$\alpha$, ppt</th>
<th>$\beta$, ppt yr$^{-1}$</th>
<th>$\chi$, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper limit</td>
<td>538</td>
<td>$-1.2 \times 10^{-4}$</td>
<td>2</td>
</tr>
<tr>
<td>Best fit</td>
<td>536</td>
<td>$-1.6 \times 10^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>Lower limit</td>
<td>530</td>
<td>$-2.0 \times 10^{-4}$</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$These constants are derived using the method of the least squares through the measured concentration profile of Figure 4. Uncertainties in the measured profiles and scaling factors (Table 1) for the molecules are incorporated in these values.

1975 to 2000 deduced from model age at pore close-off depth (Figure 6). All gases show a strong decrease in concentration toward the surface in the top 20 m of the firn layer. This part of the firn air is influenced by seasonal variations in gas mixing ratios at the surface and seasonal variations in meteorological parameters.

[25] A close examination of the middle and deeper part of the concentration profile (from 30 to 100 m) reveals some fluctuation superimposed on any long-term trend in the concentration with depth. This fluctuation seems similar for methyl chloride, ethane and propane. Ethane and propane are measured both on a FID detector with gas chromatography, while methyl chloride and CFC-12 were measured by an ECD detector. Therefore this coherent variation seems not to be caused by the sampling or detection.

[26] In order to test whether the fluctuation in the concentration profiles was the result of regular long-term variability in the records we tried to fit the data to sine functions with periods ranging from 1 to 10 years superimposed on the time series for these gases in the diffusion model. However this could not completely explain the observed variability in the concentration profiles. Instead, it appears that fluctuations at the surface diffuse strongly to yield a smooth gradual concentration gradient in the lower parts of the column. Although we could not find a simple explanation for the observed co-variances in the concentration profiles, they are within the 1σ range of the measurements, so we choose to ignore them in order to obtain time series for the gases of Figure 6. For this purpose we used the inverse modelling method described in section 3.2 using a linear time series for the NMHCs and methyl chloride to retrieve the concentration profiles shown in Figure 6. Superimposed on these linear time series we placed a sine function to account only for the seasonal variations of the NMHCs and methyl chloride.

[27] Our computed profiles generally agree well with the observations (Figure 6). These profiles yielded the time series for ethane, propane, acetylene and methyl chloride in the atmosphere shown in Figure 7. Along with our derived concentrations from Figure 7, Table 3 presents direct atmospheric measurements at South Pole [Clarkson et al., 1997; Khalil and Rasmussen, 1999] and Neumeyer station [Rudolph et al., 1992] at Antarctica and from Cape Grim [Lewis et al., 2001] and Baring Head [Clarkson et al., 1997]. The measurements done by Gros et al. [1998] represent marine boundary layer air measured during a cruise in the summer of 1993 and Blake et al. [1999] measured marine boundary layer air during an aircraft campaign in 1995. The measured values from these studies vary strongly with location obscuring a direct comparison. It is therefore important to gain more and longer records for these gases in the Southern Hemisphere. From our firn air analyses we were able to lengthen the records significantly to 25 years for the NMHCs and methyl chloride. The results we added to this list represent free atmospheric concentrations and agree well with the other studies. Although the background concentration for ethane seems to be significantly lower than earlier observations by Rudolph et al. [1992] from Neumayer station over the period 1984–1990. On the other hand, our result, for ethane are in line with the observations from two stations (South Pole and Baring Head) measured by Clarkson et al. [1997] and the marine boundary layer air measured by Gros et al. [1998].

[28] Because this is the first time that NMHC are analysed from firn air, some indication about the stability of these gases in the firn layer is needed. Seinfeld and Pandis [1998] describe the tropospheric chemistry of NMHC to be highly reactive to OH radicals and other oxidizing species. Dibb et al. [2002], Swanson et al. [2002], Sunner et al. [2002] and Honrath et al. [2002] describe the concentration of reactive gases in the snow layer and emission of OH radicals and other reactive gases like NO$_x$, HONO, HNO$_3$ from the snow pack into the atmosphere above an ice cap. Reactions of NMHC and methyl chloride with these emitted oxidizing species like OH might therefore explain the low concentration in the atmosphere of the NMHC over Antarctica. Though deeper in the firn layer, reactions with these oxidizing species are not to be expected because of the following: (1) OH radicals are photo chemically produced.
and sunlight only penetrates the snow layer for less than 1 m [Warren, 1982]. We can therefore safely assume that there will be no formation of OH radicals deeper in the firm layer. (2) The lifetime of OH radicals in the atmosphere is only a few seconds [Seinfeld and Pandis, 1998]; therefore it is safe to assume that the OH radicals will not diffuse deep in the firm layer and that reactions with these radicals are insignificant at 8 m depth (first firm air measurement). This concept is confirmed by Swanson et al. [2002], who showed the concentration profile of ethane and propane from 0–2 m in the snow and firm on Summit (Greenland). Their profiles do not show any loss or production in this part of the firm.

[29] Below this upper zone, NMHC, are stored in the firn layer, which is a dark and cold environment. We can therefore expect that these gases remain stable in concentration simply because of the lack of reactive oxidizing gases and radicals like OH. We assume that the firm air concentrations represents smoothed mean annual concentrations except for the first 20 m from the surface, which is influenced by the seasonal variations.

[30] Linear trends of ethane, propane, acetylene and methyl chloride over the past 25 years (1975–2000) over DML are presented in Figure 8. For methyl chloride we derived a decrease of $1.2 \pm 0.6$ ppt per year. A study of methyl chloride by Khalil and Rasmussen [1999] reports a similar decreasing trend; the concentrations measured at South Pole between 1984 and 1994 according to Table 3 varied between 477 and 596 ppt. The trends observed for several locations in that study however strongly deviate from the average global trend. Butler et al. [1999] performed a firm air study at South Pole. In their study they found an increasing trend from the beginning of the twentieth century to the 1970s. From approximately 1975 to 1999, their derived history for methyl chloride seems to stabilize and becomes more comparable to our data, though Butler et al. [1999] had derived a somewhat lower concentration range of 480–521 ppt for the same period (1975–1999) (Table 3). Because of the uncertainties for measuring methyl chloride our obtained concentration range is inline with the other studies for this gas.

[31] A nearly constant level for acetylene and propane was derived for the period of 1975–2000. These gases are produced mainly by biomass burning and fossil fuel use.
However propane and, to a lesser extent, acetylene
[Kanakidou et al., 1988] are also emitted by the ocean
[Lewis et al., 2001], which is the only local source for our
samples. The measurements for propane and acetylene can
therefore only be used to determine background concentration
over DML, as the lifetime for these gases is only
1 month in the atmosphere [Boissard et al., 1996].

In contrast to acetylene and propane, the concentration of ethane appears to have increased in the troposphere (1.6 ± 0.6 ppt per year). Because of the longer lifetime of ethane (τ = 92 days in the atmosphere) relative to propane and acetylene, transport from a larger area can be expected [Boissard et al., 1996] and, hence, a stronger influence of biomass burning and natural gas use. According to the IPCC report [Houghton et al., 2001], the use of land has changed significantly in the Southern Hemisphere in the last 25 years, leading to an increase in biomass burning and fossil fuel use. This is consistent with increased NMHC emission from these anthropogenic sources [Rudolph et al., 1992; Clarkson et al., 1997], yielding the increasing trend observed for ethane in the Antarctic firm.

5. Conclusions

We used a measured concentration profile for CO₂ and the South Pole atmospheric measurements to optimize a numerical diffusion model, and determined the mean age of CO₂ at pore close-off to be 28 ± 3 years. An inverse modeling approach, verifying the CFC-12 measurements, was used to retrieve time series from the measured concentration profiles in firn for ethane, propane and acetylene, yielding the atmospheric trends for these gases between 1975 and 2000 over DML. Background concentrations of 24 ± 2 ppt for acetylene and 30 ± 4 ppt for propane appeared fairly constant during the past 25 years. In contrast to acetylene and propane, methyl chloride and ethane show significant trends. We derived an increase of ethane, of 1.6 ± 0.6 ppt per year with a background surface concentration of 241 ± 12 ppt in 2000. This background concentration seems to be significantly lower than earlier observations by Rudolph et al. [1992] for Neumayer station over the period 1984–1990. On the other hand, the ethane result is consistent with the observations by Clarkson et al. [1997] and Gros et al. [1998]. For methyl chloride analyzed from firn air, we deduced a background surface concentration of 548 ± 32 ppt in 2000 and a decrease of 1.2 ± 0.6 ppt per year over the past 25 years. This result is in reasonable agreement with earlier published observations by Khalil and Rasmussen [1999] and Butler et al. [1999] for the period between 1976 and 1999 given the expected variability in this gas. The concentration range for methyl chloride from Butler et al.’s study appears to be a slightly lower (480–521 ppt; from 1900 to 1999) than our results. Clearly, more extracted time series from firn air analyses in combination with atmospheric chemical transport models are needed to study the atmospheric trends of methyl chloride and light NMHCs over the Southern Hemisphere during the last decades.

### Table 3. Annual Mean Concentrations for Ethane (C₂H₆), Propane (C₃H₈), Acetylene (C₂H₂), and Methyl Chloride (CH₃Cl) Measured at Different Remote Locations in the Southern Hemisphere for Comparison With the Obtained Annual Surface Concentrations for the Period of 1975–2000 Over DML (Site M)^

<table>
<thead>
<tr>
<th>Period</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₂H₂</th>
<th>CH₃Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan.–Feb. 1999</td>
<td>142²</td>
<td>8.8²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1991–1996</td>
<td>296</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990–1996</td>
<td>288</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cruise 1993</td>
<td>291 ± 7b</td>
<td>61 ± 53b</td>
<td>48 ± 35b</td>
<td>540–560w</td>
</tr>
<tr>
<td>Aircraft 1995</td>
<td>300–360</td>
<td>6–12e</td>
<td>15–30º</td>
<td>540–560w</td>
</tr>
<tr>
<td>1982–1990</td>
<td>380–400</td>
<td>50–84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1984–1994</td>
<td>477–596</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1975–1999</td>
<td>480–521</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values for methyl chloride have been corrected according to Montzka et al. [2003].

Summer values.

November and December values.

Figure 8. Results from the model calculations, representing the linear trend in atmospheric surface concentration over Dronning Maud Land in the past 25 years (1975–2000). The error bars represent the modeled upper and lower limits as shown in Figure 7.
Acknowledgments. Words of gratitude should go to the Norwegian Polar Institute (NPI) for their leadership and logistics during the NARE EPICA expedition 2000/2001 and to Jacob Schwander for his firm diffusion model which would have liked to thank James Butler. The Max-Planck-Institut für Meteorologie in Hamburg, the Max-Planck-Institut für Meteorologie (NWO), the Norwegian Polar Institute (NPI) and the budget from ESF/EC scientific program, funded by the European Commission under the reviewers of this paper for their effort and the constructive comments for methyl chloride we would like to thank James Butler. The latest atmospheric chemistry, we would like to thank Bert Scheeren and the other technicians of IMAU for their work on the Licor CO2 analyzer. All participants in the field are gratefully acknowledged for their assistance other other technicians of IMAU for their work on the model. Further, we would like to thank the Instrumentele Groep Fysica Boissard, C., B. Bonsang, M. Kanakidou, and G. Lambert (1996), D02307 KASPERS ET AL.: NONMETHANE HYDROCARBON TRENDS FROM FIRN AIR Bra¨unlich, M., O. Aballain, T. Marik, P. Jo¨ckel, C. A. M. Brenninkmeijer, J. Chappellaz, L. Arnaud, and J. Chappellaz (2000), Determina-

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