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Long-term measurements of light alkanes and acetylene in the Antarctic troposphere

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ABSTRACT

Between 1982 and 1989, biweekly whole air samples were collected at the German Antarctic station "Georg von Neumayer". In addition, a smaller number of samples were taken in 1988 and 1989 at Scott Base, the New Zealand Antarctic station. These samples were analyzed for several light hydrocarbons and halocarbons. For the light alkanes and acetylene, the average results from the two stations which are located at opposite coasts of Antarctica agree. The annual mean values for ethane, propane, n-butane, i-pentane and acetylene are 380 ± 8 ppt, 84 ± 4 ppt, 50 ± 4 ppt, 15 ± 2 ppt, and 17 ± 1 ppt, respectively. The mixing ratios of ethane, propane, and i-pentane show a seasonal cycle with a peak in August, a minimum in February and an average maximum to minimum variation of 40%–50%. Acetylene also shows a maximum around August, but its seasonal variation is higher by a factor of three. For ethane, propane and acetylene, the measurements indicate that during the last few years, the average mixing ratios in austral winter have slightly increased. A possible explanation of this secular trend is the increase of biomass burning in the Southern Hemisphere. This is also consistent with the assumption that part of the seasonal variation found for ethane, propane and acetylene reflects the seasonal dependence of biomass burning.

1. Introduction

Nonmethane hydrocarbons (NMHC) are important participants in the photochemical reaction cycles in the troposphere, on local as well as on global scales. Furthermore, the knowledge of their large scale distributions can be used to improve our understanding of atmospheric transport processes (cf. Ehhalt et al., 1985; Rudolph, 1988; Rudolph and Johnen, 1990) and are important to validate model predictions. In recent years a number of papers presenting measurements of NMHC in the remote troposphere have been published and we are beginning to get some reasonable idea of their temporal and spatial distributions. Still, our knowledge is far from being complete. Most of the measurement series were made in the Northern Hemisphere and the data base which is available for the Southern Hemisphere is extremely limited. Apart from two investigations (Bonsang et al., 1990, Rudolph et al., 1989) the published measurement series from the Southern Hemisphere are limited to periods of a few weeks or less. They therefore do not give any information about the seasonal variability of NMHC let alone long term trends.

In a previous paper (Rudolph et al., 1989), we presented measurements of C_2- and C_3-hydrocarbons made at the German Antarctic station "Georg von Neumayer" between 1982 and 1985. Since then we have continued these measurements and expanded the range of compounds investigated. In this paper we present results from measurements of several light alkanes and acetylene at the Neymayer station. The observation periods range from more than 8 years for ethane and propane to about 3 years for some of the less abundant hydrocarbons.

2. Experimental procedure

Between 1982 and 1989, about 150 whole air samples were collected at Neumayer station (70°36′S, 8°22′W). On the average the interval between the collection of two samples was 2 weeks. However, samples were only collected under meteorological conditions where contamination from the station and the surrounding facilities could be excluded. Therefore the sampling intervals were not always precisely two weeks. Details of the locaton of the station, sampling site and sampling procedure are given by Rudolph et al. (1989). In addition to the measurements at the Neumayer station, in 1988 and 1989 a limited number of samples were taken at Scott Base (78° S, 167° E), the New Zealand Antarctic station.

The air samples were collected in evacuated stainless steel canisters with metal bellows valves. Once a year, they were transferred to the laboratory in Jülich and analyzed by gas-chromatography in combination with a cryogenic preconcentration procedure. Several tests were made to verify that the long storage periods did not affect the composition of the sampled air. Sample containers were returned empty and then filled with clean synthetic air. They showed no detectable amounts of the substances investigated in this work. Repeat analyses of some air samples several months after the first measurement showed no indication of a significant change. However, the amount of sample which was available for the second analysis was always relatively small and therefore the precision of the second analysis for substances at mixing ratios close to the lower limit of detection was not very good. For these substances we would not have been able to detect a change of less than 25%.

The samples collected in 1982 and 1983 were analyzed on a packed column (Rudolph and Jebson, 1983), and from 1984 on with a combination of packed and capillary columns (Rudolph et al., 1986). This improved the detection limit and also increased the range of compounds which could be measured.

The detection limit for hydrocarbons is between 1 and 10 ppt, depending on the type of compound. For most halocarbons the theoretical detection limits are below 0.1 ppt. The reproducibility for mixing ratios exceeding the detection limit by a factor of more than 5 was between 5% and 10%. The linearity of the measuring procedure was checked by dilution series. It was sufficient to allow the extrapolation down to the detection limits. In general the blank values were below the detection limit. However, sometimes detectable blank levels were found as a result of leaking valves, contamination of the inlet system or carrier gas impurities. Since our system was operated automatically, occasionally samples were analyzed before such problems were noticed and solved. In these cases, the measurements were corrrected for the blank values if the blank contributed less than 20% to the measurement. If the blank exceeded 20% of the peak area for a given substance, the measurement was eliminated from the data set.

All the measurements were evaluated quantitatively by comparison of the sample with a reference air standard of known composition. This reference gas is stored in a high-pressure gas cylinder. The trace gas mixing ratios in the reference air standard are in the range of a few ppb to a few tenths of a ppb. They were determined by comparison with standards prepared by a three step static dilution procedure. The stability of the reference air was occasionally checked by comparison with freshly prepared mixtures. We estimate, that the accuracy of our calibration is better than 20%, the reproducibility better than 10%, and the change of the trace gas mixing ratios in the reference air less than 5% for the whole time period.

3. Results

The total average mixing ratios of the light alkanes, acetylene and some chlorocarbons at Neumayer station are shown in Fig. 1. Also shown are the standard deviations and the errors of the mean. These values are based on at least 60 individual measurements, sometimes (for ethane, propane) on nearly 150 data points. The mixing ratios of alkanes heavier than pentane and of benzene, toluene, and the xylenes were generally below 10 ppt and in most cases below the detection limit. We estimate that the average value for these compounds is less than 5 ppt, but the numerous samples with mixing ratios below the detection limit prevent the calculation of a meaningful average. In contrast to the measurements from Neumayer station, we observed in several of the

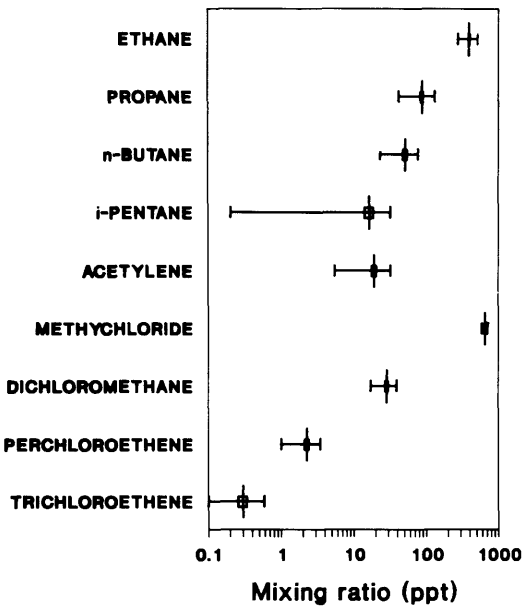

Fig. 1. Average mixing ratios for several trace gases at Neumayer station (Antarctica) from measurements between 1982 and 1989. The vertical bars show the mean value, the width of the rectangles indicate the error of the mean and the horizontal bars the standard deviation.

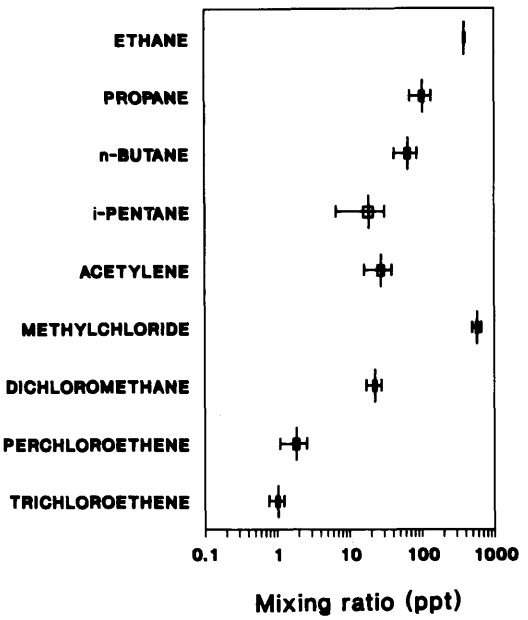

Fig. 2. Same as Figure 1, but for Scott Base (Antarctica). Measurements were made in 1988 and 1989.

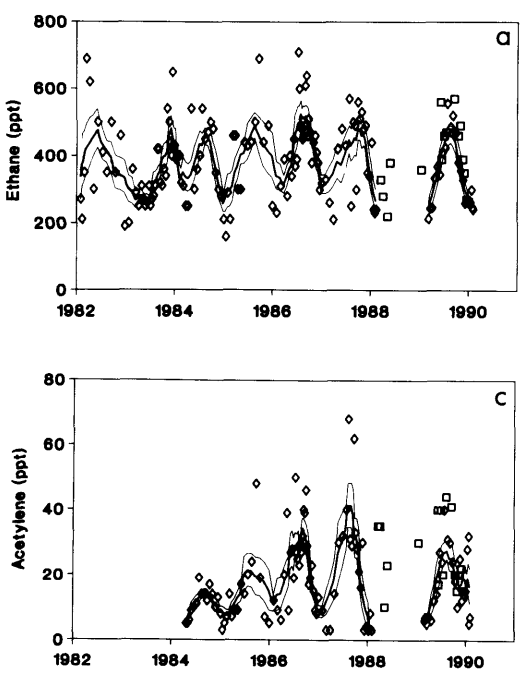

Fig. 3. Trace gas measurements from Antarctica. The diamonds are measurements from Neumayer, the squares measurements from Scott Base. The thick solid line is the running average of the Neumayer data, the thin lines indicate the range of error of the mean values. The tick marks on the time-axis always indicate January 1. (a) Ethane. (b) Propane. (c) Acetylene.

samples from Scott Base toluene and xylene mixing ratios exceeding some 10 ppt. These elevated mixing ratios of the alkylbenzenes were accompanied by rather high levels of light alkanes, acetylene and sometimes of halocarbons. This strongly indicates that these samples were contaminated. A possible source of contamination is the vicinity of Scott Base to another, large, Antarctic station (McMurdo). We have not yet been able to identify sampling conditions which would allow the collection of definitely uncontaminated samples. Therefore we used the alkylbenzenes to discriminate against contamination effects and rejected all samples with more than 20 ppt of toluene or 10 ppt of one of the xylenes. This reduced the number of useful measurements from Scott base to 16. In Fig. 2 the average mixing ratios of the light alkanes, acetylene and some chlorocarbons are shown for Scott Base (78°S, 167°O).

In Fig. 3a–c, the Neumayer measurements of ethane, propane, and acetylene are plotted as a function of time. Also shown are the running averages with an averaging time of 3 month and

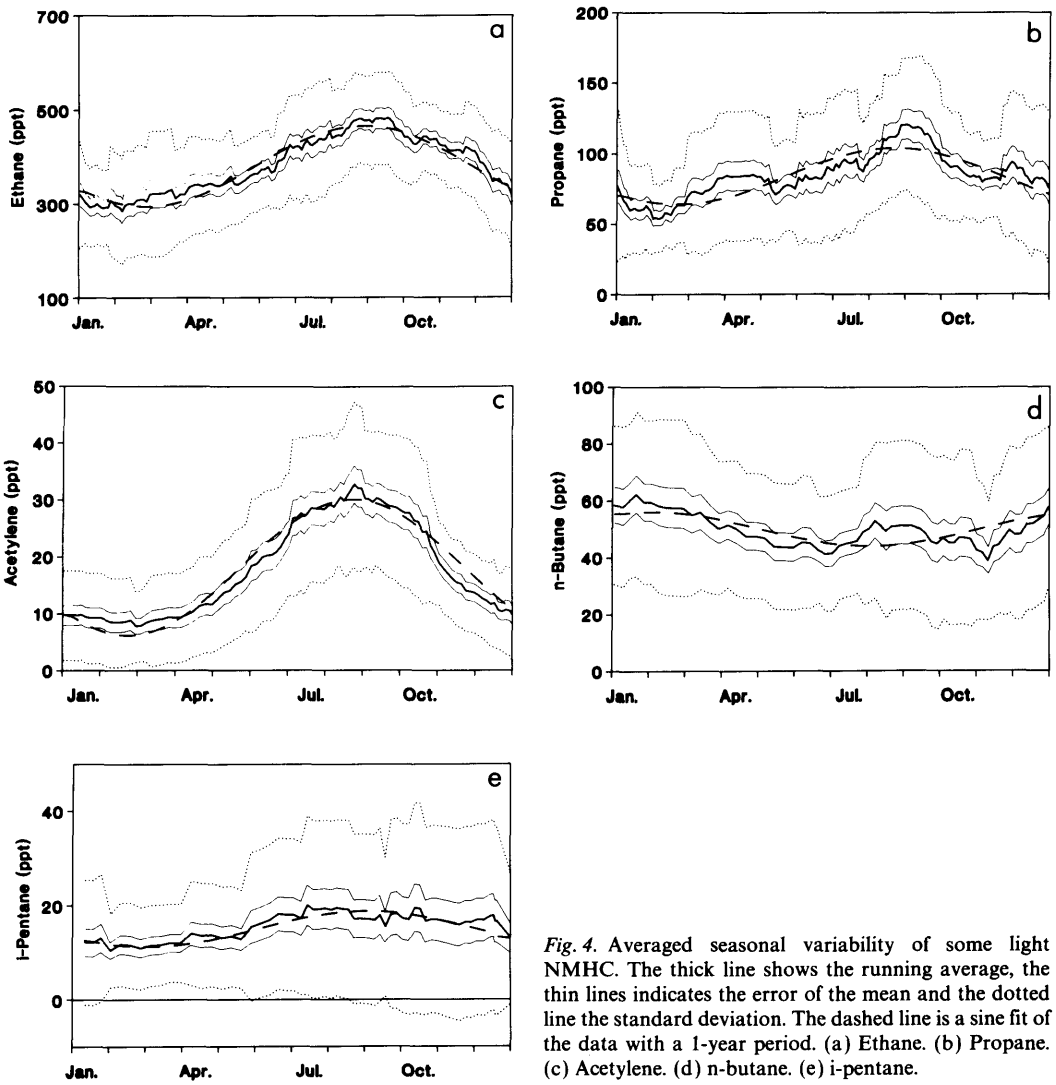

Fig. 4. Averaged seasonal variability of some light NMHC. The thick line shows the running average, the thin lines indicates the error of the mean and the dotted line the standard deviation. The dashed line is a sine fit of the data with a 1-year period. (a) Ethane. (b) Propane. (c) Acetylene. (d) n-butane. (e) i-pentane.

the error of the mean. For comparison we also included the results from Scott Base. The gap in the Neumayer data for 1988 is due to shipping problems.

To show possible systematic seasonal variations we combined the data from all the different years and calculated a running average with an averaging period of 6 weeks as a function of time of the year. The results are presented in Fig. 4 for the light alkanes and acetylene. Also included is a least square fit to a sine function with a one-year period.

4. Discussion

Apart from a few research stations and related activities there are no anthropogenic trace gas sources on the Antarctic continent. Furthermore, the only land areas located south of 40°S are Tasmania, the South Island of New Zealand, and southern Patagonia. These are rather small areas which are sparsely populated and not industrialized. Consequently the only potentially important regional trace gas source for Antarctica are ocean emissions.

The trace gases discussed in this paper are removed from the atmosphere primarily by the reaction with OH-radicals. From model calculations (cf. Hough, 1991; Volz et al., 1981) we can expect only low OH-radical concentrations in the Antarctic troposphere. In the austral winter they are negligible. Thus, for Antarctica, the tropospheric residence times of these trace gases are quite long (cf. Rudolph et al. 1989) and in general, they exceed the timescales of meridional transport.

The average atmospheric lifetimes of the different compounds vary by nearly two orders of magnitude. They range from about one week to more than one year. As expected the variability of the trace gas mixing ratios increases systematically with increasing reactivity (see Fig. 5). However, due to the substantial number of measurements the average values for Neumayer Station are reasonably representative. The errors of the mean values are between 1% for methylchloride and about 10% for i-pentane and trichloroethene. The data set from Scott Base is much smaller and consequently the average mixing ratios have larger errors. Nevertheless, the results agree very well (Figs. 1 and 2). In general the differences are less

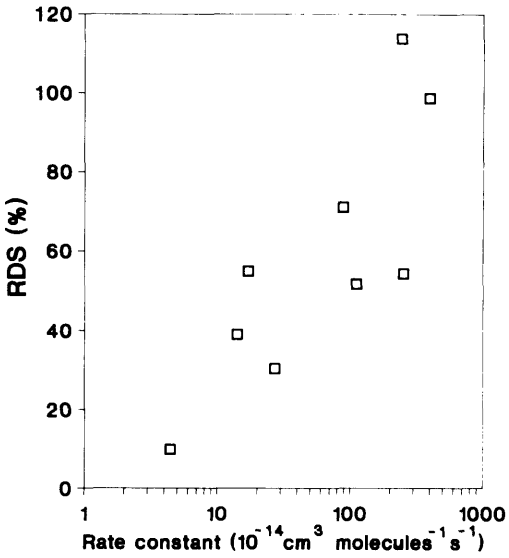

Fig. 5. Plot of the relative standard deviation (RSD) of the trace gas mixing ratios (Neumayer station data) as a function of the rate constants for the reaction with OH-radicals. The rate constants are taken from Atkinson (1986) and Atkinson et al. (1989).

than 20%, for ethane less than 2%. There is no statistically significant difference, except for trichloroethene. The two stations are separated by the Antarctic continent. Therefore the good agreement indicates that these results are representative for high southern latitudes. For trichloroethene mixing ratios from Scott Base are a factor of three higher than for Neumayer station. We cannot completely exclude that this is due to contamination during sampling. Our criterion for uncontaminated samples from Scott Base was based on the concentrations of alkylbenzenes. Due to the different types of potential contamination sources, this is not a very strict criterion for the exclusion of halocarbon contaminations at the sub ppt level.

For several of the trace gases a substantial part of the observed variability is systematic with season. For ethane the seasonality is clearly visible in the time series shown in Fig. 3a. A sine fit to the data shows an average of 380 ± 8 ppt with an amplitude of 88 ± 12 ppt corresponding to a relative change of $23\% \pm 3\%$. On the average the maximum occurs in August, but the occurrence of the maximum can shift by about ± 1 month from year to year. These results give a more detailed and

precise picture, but otherwise agree with previous findings which had been based only on the measurements made between 1982 and 1986 (Rudolph et al., 1989).

The presently available data set covers a period of 8 years and allows a preliminary analysis for long term trends. The deseasoned ethane data indicate a linear trend with a slope of 2 ± 3 ppt/year. Thus the secular trend of ethane in the Southern Hemisphere is quite small (0.5%/year) and not significantly different from zero. However, if we look at the trend of the annual maximum ethane concentrations (mid of July to October) separately, we find an average increase of 20 ± 7 ppt/year. The ethane measurements outside the annual maximum show no increase at all. We can rule out experimental problems such as a drift in our reference air as possible explanation because this would affect all measurements and not only the annual maximum.

Rudolph et al. (1989) point out that the annual maximum of the mixing ratios of ethane and acetylene over Antarctica coincides with the maximum in Southern Hemispheric biomass burning activities. In tropical regions the maximum in biomass burning generally occurs during the dry season, this is August to October in South America and June to October in southern tropical Africa (cf. Cros et al., 1988; Fishman and Larsen, 1987). A substantial fraction of the biomass burned in the Southern Hemisphere is due to shifting agriculture and deforestation (Seiler and Crutzen; 1980). Deforestation rates and the burning of savannah and brushland are presently increasing (cf. Crutzen and Andreae, 1990) and consequently the NMHC emission rates from biomass burning are increasing. This might well explain the observed trend in the August/September maxima of the ethane concentrations.

The impact of biomass burning on the ethane concentration in the remote marine atmosphere has been observed recently by Koppmann et al. (1991). They found ethane levels of sometimes more than 600 ppt over the open Atlantic between the equator and 20° S in September/October 1988. This exceeds our Antarctic average ethane concentration by nearly a factor of two. From the composition of the air mass and back trajectories Koppmann et al. (1991) concluded that this enhancement was due to an aged, very widespread plume from biomass burning.

For propane, the variability is higher and we cannot see a very clear seasonal signal in the time series (Fig. 3b). Nevertheless, the averaged seasonal dependence of the propane mixing ratio (Fig. 4b) shows a systematic seasonality which is very similar in shape to that of ethane. With an annual mean value of 84 ± 4 ppt the absolute concentrations are a factor of four lower, but the relative amplitude of $24\% \pm 6\%$ (20 ± 5 ppt) and the location of the maximum in August/September is very similar. A least square fit to the deseasoned data indicates an average increase of 4 ± 3 ppt/year. Similar to ethane, the trend is more pronounced for the seasonal maximum, here we observe an increase of 8 ± 3 ppt/year. If we assume that biomass burning is the main reason for the increasing ethane and propane maxima and neglect the different atmospheric removal rates, we can calculate an expected propane increase of 11 ppt/year from the observed ethane change and the NMHC emission pattern of biomass burning (Crutzen et al., 1985). This is very close to the observed value of 8 ppt/year. Moreover, the somewhat lower measured value for propane is compatible with its faster removal during transport.

For the other alkanes and acetylene, the measurements started in spring 1984 and the data coverage is not as complete as for ethane and propane. Nevertheless, we can see a definite seasonal cycle in the acetylene time series (Fig. 3c). The average seasonal cycle (Fig. 4c) is well established, showing an amplitude of 11 ± 2 ppt compared to an annual mean value of 17 ± 1 ppt. The relative seasonal change is with $65\% \pm 12\%$ about three times larger than for ethane or propane. Again, the maximum occurs around August.

In contrast to ethane and propane, acetylene has only marginal oceanic sources (cf. Ehhalt and Rudolph; 1984). Measurements by Kanikidou et al. (1988) indicate that oceans may be a weak acetylene source, more recent results by Plass et al. (1991) showed that this source does not contribute significantly to the global acetylene budget. Since urban and industrial acetylene sources are of minor importance in the Southern Hemisphere (cf. Hough, 1991), biomass burning is probably the dominant source of acetylene in the Southern Hemisphere. We can therefore expect that acetylene reflects the seasonal variation of the biomass burning emissions even stronger than

ethane or propane. This is also supported by the observations of Koppmann et al. (1991). Over the open Atlantic between the equator and 20°S they found between 150 ppt and 60 ppt of acetylene in an airmass which was influenced by biomass burning. This a factor of 4 to 9 higher than our Antarctic average. This compares with a factor of only two for ethane.

The acetylene time series measurements in Fig. 3c indicate a substantial change of the acetylene mixing ratios with time. On the average, there is an increase of 1.6 ± 0.6 ppt/year between 1984 and 1989, but there seems to be a significant, non-systematic interannual variability. The average mixing ratios in 1989 exceed those from 1984 and 1985 by 30 to 50%, but are lower than those from 1986 and 1987. We also have to consider, that several of the acetylene measurements gave results close to the detection limit which introduces a substantial experimental uncertainty. This prevents a more detailed analysis of the acetylene trend.

For n-butane and i-pentane, the available data set is smaller than for acetylene and there is a large variability. Nevertheless, the available data are sufficient to give a preliminary picture of their seasonal variability. For i-pentane a sine fit with an annual average of 15 ± 2.3 ppt, a relative amplitude of $25\% \pm 21\%$ ($4 \text{ ppt} \pm 3 \text{ ppt}$), and a maximum around August seems to give an acceptable description of the measurements (Fig. 4e). This indicates that i-pentane behaves very similar to ethane and propane. However, the uncertainty of the amplitude and of the phase is rather high and we cannot exclude that part of these similarities are fortuitous.

For n-butane, a sine fit with a one year period does not give a good representation of the measurements (Fig. 4d). The average n-butane mixing ratio is $50 \text{ ppt} \pm 4 \text{ ppt}$ with a standard deviation of 27 ppt. The highest monthly average values are observed during January and February with $60 \text{ ppt} \pm 7 \text{ ppt}$. A secondary, very weak maximum of $52 \text{ ppt} \pm 8 \text{ ppt}$ is indicated around August. Lowest average values around $40 \text{ ppt} \pm 7 \text{ ppt}$ are seen in June and October. There is no evident explanation for these observations. The seasonality of the atmospheric removal by reaction with OH-radicals or a biomass burning source of n-butane would explain elevated n-butane mixing ratios in austral winter, but not the rather high summer values. To explain this we have to assume that there is a peak in the NMHC emissions during summer at mid and high southern latitudes. Indeed, there are some indications of a seasonal cycle of oceanic NMHC emissions near Antarctica. Rudolph et al. (1989) explained the observation of high alkene mixing ratios in Antarctica during March and April with higher oceanic emissions resulting from lower sea ice coverage during this time. Bonsang et al. (1988) estimated the global n-butane flux from the oceans to about 2×10^{12} g/year. Considering the very low atmospheric OH-radical concentrations at high latitudes even a considerably smaller oceanic source would be sufficient to explain the concentrations of n-butane observed over Antarctica. However, the atmospheric lifetime of n-butane by far exceeds those of the alkenes and is sufficient to allow transport over very large distances, especially at mid and high latitudes. Sea ice coverage only affects a restricted area which is small compared to these distances and it is not yet possible to estimate the seasonal cycle of oceanic NMHC emissions on a larger scale.

5. Comparison with other measurements and model calculations

There are a few studies of NMHC in the remote marine atmosphere of the Southern Hemisphere. Bonsang et al. (1990) used the results of 23 NMHC measurements made at Amsterdam Island (38°S, 78°E) between 1984 and 1986 to derive seasonal averages of NMHC mixing ratios. For ethane their measurements show a mean value of 395 ppt with a standard deviation of 158 ppt. This agrees very well with our measurements from Antarctica. Also the seasonal variability at Amsterdam Island with a summer average of 350 ppt and a winter and spring value of 450 ppt and 447 ppt respectively is very similar. This agrees with the findings of Rudolph et al. (1989). They compared published ethane measurements in the Southern Hemisphere and concluded, that their measurements over Antarctica give a fairly representative picture.

For acetylene Bonsang et al. (1990) found an average of 37 ppt with a standard deviation of 22 ppt. This is about twice our Antarctic annual mean, but the shape of the seasonal cycle with a

summer value of 25 ppt and a winter and spring average of 51 ppt and 64 ppt respectively is very similar. These observations are compatible with the existence of a systematic latitudinal acetylene gradient in the Southern Hemisphere as suggested by Rudolph et al. (1989).

The average propane mixing ratio reported by Bonsang et al. (1990) is 151 ppt with a standard deviaton of 131 ppt. Our results from Antarctica are about 40% lower. This difference is still in the range of variability which is found for propane in the remote marine atmosphere (cf. Rudolph and Johnen, 1990; Rudolph et al., 1989; Bonsang et al., 1991). However, with highest values in Southern Hemispheric autumn, the seasonal cycle of propane at Amsterdam Island is different from that over Antarctica.

The average n-butane mixing ratios at Amsterdam Island are 49 ppt with a standard deviation of 39 ppt. They show only a marginal seasonal variability of a few ppt. This is surprisingly similar to our observations over Antarctica. The few available measurement series of n-butane in the remote marine troposphere of the Southern Hemisphere generally range around several 10 ppt (Rudolph and Johnen, 1990; Singh and Salas, 1982; Bonsang and Lambert, 1985; Rudolph et al., 1982; Bonsang et al., 1991; Singh et al., 1988) but show a variability of roughly a factor of five.

Bonsang et al. (1990) give no results for i-pentane, but there are a few other published measurements from the remote troposphere of the Southern Hemisphere. Rudolph and Johnen (1990) observed that over the open southern Atlantic the i-pentane mixing ratios were generally below their detection limit of about 15–20 ppt. This agrees with an earlier measurement series from the South Atlantic where Rudolph et al. (1982) found levels around 10 ppt. Equally low values of generally less than 20 ppt were observed in the Southern Hemisphere for the free troposphere (Ehhalt et al., 1985; Rudolph, 1988). These results are compatible with our measurements from Antarctica. But there are also some reports of significantly higher i-pentane mixing ratios. Singh and Salas (1982) observed over the Pacific nearly 200 ppt of i-pentane at low southern latitudes decreasing to 50 ppt between 20°S and 32°S. For the South Pacific Bonsang and Lambert (1985) report an average of about 100 ppt with occasionally low values of some 10 ppt. Even higher values ranging from several 10 ppt to a few ppb with averages of about 500 ppt and 200 ppt were observed by Bonsang et al. (1988, 1991) near Madagascar and at Hao atoll (18°S, 141°W) respectively. The authors explain these observations with strong regional oceanic sources. Therefore these rather high i-pentane mixing ratios cannot be considered as representative Southern Hemispheric background air.

We can compare our measurements with model predictions. Hough (1991) presented model calculations of the distributions of several light NMHC based on a 2-dimensional photochemical model. For 70°S at groundlevel this model predicts ethane mixing ratios of about 600 ppt for January and April and between 800 ppt and 1000 ppt for July and October. These estimates are nearly a factor of 2 higher than our measurements but show a similar seasonal cycle. Since our measurements agree with most other published ethane data for the Southern Hemisphere this difference cannot be due to an error in calibration. This points towards some error in the model. Since the model gives an adequate description of the Southern Hemispheric mixing ratios of methane and CO, we can rule out an error in the average OH-radical concentrations which could explain a difference of a factor of 2. A slower latitudinal exchange in the model would cause a steeper north-south gradient and lower ethane mixing ratios over Antarctica. However this would not be compatible with our knowledge of the distribution of ethane in the Southern Hemisphere. The most likely explanation are an overestimate of the Southern Hemispheric ethane emissions in the model.

For propane, the model calculations of about 50 ppt to 70 ppt for January and April are compatible with our measurements. However, for July and October, the model overpredicts propane by about 150 ppt. With about 10 ppt acetylene in April and 30 ppt–40 ppt in July, the model adequately describes our observations.

The model of Hough (1991) does not differentiate between n-butane and i-butane, but in general i-butane contributes only about 25% to the sum of both butanes (cf. Rudolph and Johnen, 1990). As a first approximation, we can therefore compare our n-butane measurements with the model calculations for butane. With about 10 ppt for April and 25 ppt for July, the model predictions

are not only by a factor of two lower than our measurements but also show a strong seasonal cycle which is not visible in our data. However, the model of Hough does not include an oceanic emission of butane. The results of Plass et al. (1991) and Bonsang et al. (1988) show that the oceans are a source for butane, although the magnitude of the source is still rather uncertain. This might well explain the discrepancy between our observations and the model.

6. Conclusions

The long-term measurements of organic trace gases at the Neumayer Station in Antarctica allow the determination of well defined average mixing ratios even for compounds with relatively short atmospheric residence times and a large variability, e.g., n-butane and i-pentane. For acetylene, the light alkanes, and several chlorocarbons the average mixing ratios from Neumayer station agree with the results from Scott Base which is located more than 2000 km away on the opposite coast of Antarctica. This shows that these average mixing ratios are reasonably representative for high southern latitudes. For ethane the results from Antarctica are representative for the remote marine atmosphere at mid and high southern latitudes. On the average ethane and propane show similar seasonal cycles with relative amplitudes of nearly 25% and maxima around August. However, ethane is about a factor 4 more abundant than propane.

The observed seasonality of the NMHC is compatible with biomass burning and ocean emissions being the dominant Southern Hemispheric sources and the reaction with OH-radicals being the sink mechanism. This also explains the more pronounced seasonal cycle of acetylene which has no significant ocean source and therefore more strongly shows the seasonality of the biomass burning emissions.

There are indications of a slight secular trend in the mixing ratios of ethane, propane, and acetylene during the observation period. This increase seems to be most pronounced for the austral winter. These observations can be explained by increasing NMHC emissions as a result of increasing biomass burning in the Southern Hemisphere.

Our NMHC measurements from Antarctica give a sufficiently well defined average to allow a meaningful comparison with model calculations. For several NMHC the model predictions of Hough (1991) are in reasonable accordance with our measurements, but there are also differences which point towards some inadequacies in the model. A probable explanation could be the uncertainties in the models NMHC emission data for the Southern Hemisphere. We think that detailed and representative NMHC distributions are extremely useful to constrain model calculations and atmospheric budgets.

7. Acknowledgements

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