

ETHANE AND PROPANE IN THE SOUTHERN MARINE TROPOSPHERE

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Abstract—Nearly 500 measurements of the ethane and propane mixing ratios have been made in clean marine air at Baring Head (New Zealand) and Scott Base (Antarctica) between 1991 and 1996. The annual averages of the mixing ratios (285 and 40 ppt) are lower than previously reported for the Southern Hemisphere. A striking feature of the seasonal cycle is the abrupt drop in mixing ratios of both compounds around November and a corresponding increase in the ethane/propane ratio (from about 7 in winter to > 10 in summer), suggesting a sharp decrease in Southern Hemisphere sources (e.g. biomass burning or fossil gas emissions) of these compounds in the spring. From a simple budget estimate it is concluded that biomass burning is most likely the dominant source of ethane and propane in the Southern Hemisphere. The seasonal variability of the emissions which are required to balance the Southern Hemisphere propane budget agrees very well with the seasonality derived for ethane emissions in a previous study.

Key word index: Non-methane hydrocarbons, Southern Hemisphere.

INTRODUCTION

Non-methane hydrocarbons (NMHC) are important participants in the trace gas chemistry of the troposphere, on local and global scales. Their photochemistry has not been studied as intensively as it has for methane in spite of their reactive nature.

The NMHCs make a significant contribution to the production of carbon monoxide (e.g. Graedel and Crutzen, 1993) and are influenced by changes in global or regional hydroxyl radical mixing ratios. Knowledge of their distribution on a large scale can thus be used to improve our understanding of atmospheric oxidation and transport processes. Global distributions have been estimated and models applied to deduce ethane and propane budgets and chemistry (e.g. Kanakidou *et al.*, 1991; Rudolph, 1995). In spite of the numerous studies of the large-scale distributions of NMHC, there are still substantial gaps in our knowledge, particularly as adequate data from the Southern Hemisphere are lacking.

The first constructs of latitude and altitude profiles which covered the middle or high latitudes of the Southern Hemisphere for a range of NMHCs were those from data collected during the STRATOZ II

flights circumnavigating South America in 1980 (Schmidt *et al.*, 1982) and cruises of R.V. Meteor to the South Atlantic in 1979–81 (Rudolph *et al.*, 1982). The results are summarised by Ehhalt *et al.* (1984, 1985). Latitude profiles from a ship cruise in the South Pacific in November 1982 (Bonsang and Lambert, 1985) showed small numbers of samples with particularly low NMHC mixing ratios in the South Pacific around 35°S, but no samples were taken south of 40°S.

Measurements taken in late spring and early summer at the South Pole in 1984–85 (Khalil and Rasmussen, 1986) showed ethane mixing ratios decreasing through more than a factor of two between early October and mid January each year and indicated both very low hydrocarbon mixing ratios and a strong seasonal cycle.

Since the early 1980s there have been other collections of Southern Hemisphere samples on sea or airborne campaigns, (e.g. Singh *et al.*, 1988; Rudolph *et al.*, 1988) but measurements through a range of seasons at fixed clean air sites have been infrequent (e.g. Blake and Rowland, 1986; Bonsang *et al.*, 1990; Rudolph *et al.*, 1989, 1992) and the spatial and temporal distributions of the most common NMHCs is still uncertain.

The available data for surface mixing ratios of ethane and propane in clean air were reviewed by Kanakidou *et al.* (1991) and Rudolph (1995) and very recently by Boissard *et al.* (1996). It has become clear that the mixing ratios of these non-methane alkanes are very much less in the Southern than the Northern Hemisphere and that the latitudinal gradients within the Southern Hemisphere are not large. Nevertheless the measurements so far have shown large variations in absolute mixing ratios between experiments and sites, which could be attributable to seasonal variation, variation with air mass trajectories, longitudinal variation, or experimental techniques. Rudolph (1995) reviewed global ethane tropospheric distribution including detailed information on interhemispheric differences, but conclusions relating to the southern hemisphere were still based on small numbers of measurements.

This work introduces longer and denser time series of ethane and propane mixing ratios at southern hemisphere sites which enable revision of past estimates of the budgets.

EXPERIMENTAL

Air samples have been taken at two Southern Hemisphere sites. The first is Baring Head in New Zealand (41°24'S, 174°52'E). The Baring Head facility is at an unmanned lighthouse station, on the edge of an 80 m cliff, with the prospect of a clean air fetch between SE and SW directions. This site is already proven as subject to clean air representative of large areas of the southern oceans (e.g. Lowe *et al.*, 1994) and has been used for studies of aromatic hydrocarbons (Clarkson *et al.*, 1996).

The second site used was Scott Base, Antarctica, (77°51'S, 166°45'E). The prevailing light wind at this site is north east, although the trajectory beyond a range of a few kilometres is generally from the south across the Ross Ice Shelf for hundreds of kilometres (Sindlar, 1988). In order to avoid effects from Scott Base itself and McMurdo Station to the north-west, collections of flask samples were only made from positions and at times when a clean trajectory from the Ice Shelf was reasonably assured.

An automatic air sampling and gas chromatograph system was established at Baring Head from December 1991 to September 1993. It was based on a Siemens Sichiromat with cryogenic sample trapping by liquid nitrogen. It depended on a system of automatic trapping and injection described in detail by Rudolph *et al.* (1990) for unattended operation. It is the same system as described by Clarkson *et al.* (1996) and the performance was virtually identical to that described by Rudolph *et al.* (1990).

Wind speed and direction at Baring Head were logged as ten-minute averages and four-day back trajectories are routinely estimated from analysed wind fields. The equipment operated automatically, but required a visit at least once a week to replenish the coolant and to measure a reference gas sample (air with known NMHC mixing ratios from a high pressure cylinder). Because of the concerns about ozonolysis of alkenes in a real-time cryo-trapping system (Koppmann *et al.*, 1995) we have passed the sample stream through a tube packed with potassium iodide. This reduced ozone effects on alkenes and had no observed effect on the alkanes reported here.

Calibration has been by comparisons with the reference mixtures containing about 30 NMHCs in ppb amounts. To

establish a reliable and stable calibration, several air samples were exchanged between NIWA and KFA Jülich. Local working standards have been prepared from mixtures of light hydrocarbons supplied by BOC Gases in New Zealand and NIST in the U.S. During the period of these analyses we also took part in the international intercomparison exercise for NMHCs, NOMHCE (Apel *et al.*, 1994). As part of NOMHCE Phase 2, in July 1992 we analysed a test mixture of NMHCs provided by NCAR, Boulder. Our results for ethane and propane agreed within 2% of NIST gravimetric analyses.

In addition to the automated samples collected at Baring Head, we have collected flask samples at the same site (May 1993–May 1996) and also from Scott Base (January 1990–November 1995). Flasks used in most cases were 800 ml electropolished stainless steel canisters fitted with Nupro SS-4H4 valves for flow-through sample collection. Flask preparation was carried out at 100°C and involved flushing with dehumidified zero air followed by evacuation. These flasks were filled by flushing with ambient air and pumping to 38 psi above atmospheric pressure. A small number of the Antarctic samples were filled to ambient pressure only.

The flask samples have been analysed on a different GC system, based on a Varian 2740-20, with a two stage cryogenic trapping and transfer system, similar to that described for light hydrocarbon analysis by Greenberg *et al.* (1994). This system had a 0.08" i.d. 20 ft phenyl isocyanate; Porasil C column with 7 ml min⁻¹ helium carrier used isothermally at 50° which provided good separation for C₂ to C₅ alkanes and alkenes.

ETHANE AND PROPANE MIXING RATIOS

Automatic and continuous monitoring began in December 1991 at Baring Head. All alkanes to C₅ are identifiable from the FID in most samples and also a range of alkenes and methyl chloride. Here we present only mixing ratio data for ethane and propane, the longest lived NMHCs.

Baring Head is subject to frequent storms from the south. An analysis of four-day back trajectories for southerly winds at Baring Head shows that air is descending and typically originates south of 50°S between Australia and Antarctica. Figure 1 shows a trajectory of this sort from a three-day southerly event in January 1992. Figure 2 illustrates the way in which the hydrocarbon mixing ratios measured change their characteristics during such a southerly event. The highly variable mixing ratios measured in other winds at Baring Head appear to be the result of land sources, possibly the urban sources of Lower Hutt and Wellington cities about 20 km to the north and north-west. In this work only samples collected from wind directions between 135° and 225° are included in the dataset for further analysis.

Although low NMHC mixing ratios have been observed in all wind regimes, it is conspicuous that none of the higher mixing ratios (e.g. ethane > 600 ppt [parts per trillion]) occur in southerly conditions.

In Fig. 3 we have plotted ethane and propane mixing ratios for both sites against time of the year using only southerly wind data from Baring Head but all the Scott Base data. For these plots we have fitted

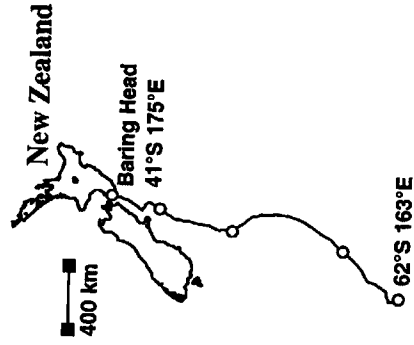


Fig. 1. A typical southerly trajectory at Baring Head. This example shows the trajectory for the four days up to local noon, 3 January 1992. The air originated well south of New Zealand.

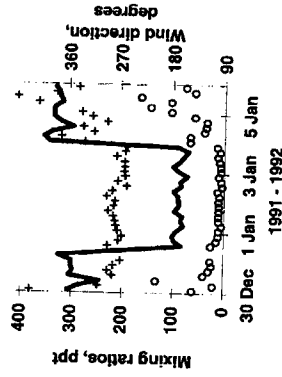


Fig. 2. An example of the variation of the mixing ratios of ethane (crosses) and propane (circles) during an episode with wind directions changing from north to south (continuous line). Wind speeds through the southerly period were over 15 m s^{-1} until 3 January when speeds decreased to 5 m s^{-1} .

an harmonic curve to the monthly medians to aid interpretation. These fits, as well as those for each site separately, are summarised in Table 1.

The fitting of a simple annual harmonic curve has limitations for describing the observations. For example, Fig. 3a for both sites shows that a better estimate for the occurrence of the ethane minimum would be Day 30 to Day 60 (February), similar to propane. For the reducing mixing ratios late in the year, the harmonic does not adequately describe the rapid drop after Day 300 (in November). In any case it is conspicuous that all outliers (whether from local or experimental effects) are high and the lower envelope of the data, somewhat lower than the curve of monthly medians plotted, appears to describe a seasonal variation which could be taken as more representative of clean marine air at mid latitudes in the Southern Hemisphere. An indication of the age of the air encountered at Baring Head and Scott Base can be

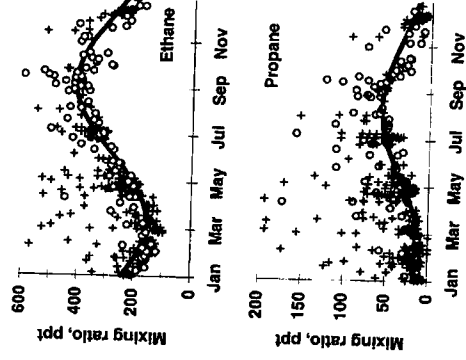


Fig. 3. (a) Ethane and (b) propane mixing ratios at Baring Head during southerly winds and at Scott Base, 1991–1996. The smooth curve is a simple harmonic fitted to the monthly medians. Crosses represent Baring Head samples and open symbols represent Scott Base.

obtained from the ratios of the ethane/propane mixing ratios. This ratio is on average around 1.5 for fossil fuel derived emissions (Hough, 1991) and about 2, with a range from 1 to 5, for emissions from biomass burning (Rudolph *et al.*, 1995). The only relevant atmospheric removal process for ethane and propane is the reaction with OH-radicals. Since propane reacts with the OH-radical about 4 times faster than ethane (Atkinson, 1990), the ethane-propane ratio will increase, depending on transport time and OH-radical mixing ratios with increasing distance from the sources. The atmospheric lifetime (τ) calculated for the reaction with OH-radicals ($\tau = k_{\text{OH}}^{-1} [\text{OH}]$, with k_{OH} being the rate constant for the reaction with OH radicals and $[\text{OH}]$ the average tropospheric OH-radical concentration) for ethane is about two months and for propane about two weeks (Rudolph and Ehhalt, 1981). The mean value of all ethane to propane ratios is 9.8 (standard deviation 7) which is well above the emission ratio of the dominant ethane and propane sources. In a very simplified picture this would correspond to an average age of 4–6 weeks for the sampled air masses.

The observed variability of the ethane/propane ratio is quite substantial, but a major part of this variability is due to a significant seasonal variation with higher ethane to propane ratios in the Southern Hemisphere summer (Fig. 4). This systematic change of the ethane to propane ratio may be explained by the faster removal of propane relative to ethane during transport as a result of the higher OH-radical mixing ratios in summer. Moreover, the absolute mixing ratios of both ethane and propane are significantly lower in summer than in winter. Qualitatively these

Table 1. Seasonal variations derived from simple harmonic fits to monthly medians of mixing ratios

| | Number of samples | Mean, ppt | Amplitude, ppt | Date of minimum, Julian day |
|----------------------|-------------------|-----------|----------------|-----------------------------|
| | | | ETHANE | |
| Baring Head, 1991-96 | 377 | 296 | 138 | 88 |
| Scott Base, 1990-96 | 89 | 288 | 120 | 70 |
| Both sites | 466 | 285 | 128 | 72 |
| | | | PROPANE | |
| Baring Head, 1991-96 | 376 | 38 | 24 | 66 |
| Scott Base, 1990-96 | 88 | 43 | 23 | 30 |
| Both sites | 464 | 34 | 23 | 45 |

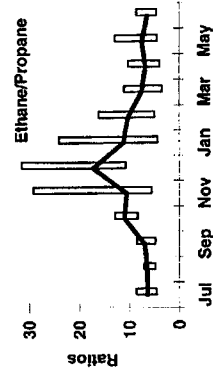


Fig. 4. Monthly medians of ratios of ethane/propane mixing ratios (continuous line) for samples collected 1990-96 at Baring Head and Scott Base. The vertical bars span the 10 to 90 percentile range of the data.

observations are compatible with a faster removal of the NMHC in summer as a result of the higher average OH-radical mixing ratios. However, a simple quantitative estimate shows that there must be other factors which affect the ethane and propane mixing ratios at mid and high southern latitudes. The ethane/propane ratio is on average 7 for April to September and on average 10-13 for October till March with the highest values of over 15 in December. Assuming that the transport patterns and the source strength do not change, an increase of the OH-radical concentration by roughly 50% would be required. However, this alone can only explain a part of the observed change of more than a factor of two in the ethane mixing ratios between winter and summer. Another possibility is a change in the emissions of ethane and propane with season. A larger contribution of a source with a higher ethane/propane ratio, e.g. an increase of biomass burning compared to man-made/industrial emissions, would also result in a larger ethane/propane ratio in the troposphere. Finally, we should remember that about half of the ethane turnover in the Southern Hemisphere is balanced by transport from the Northern Hemisphere (Rudolph, 1995). The ethane/propane ratio at low latitudes of the Northern Hemisphere (north of the ITCZ) is quite high, generally around 5-10 (Rudolph and Johnen, 1990; Koppmann *et al.*, 1992). Consequently increased transport of ethane from the Northern Hemisphere would have the same effect as a larger contribution from a source with a high ethane/propane ratio. We

note that the interhemispheric gradient of ethane, which is one of the driving factors for the north-south transport of ethane, has its maximum in late Southern Hemisphere summer (Rudolph, 1995).

Rudolph (1995) derived the global latitudinal and seasonal variations of the ethane mixing ratios from several series of tropospheric measurements. For the latitude range from 40 to 80°S this distribution shows only a marginal gradient ($< 1\%/10^\circ$ latitude) which is in very good agreement with the observation of nearly identical ethane mixing ratios at Baring Head and Scott Base. Also the phase of the seasonal cycle with the minimum in March and the maximum in September agrees very well with our observations. The mean value and the amplitude of 374 and 90 ppt, respectively, derived by Rudolph (1995) differ by about 30% from our observations. Considering the very limited data set for the Southern Hemisphere which was available to Rudolph, the agreement is surprisingly good and within the error estimate given by Rudolph.

The bias introduced by our use of monthly medians (rather than means) to reduce the influence of high outliers is only marginal. If monthly means had been used for curve fitting, then the calculated annual average mixing ratio would be 303 ppt instead of 285 ppt. There are very few measurements of the seasonal variation of NMHCs in the Southern Hemisphere. Rudolph *et al.* (1989, 1992) report measurements of ethane measured by Rudolph *et al.* (1989, 1992) at Neumaier, (70°36'S, 8°22'W) is nearly identical to the seasonal variation of ethane given by Rudolph (1995) for mid and high southern latitudes. This is not surprising since these data were the most extensive investigations of the seasonal variations of ethane at these latitudes which were available at that time. Bon-sang *et al.* (1990) measured the seasonal variation of light NMHC at Amsterdam Island (38°S, 78°E). From the limited data set of 23 measurements an annual mean ethane mixing ratio of 395 ppt (standard deviation 158 ppt) was derived. This is somewhat higher than our results for mid and high southern latitudes. Also the seasonal variability at Amsterdam Island is somewhat less pronounced, the late summer values range around 300 ppt, the spring values around 450 ppt. These differences may be due to systematic

Table 2. Comparison of modelled ethane and propane mixing ratios for the tropospheric boundary layer and 40–70°S with our measurements

| Month | Ethane mixing ratio, ppt | | | Propane mixing ratio, ppt | | |
|----------|--------------------------|-----------------------------------|------------|---------------------------|-----------------------------------|------------|
| | Hough (1991) | Kanakidou <i>et al.</i> (1991) | This work* | Hough (1991) | Kanakidou <i>et al.</i> (1991) | This work* |
| January | 500–750 | | 200 ± 6 | 25–50 | | 25 ± 3 |
| March | | 350–400 | 203 ± 17 | | 50–80 | 43 ± 8 |
| April | 500–750 | | 240 ± 9 | 75–100 | | 45 ± 5 |
| June | | 400–500 | 333 ± 9 | | ca. 100 | 57 ± 5 |
| July | 750–1000 | | 356 ± 7 | 100–250 | | 60 ± 4 |
| October | | | 343 ± 12 | ca. 100 | | 33 ± 2 |
| December | 750–1000 | 350–400 | 248 ± 5 | | ca. 50 | 15 ± 1 |

*Means and the errors of the mean

effects, e.g. the results of longitudinal or latitudinal gradients, but in view of the small number of measurements from Amsterdam Island the significance of these differences is very low. For January Boissard *et al.* (1996) report ethane values ranging around 500 ppt at 40–50°S. These values are significantly higher than our observations at Baring Head or Scott Base which probably reflects that most of the measurements were made over the coastline of South America. It therefore is plausible that these observations are biased by strong regional sources.

The phase of the seasonal cycle Rudolph *et al.* (1989, 1992) report for propane is similar to our results, but with a mean value of 85 ppt they are factor of two higher than our annual averages. The annual mean propane mixing ratios of 151 ppt (standard deviation 131 ppt) which are reported by Bonsang *et al.* (1990) for Amsterdam Island are surprisingly high. In contrast to our results they are highest in the Southern Hemisphere autumn. Surprisingly high Southern Hemisphere propane mixing ratios were also reported by Boissard *et al.* (1996) for January. At 40–50°S they observed mixing ratios in the range of 250–400 ppt, more than an order of magnitude higher values than we observed at Baring Head and Scott Base. As mentioned above, this is most probably due to the impact of strong regional sources.

It should be noted that all propane data sets for the Southern Hemisphere background troposphere reported in the literature show substantial, seemingly unsystematic, variations. Moreover, from the relatively short atmospheric residence time of propane we can not rule out substantial changes of the propane mixing ratios as a function of latitude and longitude. Thus the differences between the different data sets may be an indication of systematic differences between the sampling locations.

It is interesting that the ethane to propane ratio which can be derived from the measurements of Rudolph *et al.* (1989, 1992) is around 5 and shows no major systematic variations with season. This, and the higher mixing ratios for ethane and propane indicate some impact from less remote sources (e.g. from southern Africa or South America) at Neumaier.

Nevertheless, the very good agreement between the average values from Baring Head and Scott Base combined with the large number of measurements give confidence that our propane mixing ratios are representative for a major part of the mid and high latitudes of the Southern Hemisphere. The bias from using monthly medians instead of means has a only a small effect (47 ppt instead of 35 ppt) on the average propane mixing ratio and cannot explain the differences to the previously published data sets. We attribute these differences to the much larger numbers of samples in the present work, collected over several years, and the opportunities in this work for identifying ideal clean marine air conditions.

Hough (1991) and Kanakidou *et al.* (1991) used two dimensional models to calculate the tropospheric distributions of ethane and propane. In Table 2 the results of these models are compared with our measurements.

In general, the observed ethane and propane mixing ratios are on the lower side of the model distributions. The mixing ratios calculated by Hough (1991) are a factor of 2–3 too high. However, they are based on a global ethane source strength of 29 Tg yr⁻¹ whereas a more recent estimate of the ethane sources gave a global emission rate of about 13 Tg yr⁻¹ (Rudolph, 1995). The results of Kanakidou *et al.* (1991) which are based on a global ethane source strength of only 16 Tg yr⁻¹ are also about 50% higher than our observations. For propane the mixing ratios in both models are on average about a factor of two higher than the observations.

It is obvious that our observations of relatively low mixing ratios of ethane and propane at mid and high southern latitudes will have some consequences on estimates of the impact of these compounds on the atmospheric chemistry in the southern hemisphere, e.g. for the mixing ratios of PAN or acetone which can be formed during the photo-oxidation of ethane and propane, respectively. However, the relationships between precursor mixing ratios, photo-chemistry and transport are quite complex (e.g. Kanakidou *et al.*, 1991) and sufficiently representative measurements of the seasonal variation of ethane and propane

from remote sites at low southern latitudes are still lacking.

THE SOUTHERN HEMISPHERE BUDGET OF ETHANE AND PROPANE

Rudolph (1995) presented calculations of global and hemispheric budgets for ethane. The estimated emissions for 35–90°S are 0.35 Tg yr^{-1} , nearly a factor of two lower than the 0.6 Tg yr^{-1} which are required balance the budget. Due to the limited database for mid and high southern latitudes which was available to the author this was not considered significant. But it is interesting to note that with the lower ethane mixing ratios observed in this study the gap in the ethane budget for mid and high southern latitudes is strongly reduced. In a revised budget the lower ethane mixing ratios result not only in a lower removal rate of ethane, but also in increased atmospheric transport from north to south due to a steeper ethane gradient. Both effects together would reduce the required ethane source by roughly one third to about 0.4 Tg yr^{-1} and thus result in a reasonably well balanced ethane budget for the region south of 35°S. However, even this revised estimate remains uncertain since the ethane mixing ratios at low southern latitudes, and thus the exact shape of the latitudinal gradient, are still not very well known.

The analysis of the seasonal cycle of the Southern Hemisphere ethane mixing ratios requires ethane sources which peak around September (Rudolph, 1995). If biomass burning indeed is the dominant Southern Hemisphere source for both ethane and propane we would expect a similar seasonality for propane emissions. We can use our measurements to derive a rough estimate of a propane budget for the Southern Hemisphere. This requires the knowledge of the Southern Hemisphere concentration field for propane. Our data do not cover the whole Southern Hemisphere and therefore we have to extrapolate from our observations. This may result in large uncertainties, but the very good agreement between the average seasonal cycles for Scott Base and Baring Head which are located more than four thousand kilometres apart gives us confidence that the measurements are reasonably representative for clean Southern Hemisphere air. Furthermore, the measurements of Donahue and Prinn (1990) over the Pacific in February/March 1990 at 10°S showed propane mixing ratios between 15 and 30 ppt, very close to the values we observed at Baring Head and Scott Base for the same month. As a first approximation we therefore assume that our measurements represent the Southern Hemisphere background mixing ratios of propane at ground level. There are very few measurements of the vertical profiles of propane in the remote Southern Hemisphere. The measurements made by Rudolph (1988) in the Southern Hemisphere at different altitudes over remote areas indicate that the verti-

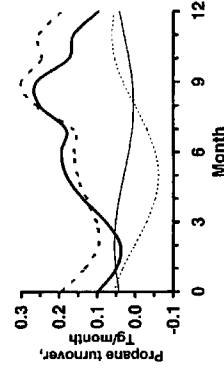


Fig. 5. Seasonal variation of the budget of propane for the Southern Hemisphere. The thick solid line shows the required source strength, the thick broken line the removal by reactions with OH-radicals. The thin solid and broken lines show the flux from the Northern Hemisphere and change of the Southern Hemispheric propane content, respectively.

cal gradient of the propane mixing ratio is quite small, around 2–3% per kilometre. We use this small gradient to derive the tropospheric propane concentration field from our ground level measurements.

Propane is removed from the troposphere primarily by reaction with OH-radicals. Thus we can calculate the chemical loss from the propane concentration field, the OH-radical concentration field, the temperature distribution and the rate constants for the reaction of propane and OH-radicals. We use the shape of the OH-radical distribution published by Taylor *et al.* (1991) which was adopted from Brasseur *et al.* (1990). In order to be compatible with recent estimates of the average global OH-radical concentration based on methylchloroform budgets (Prinn *et al.*, 1995) the distribution was scaled to a mean global OH-radical concentration of $1 \times 10^6 \text{ cm}^{-3}$. The temperature field was extracted from the GISS three-dimensional model (Hansen, 1983) and for the rate constant and its temperature dependence we used the values recommended by Atkinson *et al.* (1992). We calculate the removal rate of propane for the Southern Hemisphere for each month in intervals of 10° latitude and 1 km altitude. The total tropospheric loss rate of propane due to reactions with OH-radicals is 2.2 Tg yr^{-1} with a range of 1.2–3.7 Tg yr^{-1} . Its seasonal variation is shown in Fig. 5.

As well as propane removal by OH-radicals a few other lesser contributions to the Southern Hemisphere propane budget have to be considered in order to calculate the required source strength. The loss to the stratosphere can be estimated from the average propane concentration in the troposphere and the troposphere-stratosphere exchange rate of 0.8 yr^{-1} (e.g. Warneck, 1988). This loss is between 0.01 and $0.02 \text{ Tg month}^{-1}$ and thus negligible compared to the turnover due to OH-radical reactions. Interhemispheric exchange will result in a flux of propane into the Southern Hemisphere since the propane concentrations in the Northern Hemisphere are generally higher than in the Southern Hemisphere (Rudolph, 1988; Rudolph and Johnen, 1990; Rudolph *et al.*,

Table 3. Main contributions to the Southern Hemispheric budget of ethane and propane. Given is the best estimate and the range of the estimate

| | Ethane ^a (Tg yr ⁻¹) | Propane (Tg yr ⁻¹) |
|-------------------------------------|---|-----------------------------------|
| Removal by OH reaction | 4.9 (3.2–7.8) | 2.2 (1.2–3.7) |
| Flux from Northern Hemisphere | 1.5 (0.9–2.1) | 0.3 (0.15–0.6) |
| Required Southern Hemisphere source | 3.4 (1.6–5.2) | 1.9 (0.9–3.4) |
| Biomass burning emissions | 2.7 (1.3–4.2) | 2.1 (1.2–3) |

^aData are taken from Rudolph (1995) and corrected for the slightly lower ethane mixing ratios found for the Southern Hemisphere in this study. Furthermore the removal rate by reaction with OH-radicals is recalculated for a global mean OH-radical concentration of 10^6 cm^{-3} in order to be compatible with the more recent global lifetime estimates of CH_3CCl_3 (Prinn *et al.*, 1995).

1982, 1984; Singh and Salas, 1982; Singh *et al.*, 1988; Donahue and Prinn, 1993; Boissard *et al.*, 1996; Blake *et al.*, 1996a, b). In order to estimate the interhemispheric exchange rate of propane we use an average Northern Hemisphere propane mixing ratio of 200 ppt and a seasonal cycle which is similar in shape to the Southern Hemisphere seasonality for propane but shifted in phase by six months. The minimum of about 80 ppt is found in August, the maximum of 320 ppt in February. Based on this crude average Northern Hemisphere propane seasonality and from an interhemispheric exchange time of 1.5 years (Mais and Levin, 1994) we deduce that the propane flux from the Northern to the Southern Hemisphere is around 0.3 Tg yr^{-1} with an uncertainty of roughly a factor of two. The seasonal variability of this interhemispheric exchange is included in Fig. 5. Due to the large temporal and spatial variability of the propane mixing ratios in the Northern Hemisphere and the limited number of studies, this value is very uncertain. However, interhemispheric exchange contributes only about 15% to the Southern Hemispheric propane turnover and consequently this contribution is of minor importance for the propane budget. The remaining propane source which is needed to balance the Southern Hemisphere propane budget is 1.9 Tg yr^{-1} . Its seasonal variability is shown in Fig. 5. We can compare this with an estimate of the emission rates of propane from biomass burning in the Southern Hemisphere. The propane/carbon dioxide emission ratios range from 0.01% (by volume) to 0.19% with a best estimate around 0.05% (e.g. Rudolph *et al.*, 1995). The carbon dioxide emissions from biomass burning are estimated to be between $1600\text{--}4100 \text{ Tg C yr}^{-1}$ (Crutzen and Andreae, 1990). From the latitude dependence of the biomass burning emissions given by Hough (1991) we derive that about 40% of the total emissions occur in the Southern Hemisphere. Based on these data the annual mean propane emissions from biomass burning in the Southern Hemisphere is in the range of $1.2\text{--}3 \text{ Tg yr}^{-1}$, with a best estimate of 2.1 Tg yr^{-1} . Evidently, the biomass burning source and the required emissions match. There are a few other, minor sources of pro-

pane in the Southern Hemisphere. However, they are negligible compared to biomass burning. Global oceanic emissions of propane are about 0.1 Tg yr^{-1} and also the contribution of civilisation related emissions of light alkanes in the Southern Hemisphere (e.g. natural gas losses) is marginal (Ehhalt and Rudolph, 1984; Rudolph, 1995). We thus conclude that the Southern Hemisphere propane budget is reasonably well balanced although both the source and the sink estimates have substantial uncertainty.

Table 3 summarises the main budget items for ethane and propane in the Southern Hemisphere. There are substantial uncertainties in these budget estimates. Nevertheless, both from the absolute magnitude and the relative ethane to propane source strength, biomass burning is probably the dominant emitter of ethane and propane in the Southern Hemisphere. Furthermore, interhemispheric exchange is far more important for ethane than for propane. The budgets are still not sufficiently constrained to allow conclusive estimates of the magnitude of contributions from other minor sources, e.g. oceans or natural gas leakage. The seasonal variation of the derived propane source strength has a pronounced maximum in August/September and a minimum around February. The shape of this seasonal cycle is very similar to the seasonality derived for the Southern Hemisphere ethane emission rates (Rudolph, 1995). This is consistent with the concept that biomass burning is the dominant Southern Hemisphere source for both ethane and propane.

Based on their measurements during the TROPOZ II aircraft campaign in January 1991, Boissard *et al.* (1996) derived flux estimates for different zones of the Earth's surface. They deduced that there are substantial oceanic propane emissions, $0.85 \text{ Tg month}^{-1}$, from the Southern Ocean ($30\text{--}60^\circ\text{S}$) in January. The high source strength Boissard *et al.* deduced are probably the consequence of the rather high propane mixing ratios they observed in the Southern Hemisphere (see above). This large oceanic propane source is not compatible with our observations of propane mixing ratios as low as 10–20 ppt in marine air in January through several years at Baring Head (41°S).

CONCLUSIONS

Levels of ethane and propane measured at mid and high latitudes of the Southern Hemisphere through 1990–1996 are consistently lower than in previously reported measurement series. The observations reinforce earlier work which indicates that sources of NMHC in the Southern Hemisphere are much smaller than in the Northern Hemisphere. High ethane/propane ratios are consistent with interhemispheric exchange being an important source of ethane south of the equator. The nearly identical mixing ratios and seasonal cycles at Baring Head and Scott Base suggest that the air at mid and high southern latitudes is mixed rapidly relative to the lifetime of propane at these latitudes, and is also compatible with the absence of any major source of light hydrocarbons south of 45°S.

The seasonal cycles are now well defined and feature a regular abrupt fall in mixing ratios at the end of each year. This observation can possibly be attributed to the cessation of a Southern Hemisphere source, such as biomass burning during spring each year. The seasonal variation of the required sources for ethane and propane are very similar. Moreover, the magnitude of the mean annual emission rate is compatible with an estimate of the biomass burning source strength. Seasonal changes in the large-scale transport patterns cannot completely be ruled out as an explanation for these rather abrupt changes. However, the existing evidence is fully compatible with the idea that biomass burning is by far the most important source of ethane and propane in the Southern Hemisphere. The analysis of the seasonal cycles of these two trace gases suggests a substantial seasonal variability of the intensity of biomass burning with a maximum in August/September and a minimum around February. Due to the still limited spatial coverage of ethane and propane measurements in the background troposphere of the Southern Hemisphere these estimates still have a substantial uncertainty. Nevertheless, the available results indicate that ambient observations of ethane and propane can be very useful tools to study the intensity and seasonality of biomass burning in the Southern Hemisphere.

REFERENCES

- Apel, E. C., Calvert, J. G. and Fehsenfeld, F. C. (1994) The non-methane hydrocarbon intercomparison Experiment (NOMHICE): Tasks 1 and 2. *Journal of Geophysical Research* **99**, 16,651–16,664.
- Atkinson, R. (1990) Gas-phase tropospheric chemistry of organic compounds: a review. *Atmospheric Environment* **24A**, 1–41.
- Blake, D. R. and Rowland, F. S. (1986) Global atmospheric concentrations and source strength of ethane. *Nature* **321**, 231–233.
- Blake, D. R., Chen, T.-Y., Smith, Jr., T. W., Wang, C. J.-L., Wingenter, O. W., Blake, N. J., Rowland, F. S. and Mayer, E. W. (1996a) Three-dimensional distribution of non-methane hydrocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A). *Journal of Geophysical Research* **101**, 1763–1778.
- Blake, D. R., Blake, N. J., Smith, Jr., T. W., Wingenter, O. W. and Rowland, F. S. (1996b) Non-methane hydrocarbon and halocarbon distribution during Atlantic Stratospheric Transition Experiment/Marine Aerosol and Gas Exchange, June 1992. *Journal of Geophysical Research* **101**, 4501–4514.
- Boissard, C., Bonsang, B., Kanakidou, M. and Lambert, G. (1996) TROPOZ II: global distribution and budgets of methane and light hydrocarbons. *Journal of Atmospheric Chemistry* **25**, 115–148.
- Bonsang, B., Kanakidou, M. and Lambert, G. (1990) NMHC in the atmosphere: preliminary results of monitoring at Amsterdam Island. *Journal of Atmospheric Chemistry* **11**, 169–178.
- Bonsang, B. and Lambert, G. (1983) Non-methane hydrocarbons in an oceanic atmosphere. *Journal of Atmospheric Chemistry* **2**, 257–271.
- Brasseur, G., Hitchman, M. H., Walters, S., Dymek, M., Falise, E. and Pirre, M. (1990) An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere. *Journal of Geophysical Research* **95**, 5639–5655.
- Clarkson, T. S., Martin, R. J., Rudolph, J. and Graham, B. W. L. (1996) Benzene and toluene in New Zealand air. *Atmospheric Environment* **30**, 569–577.
- Cutzen, P. J. and Andreae, M. O. (1990) Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science* **250**, 1669–1678.
- Donahue, N. M. and Prinn, R. G. (1990) In situ non-methane hydrocarbon measurements on SAGA 3. *Journal of Geophysical Research* **98**, 16,915–16,932.
- Ehhalt, D. H. and Rudolph, J. (1984) On the importance of light hydrocarbons in multiphase atmospheric systems. *Berichte der Kernforschungsanlage Jülich*, D-5170, Jülich, FRG, Jül-1942.
- Ehhalt, D. H., Rudolph, J., Meixner, F. X. and Schmidt, U. (1985) Measurements of selected C2–C5 hydrocarbons in the background troposphere: vertical and latitudinal variations. *Journal of Atmospheric Chemistry* **3**, 29–52.
- Gracdel, T. E. and Crutzen, P. J. (1993) *Atmospheric Change: An Earth System Perspective*, p. 302, W. H. Freeman and Company, New York.
- Greenberg, J. P., Lee, B., Helmig, D. and Zimmerman, P. R. (1994) Fully automated gas chromatograph-flame ionization detector system for the *in situ* determination of atmospheric non-methane hydrocarbons at low parts per trillion concentration. *Journal of Chromatography* **A676**, 389–398.
- Hansen, J., Russell, G., Rind, D., Stone, P., Lacis, A., Lebedeff, S., Ruedy, R. and Travis, L. (1983) Efficient three-dimensional global models for climate studies: models I and II. *Monthly Weather Review* **111**, 609–662.
- Hough, A. (1991) Development of a two dimensional global tropospheric model. *Journal of Geophysical Research* **96**, 7325–7362.
- Kanakidou, M., Singh, H. B., Valentini, K. M. and Crutzen, P. J. (1991) A two-dimensional study of ethane and propane oxidation in the troposphere. *Journal of Geophysical Research* **96**, 15,395–15,413.
- Khalil, M. A. K. and Rasmussen, R. A. (1986) Temporal variability of C2-hydrocarbons at the South Pole: seasonal cycles and the possible effects of El Niño. *Antarctic Journal of the United States* **21**, 244–245.

- Koppmann, R., Bauer, R., Johnen, F. J., Plass-Dülmer, C. and Rudolph, J. (1992) The distribution of light non-methane hydrocarbons over the mid-Atlantic: results of the Polarstern cruise ANT VII/1. *Journal of Atmospheric Chemistry* **15**, 215-234.
- Koppmann, R., Johnen, F. J., Khedim, A., Rudolph, J., Wedel, A. and Wiards, B. (1995) The influence of ozone on light non-methane hydrocarbons during cryogenic pre-concentration. *Journal of Geophysical Research* **100**, 11,383-11,391.
- Lowe, D. C., Brenninkmeijer, C. A. M., Brailsford, G. W., Lassey, K. R., Gomez, A. J. and Nisbet, E. G. (1994) Concentration and ^{13}C records of atmospheric methane in New Zealand and Antarctica: evidence for changes in methane sources. *Journal of Geophysical Research* **99**, 16,913-16,925.
- Mais, M. and Levin, I. (1994) Global increase of SF_6 observed in the atmosphere. *Geophysical Research Letters* **21**, 569-572.
- Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E. and Simmonds, P. G. (1995) Atmospheric trends and lifetime of CH_3CCl_3 and global OH concentrations. *Science* **269**, 187-192.
- Rasmussen, R. A. and Khalil, M. A. K. (1982) Latitudinal distributions of trace gases in and above the boundary layer. *Chemosphere* **11**, 227-235.
- Rudolph, J. (1988) Two-dimensional distribution of light hydrocarbons: Results from the STRATOS III experiment. *Journal of Geophysical Research* **93**, 8367-8377.
- Rudolph, J. (1995) The tropospheric distribution and budget of ethane. *Journal of Geophysical Research* **100**, 11,369-11,381.
- Rudolph, J. and Ehhalt, D. H. (1981) Measurements of $\text{C}_2\text{-C}_5$ hydrocarbons over the North Atlantic. *Journal of Geophysical Research* **86**, 11,959-11,964.
- Rudolph, J., Ehhalt, D. H., Khedim, A. and Jepsen, C. (1982) Latitudinal profiles of some $\text{C}_2\text{-C}_5$ hydrocarbons in the clean troposphere over the Atlantic. *Proceedings of the 2nd Symposium on Composition of the Non-Urban Troposphere*, pp. 284-286, American Meteorological Society, Boston.
- Rudolph, J., Jepsen, C., Khedim, A. and Johnen, F. J. (1984) Measurements of the latitudinal distribution of light hydrocarbons and halocarbons over the Atlantic. In *Proceedings of the 3rd European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants*, eds B. Versino and G. Angeletti, Varese/Italy, April 1984, pp. 492-414, D. Reidel, Hingham, Massachusetts.
- Rudolph, J. and Johnen, F. J. (1990) Measurements of light atmospheric hydrocarbons over the Atlantic in regions of low biological activity. *Journal of Geophysical Research* **95**, 20,583-20,591.
- Rudolph, J., Johnen, F. J., Khedim, A. and Pilwat, G. (1990) The use of automated on-line gas chromatography for the monitoring of organic trace gases in the atmosphere at low levels. *International Journal of Environmental Analytical Chemistry* **38**, 143-155.
- Rudolph, J., Khedim, A., Wagenbach, D. (1989) The seasonal variation of light non-methane hydrocarbons in the Antarctic troposphere. *Journal of Geophysical Research* **94**, 13,039-13,044.
- Rudolph, J., Khedim, A., Clarkson, T. and Wagenbach, D. (1992) Long term trace measurements of light alkanes and acetylene in the Antarctic troposphere. *Tellus* **44B**, 252-261.
- Rudolph, J., Khedim, A., Koppmann, R. and Bonsang, B. (1995) Field study of the emissions of methyl chloride and other halocarbons from biomass burning in Western Africa. *Journal of Atmospheric Chemistry* **22**, 67-80.
- Schmidt, U., Khedim, A., Johnen, F. J., Rudolph, J. and Ehhalt, D. H. (1982) Two dimensional meridional distributions of CO , CH_4 , N_2O , CFCl_3 , and CF_2Cl_2 in the remote troposphere over the Atlantic Ocean. *Proceedings of the 2nd Symposium on Composition of the Non-Urban Troposphere*, pp. 52-55, American Meteorological Society, Boston.
- Sinclair, M. R. (1988) Local topographic influence on low-level wind at Scott Base. *New Zealand Journal of Geology and Geophysics* **31**, 237-245.
- Singh, H. B., and Salas, L. J. (1982) Measurements of selected light hydrocarbons over the Pacific Ocean. *Geophysical Research Letters* **9**, 842-845.
- Singh, H. B., Vezee, W. and Salas, L. J. (1988) Measurements of selected $\text{C}_2\text{-C}_5$ hydrocarbons in the troposphere: Latitudinal, vertical and temporal variations. *Journal of Geophysical Research* **93**, 15,861-15,878.
- Taylor, J. A., Brasseur, G. P., Zimmerman, P. R. and Cicerone, R. J. (1991) A study of the sources and sinks of methane and methyl chloroform using a global three-dimensional Lagrangian tropospheric tracer transport model. *Journal of Geophysical Research* **96**, 3013-3044.
- Warneck, P. (1988) *Chemistry of the Natural Atmosphere*, pp. 27-37, 144, and 235-236, Academic Press, New York.
- Westberg, H., Sexton, K. and Flyckt, D. (1981) Hydrocarbon production and photochemical ozone formation in forest burn plumes. *Journal of the Air Pollution Control Association* **31**, 661-664.